

Liquid-Liquid Transition in Ionic Liquids

A Dissertation Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

Matthew Albert Harris

May 2022

© by Matthew Albert Harris, 2022
All Rights Reserved.

*This work is dedicated to my parents, Frederic J. Harris and Josephine Monaco, my
brother Frederic G. Harris, and my partner Bowen Sheehan*

*In memory of C. Austen Angell, whose lucid and oftentimes almost prophetic discussion of
the complex phenomena of the liquid state and the glass transition served as a source of
inspiration for the present work.*

Beware the surface of things.

—René Damaul, Mount Analogue

Acknowledgments

Without a doubt, this dissertation would not have been possible without the influence and guidance of my research advisor, Dr. Joshua Sangoro, who encouraged me to pursue lines of questioning that led me to undertake the set of experiments that I present in this work. I also need to thank Dr. Gary Baker and Dr. Durgesh Wagle, who provided most of the samples investigated in this work, for it was they who thought to synthesize a set of ionic liquids never before studied with the hope that we would learn something new about these fascinating materials. In addition, I am grateful to Dr. Alexei Sokolov and Dr. Bamin Khomami for taking an interest in the work I have done and serving on my doctoral committee along side Dr. Sangoro and Dr. Baker. I would also need to thank the National Science Foundation for financial support through the Division of Chemistry Grant CHE-1753282. I am grateful to the University of Tennessee and the Department of Chemical and Biomolecular Engineering for providing initial financial support for my graduate studies through the Chancellor's Fellowship. I would also like to thank Dr. Yangyang Wang and the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory for aiding in the initial calorimetric studies. Wide-angle X-ray scattering measurements were performed at the Joint Institute for Advanced Materials at the University of Tennessee enabled by the Major Research Instrumentation program of the National Science Foundation under Award DMR-1827474. Finally, I would be remiss if I did not acknowledge the immense benefit I received from discussions, feedback, and guidance from my colleagues, Dr. Tyler Cosby, Dr. Thomas Kinsey, Dr. Emmanuel Mapesa, and Stephanie Spittle, throughout my graduate career at the University of Tennessee.

Abstract

The properties of liquids have been linked to the existence of the liquid-liquid transition (LLT), a first-order thermodynamic transition from one liquid phase to another in a single-component liquid. LLT is fundamental to the understanding of the liquid state and has been theorized to manifest from a two-state feature of local order in the liquid. LLT has been reported in a variety of liquids with computer simulations comprising the bulk of the evidence. Experimental evidence for LLT remains controversial because it frequently manifests in the supercooled state, obscured by crystallization. In this dissertation, evidence is presented revealing LLT in ionic liquids (ILs) based on the trihexyltetradecylphosphonium ($P_{666,14}$) cation. These studies consist of ILs containing the $P_{666,14}$ cation with a series of anions: borohydride (BH_4), propionate (Prop), nonafluoropentanoate (NFP), nonafluorobutanesulfonate (NFBS), bis(trifluoromethylsulfonyl)imide (TFSI), and camphor sulfonate (CS). These ILs are glass-formers, allowing unambiguous interpretation of the results in the supercooled state. The BH_4 , Prop, NFP, NFBS, and TFSI samples display evidence of LLT, while the CS sample shows a continuous transformation without LLT, suggesting the anions significantly influence the phase behavior of $P_{666,14}$ -based ILs. A suite of complimentary methods was employed to investigate structure, dynamics, thermodynamics, and macroscopic properties spanning a wide temperature range. Using wide-angle X-ray scattering (WAXS), the local structures and ion coordination numbers were deduced, showing abrupt changes at the LLT. Via broadband dielectric spectroscopy (BDS), an increase in the static dielectric permittivity, ϵ_s , was observed at the LLT, arising from local ion reorganization. A dynamic crossover was revealed at the LLT with an increase in fragility. Differential scanning calorimetry (DSC) revealed a peak in heat capacity, $C_p(T)$, corresponding to LLT. Comparison of the dynamic crossover with configurational entropy,

$S_c(T)$, revealed the two are governed by the same underlying two-state feature. Experimental access to the evolution of local order, dynamics, thermodynamics, and macroscopic properties across the LLT opens up unprecedented pathways to understanding the liquid state. It is argued that a two-state description of liquids is generally applicable, generating new directions for the design of neoteric liquids with bespoke properties for a host of critical applications.

M. A. Harris

Delhi, NY

January 2022

Table of Contents

1	Introduction	1
1.1	Motivation	1
1.2	Outline	5
2	Literature Review	8
2.1	The Liquid State	9
2.1.1	What is a liquid?	9
2.1.2	Liquid Structure	11
2.1.3	Dynamics in the liquid state and the dynamic glass transition	15
2.1.4	Liquid-liquid transition and the phenomenological two order parameter model	22
2.1.5	Examples of liquid-liquid transition in real liquid systems	31
2.2	Ionic Liquids	35
2.2.1	Structure of Ionic Liquids	36
2.2.2	Dynamics and Charge Transport in Ionic Liquids	41
2.2.3	Phase Behavior of Ionic Liquids	44
2.2.4	Ionic liquids as candidates for studying liquid-liquid transition	45
3	Experimental Methods	48
3.1	Broadband Dielectric Spectroscopy	49
3.1.1	Theoretical foundations	49
3.1.2	Measuring the frequency dependent complex dielectric function . . .	52
3.1.3	The stationary case	55

3.1.4	Time dependent dielectric relaxation	62
3.2	Wide-angle X-ray Scattering	69
3.2.1	Principles of X-ray scattering experiments	72
3.2.2	Theory of X-ray scattering in liquids	75
3.3	Raman Spectroscopy	78
3.4	Differential Scanning Calorimetry	80
4	Structural aspects of the liquid-liquid transition in ionic liquids	86
4.1	Temperature dependent X-ray scattering of ionic liquids	87
4.1.1	Polarity alternation	101
4.1.2	Charge alternation	105
4.1.3	Ion adjacency	111
4.1.4	Average ion coordination number	115
4.1.5	The second diffraction peak in low temperature P _{666,14} TFSI	121
4.2	Using Raman spectroscopy to probe conformational order of alkyl chains in P _{666,14} BH ₄	122
4.3	Conclusions	128
5	Dielectric aspects of the liquid-liquid transition in ionic liquids	130
5.1	Temperature dependence of the dielectric spectra	131
5.2	Static dielectric permittivity and the dipole correlation environment	134
5.3	Dynamics and dc ionic conductivity	145
5.4	Conclusions	171
6	Thermodynamics of the liquid-liquid transition in ionic liquids	173
6.1	Calorimetric Investigations of the Phase Transition and the Glass Transition	174
6.2	Heat Capacity	177
6.3	Configurational Entropy	183
6.4	Thermodynamics of the Liquid-Liquid Transition	189
6.5	Conclusions	193

7 Conclusions	194
7.1 Outlook	197
Bibliography	199
List of Publications	245
List of Conference Proceedings	246
Vita	247

List of Tables

4.1	Ionic volumes, ν^+ and ν^- [nm ³], of the P _{666,14} cation and the six anions along with molecular weights, MW [g/mol], estimated molar volumes, V^{est} [cm ³ /mol], and atomic number density, ρ_0 [Å ⁻³], at a reference temperature of 298.15 K. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	100
5.1	Effective dipole moments calculated from the Onsager equation (Equation 3.29), $\mu_{\text{Onsager}}^{\text{eff}}$ [D], and using the equation given in references [1, 2], $\mu_{\text{DRGF}}^{\text{eff}}$ [D], for the P _{666,14} cation paired with the six anions along with estimated ion pair number densities, N^{est} [nm ⁻³], at a reference temperature of 298.15 K[3]. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	139
5.2	Parameters from VFT fits to $\tau_\alpha(T)$ and $\sigma_0(T)$ including glass transition temperatures, T_g , and fragilities, m . The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit. . .	155
5.3	Parameters from TOP-VFT fits to $\sigma_0(T)$ and $\tau_\alpha(T)$. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	163
5.4	Parameters related to the dynamic crossover and the glass transition from TOP-VFT fits to $\tau_\alpha(T)$. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	167

6.1	Thermodynamic data from DSC for P _{666,14} -based ILs. A scan rate of 10 K/min was used for all measurements. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	180
6.2	Analysis of the number of dynamically correlated molecules at T_g , $N_\alpha(T_g)$, and the size of the correlated regions, $N_\alpha(T_g) \cdot (\nu_+ + \nu_-)$. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	182
6.3	Parameters from VFT-AG fits to $S_c(T)$. S_c is given in units of [J/mol K], T is given in units of [K], TS_c is given in units of [kJ/mol]. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	186
6.4	Parameters from TOP-VFT-AG fits to $S_c(T)$. S_c is given in units of [J/mol K], T is given in units of [K], TS_c is given in units of [kJ/mol]. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.	188

List of Figures

2.1	Computationally derived $S(q)$ data for a few small organic molecular solvents. Reprinted (adapted) with permission from [4]. Copyright 2015 American Chemical Society.	14
2.2	Schematic representation of a two-state liquid. The excited state (higher energy) corresponds to the normal liquid structures (NSL) characterized by energy E_ρ , volume v_ρ , and degeneracy g_ρ . The ground state (lower energy) corresponds to locally favored structures characterized by energy E_ψ , volume v_ψ , and degeneracy g_ψ	26
2.3	Prototypical phase diagram of a two-state liquid near the liquid-liquid critical point (LLCP). The top panel shows the phase diagram in the T - ψ plane at constant volume. The bottom panel shows the free-energy surface of LLT in the ρ - ψ plane. Reprinted from [5], with the permission of AIP Publishing.	29
2.4	Prototypical $P - T$ phase diagram of a two-state liquid near the liquid-liquid critical point (LLCP).	30
2.5	Computationally derived $S(q)$ data for a variety of ionic liquids. Reprinted (adapted) with permission from [4]. Copyright 2015 American Chemical Society.	37

2.6	Schematic representation of the structure of a $P_{666,14}$-based ionic liquid in the high temperature liquid state (HTLS). The polar charge network is described as a 3-D percolated network composed of alternating positive and negative ions forming filamentous structures or strands. The strands are separated by the non-polar regions composed of the 14-carbon chains and decorated by the 6-carbon chains. The resulting polarity alternation structure is described as a bicontinuous network of alternating polar and non-polar domains or a sponge-like morphology.	40
2.7	The intersection of three subsets of liquid matter, glass-formers (GF), liquids with a first order liquid-liquid transition (LLT), and ionic liquids (ILs), forming the basis for the present work.	47
3.1	Schematic diagram of the dielectric measurement cell	54
3.2	Plot of the Langevin function. $\bar{\mu}_d/\mu$ as a function of $\mu E/k_B T$ (solid line). The dashed line gives the linear approximation for low field strength.	58
3.3	Schematic diagram of the wide-angle X-ray scattering measurements. Here, λ is the wavelength of the X-rays, $\mathbf{k}_i$ is the incident momentum vector, $\mathbf{k}_s$ is the momentum vector of the scattered X-rays, 2θ is the scattering angle, and $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$ is the scattering wavevector.	74

3.4	Schematic diagram of the principle of Raman spectroscopy. Here, E_{vib} represents the energy difference between two vibrational states. E_R corresponds to the energy of the incident radiation in the process of Rayleigh scattering, where the initial and final energy states of the molecule are the same. E_S refers to the red-shifted Stokes radiation, resulting from excitation of the molecule by the incident beam from its initial state to a higher-energy virtual state and the subsequent relaxation to the higher vibrational state. E_{AS} refers to the blue-shifted anti-Stokes radiation, resulting from excitation of the molecule by the incident beam from a higher vibrational state to a higher-energy virtual state and the subsequent relaxation to a lower vibrational state. The magnitude of the Raman shift in both Stokes and anti-Stokes scattering is equal to the energy difference between the initial and final vibrational states of the molecule, E_{vib}	79
3.5	Schematic diagram of the heat-flow differential scanning calorimetry measurement cell	82
4.1	Chemical structure of the trihexyltetradecylphosphonium ($P_{66,14}$) cation and the six anions comprising the ionic liquid systems studied. The anions are (left column from top to bottom) borohydride (BH_4), nonafluorobutanesulfonate (NFBS), bis(trifluoromethane)sulfonimide (TFSI), (right column top to bottom) propionate (Prop), nonafluoropentanoate (NFP), and camphor sulfonate (CS).	88
4.2	Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{66,14}]^+[BH_4]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{66,14}]^+[BH_4]^-$ at various temperatures calculated from fits to $S(q)$ data.	90
4.3	Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{66,14}]^+[Prop]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{66,14}]^+[Prop]^-$ at various temperatures calculated from fits to $S(q)$ data.	91

4.4	Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{666,14}]^+[NFP]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{666,14}]^+[NFP]^-$ at various temperatures calculated from fits to $S(q)$ data.	92
4.5	Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{666,14}]^+[NFBS]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{666,14}]^+[NFBS]^-$ at various temperatures calculated from fits to $S(q)$ data.	94
4.6	Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{666,14}]^+[TFSI]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{666,14}]^+[TFSI]^-$ at various temperatures calculated from fits to $S(q)$ data.	95
4.7	Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{666,14}]^+[CS]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{666,14}]^+[CS]^-$ at various temperatures calculated from fits to $S(q)$ data.	96
4.8	Temperature dependence of the polarity alternation periodicity. Periodicity of polarity alternation, d_{pol} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH_4 , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	102
4.9	Temperature dependence of the polarity alternation correlation length. Correlation length of polarity alternation, ξ_{pol} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH_4 , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	104
4.10	Temperature dependence of the normalized polarity alternation correlation length. Normalized correlation length of polarity alternation, ξ_{pol}/d_{pol} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH_4 , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	106

4.11	Temperature dependence of the polarity alternation integrated peak intensity. Integrated peak intensity of polarity alternation, $(I_0 A_{TS})_{pol}$, versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	107
4.12	Temperature dependence of the charge alternation periodicity. Periodicity of charge alternation, d_{ch} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	109
4.13	Temperature dependence of the charge alternation correlation length. Correlation length of charge alternation, ξ_{ch} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	110
4.14	Temperature dependence of the normalized charge alternation correlation length. Normalized correlation length of charge alternation, ξ_{ch}/d_{ch} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	112
4.15	Temperature dependence of the charge alternation integrated peak intensity. Integrated peak intensity of charge alternation, $(I_0 A_{TS})_{ch}$, versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	113
4.16	Temperature dependence of the ion adjacency correlation length. Correlation length of ion adjacency, d_{adj} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	114
4.17	Temperature dependence of the ion adjacency peak intensity. Peak intensity of ion adjacency, $(I_0)_{adj}$, versus $1000/T$ for the six ILs studied. Top row, from left to right: BH ₄ , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	116

4.18	Temperature dependence of the ion coordination number. Ion coordination number, n_1 , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH_4 , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.	120
4.19	Temperature dependence of the structural parameters corresponding to the second diffraction peak in low-temperature $\text{P}_{666,14}$ TFSI. (A) Periodicity, d_x , of the second diffraction peak in low-temperature $\text{P}_{666,14}$ TFSI. (B) Correlation length, ξ_x , of the second diffraction peak in low-temperature $\text{P}_{666,14}$ TFSI. (C) Integrated peak intensity, $(I_0 A_{TS})_x$, of the second diffraction peak in low-temperature $\text{P}_{666,14}$ TFSI. (D) Normalized correlation length, ξ_x/d_x , of the second diffraction peak in low-temperature $\text{P}_{666,14}$ TFSI.	123
4.20	Ordering of alkyl chains across the LLT. (A) Raman spectra of $\text{P}_{666,14}$ BH_4 at various temperatures from 1040 cm^{-1} to 1530 cm^{-1} . (B) Raman spectra of $\text{P}_{666,14}$ BH_4 at various temperatures from 2835 cm^{-1} to 2955 cm^{-1} . (C) Normalized Raman spectra between 1040 cm^{-1} and 1140 cm^{-1} . (D) Ratio of the intensity of the $\nu(C-C)_T$ peak at 1065 cm^{-1} to the $\nu(C-C)_G$ peak at 1079 cm^{-1} . (E) Peak frequency of the $\nu(C-C)_T$ mode around 1130 cm^{-1} . Solid and dotted lines represent linear fits to the data to serve as guides for the eye. Vertical dashed black lines indicate the transition from liquid I to liquid II to the glassy state. Reproduced from [6].	125
4.21	Detail of Raman spectra of $\text{P}_{666,14}$ BH_4. (A) Raman spectra of $\text{P}_{666,14}$ BH_4 between 1280 and 1340 cm^{-1} showing the $\tau(\text{CH}_2)$ (twisting) modes. (B) Raman spectra of $\text{P}_{666,14}$ BH_4 between 1420 and 1485 cm^{-1} showing the $\delta(\text{CH}_2)$ (bending) modes. (C) Ratio of the integrated areas of the $\delta_a(\text{CH}_3)$ and $\delta(\text{CH}_2)$ modes. Reproduced from [6].	127

5.1	Dielectric spectra of $P_{666,14}$ BH_4. (A) Real part of the complex dielectric function, ε' versus radial frequency, ω at various temperatures. (B) Real part of the complex conductivity, σ' versus radial frequency, ω at various temperatures. (C) Derivative representation of the imaginary part of the complex dielectric function, $\varepsilon''_{der} = (-\pi/2) [\partial\varepsilon'/\partial \ln(\omega)]$ versus radial frequency, ω at various temperatures. Solid black lines show fits to the data using a combination of Havriliak-Negami (HN) functions and the Random Barrier Model (RBM) with a power law function to account for electrode polarization (see Eqn. 5.1). Dashed lines show the individual HN functions (see Equation 3.41) and RBM function (see Equation 3.43) used to fit the 210K data. Note that the sub- α relaxation only appears in the spectra at or below 220K. Reproduced from [6].	132
5.2	Derivative representation of the imaginary part of the complex dielectric function of $P_{666,14}$-based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid black lines represent fits to Equation 5.1 without including the β -relaxation term.	135
5.3	Static dielectric permittivity versus $1000/T$ for $P_{666,14}$-based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS.	137
5.4	Kirkwood-Fröhlich dipole correlation factors versus $1000/T$ for $P_{666,14}$-based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS.	140
5.5	Dimensionless dipole interaction strength, y, given by the DRGF theory[1, 2] versus $N/3\varepsilon_0 k_B T$ normalized by the value at the transition for $P_{666,14}$-based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS.	142
5.6	Fraction of LFS, $\psi(T)$, determined by the method in [2] versus T_x/T for $P_{666,14}$-based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS. Lines show the logistic ansatz for $\psi(T)$ given by Equation 5.16, discussed in Section 5.3.	144

5.7	Arrhenius plot of the relaxation rates for $P_{666,14}$ BH_4. The black circles represent $\omega_\alpha = 1/\tau_\alpha$, the structural relaxation rate. The blue squares correspond to ω_e , the characteristic charge transport rate from the RBM. The brown stars show $\omega_{sub-\alpha}$, the rate of the emergent slow relaxation appearing at the LLT. The green inverted triangles indicate ω_β , the secondary β -relaxation rate associated with the librating alkyl chains on the $P_{666,14}$ cation.	146
5.8	Arrhenius plots of the relaxation rates for $P_{666,14}$-based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.	148
5.9	BNN plots for $P_{666,14}$-based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.	150
5.10	Stickel plots of dc ionic conductivity for $P_{666,14}$-based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid and dashed lines represent VFT fits to the high temperature and low temperature regions of the data, respectively.	152
5.11	Arrhenius plots of dc ionic conductivity for $P_{666,14}$-based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid and dashed lines matching the color of the symbols represent individual high and low temperature VFT fits, respectively. The solid black lines are fits to Equation 5.17 based on the two order parameter model.	156
5.12	Arrhenius plots of the structural relaxation times for $P_{666,14}$-based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid and dashed lines matching the color of the symbols represent individual high and low temperature VFT fits, respectively. The solid black lines are fits to Equation 5.17 based on the two order parameter model.	157

5.13	Fraction of locally favored states calculated from Equation 5.16. Top panel: $\psi(T)$ versus $1000/T[K^{-1}]$. Bottom panel: $\psi(T)$ versus $T_{\psi=1/2}$ - normalized inverse temperature.	165
5.14	Static dielectric permittivity, ϵ_s, versus $\log_{10}(\tau_x/\tau_\alpha)$. Top to bottom: BH ₄ , Prop, NFBS, NFP, TFSI, CS.	170
6.1	DSC thermograms for P_{666,14}-based ionic liquids. Top row, from left to right: BH ₄ , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.	176
6.2	Heat capacity of P_{666,14}-based ionic liquids measured on heating at 10K/min. Top to bottom: BH ₄ , Prop, NFBS, NFP, TFSI, CS.	178
6.3	Configurational entropy for P_{666,14}-based ionic liquids. Top row, from left to right: BH ₄ , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.	185
6.4	The quantity TS_c^{-1} normalized by the crossover value plotted against inverse structural relaxation times normalized by the crossover time for P_{666,14}-based ionic liquids. Top row, from left to right: BH ₄ , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Dashed and dotted lines with shaded region in between serve as guides for the eye.	190

Chapter 1

Introduction

1.1 Motivation

Liquids are a part of our day-to-day lives. They are necessary for a diverse array of chemical processes and technological applications. Perhaps most importantly, the properties of the liquid state are crucial to all life as we know it. Despite the ubiquity of liquids, they are among the least well-understood of the different phases of matter. Liquids, in general, exhibit densities comparable to that of solids and yet, they flow and change their shape. On the molecular scale, this translates to a state where the constituent particles are close enough to be influenced by their neighbors while remaining mobile enough to move past each other.

Liquids are conventionally thought of as disordered, homogeneous phases lacking a well-defined internal structure, similar to a gas but with significantly higher density. However, due to the condensed nature of the liquid phase, constituent molecules are able to interact with neighboring molecules via non-covalent interactions such as hydrogen bonding, Coulombic, and van der Waals interactions. These intermolecular forces impart local order in liquids and define the so-called liquid structure. A liquid-liquid transition (LLT) is a first-order phase transition from one type of local structure to another type of local structure.[5, 7, 8, 9, 10, 11, 12, 13, 14, 15] This type of phase transition, sometimes referred to as a polyamorphic transition, has been observed in various liquid systems, including water[16, 17, 18, 19], silicon[20, 21, 22], phosphorous[23, 24], and triphenyl phosphite.[25, 26, 27, 28, 29, 30] This work will focus on the recent observations of a LLT in

ionic liquids (ILs) bearing the trihexyltetradecylphosphonium ($P_{666,14}$) cation. It is crucial to understand the effect that the LLT has on the local structure, dynamics, and macroscopic properties of these IL systems .

Ionic liquids are generally defined as materials composed entirely of ions, consisting of positively-charged cations and negatively-charged anions in molar proportionality resulting in a net neutral charge, which are in the liquid state at room temperature, i.e. salts which melt at low temperatures.[31, 32, 33, 34, 35] As such, these materials are pure liquid electrolytes, owing to their intrinsic ion conductivity in the liquid state without the need for a solvent medium, that have desirable properties for a wide array of applications, including energy storage[36, 37, 38, 39, 40], separations[41, 42, 43, 44, 45, 46, 47, 48], solvents for bio-mass processing[49, 50, 51, 52, 53, 54], catalysis[55, 56, 57, 58, 59], sensors[60, 61, 62], and solvent chemistry[63, 64, 65], to name a few. Among the properties that make ILs so appealing is their wide liquidus range, low vapor pressure, high ionic conductivity, wide electrochemical stability window, thermal stability, and tunability of their chemical structure including the capability of adding task-specific functionality.[66] With such vast variability in their chemistry, fundamental research to understand the interplay between the chemical structure of ILs and the properties of the resulting material is critically important for the development of ILs that have practical and functional advantages over conventional materials used in key technological sectors. One of the key properties of ILs that differentiates them from conventional solvents is their ability to form nanoscale structures consisting of alternating polar and apolar domains, which makes them capable of dissolving both polar and non-polar substances.[67, 68, 69, 70] Despite the fact that ILs are composed of a combination of cations and anions, imparting these materials with their unique properties, the strong electrostatic interactions that bind together ions of opposite charge in ionic substances result in associations between the cations and anions in an IL in order to achieve net charge neutrality.[67, 71, 72] A consequence of these ionic associations is that the cations and anions are inseparable; they are only stable when combined in a charge-neutralizing proportion. One could argue that this constraint makes pure ILs single-component liquids, with the fundamental liquid component consisting of the cation-anion combination possessing net

zero charge with the ionic associations between them taking the place of the covalent bond that binds atoms in molecules, only in a much weaker form.[67, 72, 73, 74, 75]

Liquid-liquid transitions in single-component liquids have been identified in a variety of materials, from atomic and metallic systems[23, 76, 77, 78, 79, 80, 81, 82, 83] to molecular liquids.[84, 85, 86, 87, 88, 89] Despite significant investigation of LLT in these disparate systems, the number of liquids that have been found to show compelling evidence of a LLT remains small. One reason for this is that most known examples of LLT occur in the supercooled liquid, meaning that in order to study the LLT one must measure the properties of the liquid without the interference of crystallization. Furthermore, since LLT is so often observed in the supercooled liquid state, it has been suggested that this phenomenon has a close relationship with the process of vitrification. Thus, in the same way that a complete understanding of the glass transition remains an open-ended problem, the precise nature of the LLT remains elusive.

The fundamental question I hope to shed light on in the present work is, “*What does the liquid-liquid transition look like in glass-forming ionic liquid systems?*” To begin to understand how to answer that question, I employed complimentary experimental methods to observe temperature driven changes in a series of quaternary phosphonium ionic liquids. Some preliminary questions need to be considered that will put the foundations of this work on firm ground. First of all, what type of ionic liquid chemical structures, specifically, would result in a liquid-liquid transition in an observable temperature range? What type of cation combined with what type of anion would lead to this type of thermodynamic phase behavior? There are an intractable number of potential combinations of different cations and anions that can be created to form ionic liquids making it a practical impossibility to experimentally test the entire sample space to measure the properties of every ionic liquid. Thus, the goal of fundamental ionic liquid research is to ascertain the range of ionic liquid behaviors and to study the interplay between chemical structure and macroscopic properties in order to develop methods to predict the properties of a new ionic liquid based on its chemical structure and to design ionic liquids with desirable properties by tweaking the moieties present in the cation and anion structures.

The ability to swap different anions, for example, paired with a given cation to generate a new ionic liquid is advantageous for the purposes of studying the possibility of a liquid-liquid transition in these systems. Once a single case is identified, a series of variations can be examined to understand the role played by, say, the anion structure in determining the presence of the liquid-liquid transition. The goal, then, is to establish a set of ILs that display polymorphic behavior in order to identify the general characteristics that typify the LLT in a particular subset of IL systems. The cation of interest in this investigation is the $P_{666,14}$ cation, due to its advantageous properties[65, 90, 91, 92, 93, 94, 95], potential technological importance[42, 96, 97, 98, 99], and the filamentous morphology exhibited by this family of ILs, as determined by molecular dynamics simulations.[4, 100, 101, 102, 103, 104, 105, 106, 107, 108] Of particular interest for this study is the filamentous nanostructure of $P_{666,14}$ -based ILs, since this cation can only form a limited number of ionic associations in the normal, high-temperature liquid state, resulting in a polar network typified by strands of alternating positive and negative charge centers with sufficient branching to form a continuously-percolating, 3-D charge network spanning the liquid.[4, 100, 101, 102, 103, 104, 107] It is my hypothesis that ILs displaying this morphology have a propensity towards LLT behavior manifesting through an increase in the number of ionic associations on the local level, leading to a reorganization of the morphology of the bulk liquid across the transition. Pairing this cation with different anions that vary in size, polarity, and charge density enables us to establish common signatures of LLT behavior in these systems as well as pinpoint aspects of the transition that are anion specific. In this work, I have investigated a series of six $P_{666,14}$ -based ILs with different anions, five of which exhibit a LLT and one which does not for comparison. Using a set of complimentary experimental methods that can be used to characterize the structural, dynamic, and thermodynamic properties of the samples, as well as measure key macroscopic properties, this investigation will yield answers to fundamental questions concerning the nature of the proposed LLT that is present in this class of ILs, enumerated as follows:

1. How does the liquid structure change across the liquid-liquid transition in ionic liquids?

2. How do the structural changes correlate with the macroscopic dielectric properties of ionic liquids?
3. How does the liquid-liquid transition affect the dynamics and transport properties of ionic liquids?
4. How is the liquid-liquid transition related to the glass transition?
5. Is the liquid-liquid transition in these ionic liquids a true first-order phase transition?
6. What role does the anion play in the liquid-liquid transition?
7. Can we identify a structural descriptor corresponding to the locally favored structures characterizing the low-temperature liquid state?

The primary aim of this fundamental scientific endeavor is to learn what defines a liquid-liquid transition in this subset of ionic liquids with the purpose of illuminating aspects of the liquid state in general that make this type of transition possible. By confirming the existence of certain ionic liquids that display polyamorphic behavior, we can begin to uncover the features of the liquid state that govern the relationship between structure and properties. The existence of the liquid-liquid transition suggests that the properties of the liquid depend strongly on highly localized interactions between the molecules that dictate their arrangement over short distances and tells us that changes in the local molecular environment can profoundly impact the bulk properties of the material. By studying the aspects of the chemical structure of the liquid that determine how and where these changes occur and what effect they have on the macroscopic properties of the system, we can gain insights that will allow us to rationally engineer novel liquids for many critical applications.

1.2 Outline

The details of the work uncovering the liquid-liquid transition in a class of ionic liquids are presented as follows. Chapter 2 gives an overview of the scientific literature pertaining to the topics of liquids, glasses, the liquid-liquid transition, and ionic liquids. Chapter 3 explains the

experimental methods and analytical procedures employed in this work, providing details to understand the results set forth in subsequent chapters. In the following chapters (Chapters 4, 5, & 6), the results of this experimental study of ionic liquids are presented, covering the structural characterization, dielectric response, and thermodynamics of the materials under consideration. In the final chapter (Chapter 7), the key results are summarized and discussed in regard to their significance and broader implications. Perspectives on the future outlook for research in the fields of ionic liquids and the liquid state in general are also given.

Chapter 2 covers topics from the scientific literature pertinent to this study of the liquid-liquid transition in ionic liquids. The relevant research discussed in this chapter includes the general nature of the liquid state, the dynamic glass transition, liquid-liquid transition, the phenomenological two order parameter model of the liquid state, and ionic liquids.

Chapter 3 outlines the experimental techniques used to study the set of ionic liquids included in this work. The methods are explained with a focus on the physical principles underlying their operation. The techniques employed in this study include broadband dielectric spectroscopy, wide-angle X-ray scattering, differential scanning calorimetry, and Raman spectroscopy. Particular emphasis is given to the application of these methods to the study of ionic liquids. In addition, details of the analysis of experimental data pertaining to the temperature dependent behavior of ionic liquids across the liquid-liquid transition are discussed.

Chapter 4 delves into characterization of the structure of ionic liquids. We begin by revisiting the hierarchical nature of $P_{666,14}$ -based ionic liquid structure before moving on to a discussion of the results obtained from temperature dependent wide-angle X-ray scattering experiments revealing the sometimes subtle and sometimes dramatic structural changes observed in a set of ionic liquids as they undergo a liquid-liquid transition. A discussion of the use of Raman spectroscopy to characterize conformational order among the alkyl chains attached to the phosphonium cation in these ionic liquids is also given.

Chapter 5 deals with the dielectric behavior of the ionic liquids in this study. We start by presenting an overview of the temperature dependence of the measured dielectric spectra of the ionic liquids in this work. The following section details the analysis of the static dielectric permittivity to understand changes in local ordering of the charges and dipoles

resulting from the liquid-liquid transition in these ionic liquid systems. Next, we provide a discussion of the charge transport properties and dynamics of the ionic liquids studied. Dynamic parameters pertinent to the liquid-liquid transition are identified.

Chapter 6 gives a discussion of the thermodynamic properties and changes observed in the set of ionic liquids under investigation starting from calorimetric data and comparing the results to the findings from structural and dielectric characterization. In particular, a detailed analysis of the configurational entropy in these systems is carried out, and a connection is made to the changes observed in the dynamic quantities reported by dielectric spectroscopy. Thermodynamic quantities relevant to the liquid-liquid transition and the glass transition are identified.

Chapter 7 concludes this work by summarizing the key findings and discussing their significance and implications for the greater scientific community. The major scientific questions presented in the introduction are addressed and potential for future research is outlined.

Chapter 2

Literature Review

In this chapter, an overview of the scientific literature will be provided in order to place the results of this experimental investigation of LLT in the $P_{666,14}$ -family of ILs in the context of the broader effort to understand the physical phenomena of the liquid state, the dynamic glass transition, the liquid-liquid transition, and the fundamental structure-property relations governing ionic liquid behavior. We begin the discussion with an introduction to the liquid state from the point of view of pair-wise interactions, an approach that draws an analogy between the weakly-interacting, low-density gaseous state and the liquid state, in which local pair interactions are amplified due to the reduced inter-particle distances in the condensed phase. Next, we provide an overview of the dynamic glass transition focusing on attempts to understand the physics of glasses in terms of the dynamics of the supercooled liquid state. We then move on to the phenomenon of the liquid-liquid transition and present the phenomenological two order parameter model of the liquid state to understand the origin of the LLT and the associated liquid-liquid critical point (LLCP). Finally, we introduce the topic of ionic liquids as a subset of liquids in general and discuss the structure, properties, and phase behavior of ILs based on current understanding of these systems.

2.1 The Liquid State

2.1.1 What is a liquid?

Liquids are one of the three fundamental states of matter, along with gases and solids (crystalline). For a pure substance, the equilibrium state will depend on the thermodynamic conditions, temperature (T) and pressure (P), applied to the system. The gas, liquid, and solid states of the system can be drawn as regions on a $P - T$ phase diagram representing the range of thermodynamic conditions under which a particular state exists in stable equilibrium. Each of these states are separated by a first-order thermodynamic phase transition. The line on the phase diagram separating two equilibrium states is referred to as the coexistence line, which defines the thermodynamic conditions of the first-order phase transition between the two phases. In general, the crystalline solid exists in the low temperature region of the phase diagram and the gaseous state occurs on the high temperature side. The liquid state exists in the region between the two extremes, and is bounded on the low temperature side by the solid-liquid equilibrium line and on the high temperature side by the vapor-liquid equilibrium line. In this simplified conception, the liquid state occupies the intermediary position between the two extremes of normal matter. The solid (crystal) state, at the low temperature extreme, is defined by long-range order of the constituent particles arranged in a periodic lattice. The gaseous (vapor) phase, at the high temperature extreme, is characterized by large inter-particle distances where the only meaningful interactions occur through particle collisions. In between, we find the liquid state, lacking long-range order but where the inter-particle distances are on the order of the size of the particles. Liquids are therefore classified as a condensed phase of matter in which the constituent particles have sufficient kinetic energy to rearrange and reorient, possessing translational and rotational degrees of freedom, but not sufficient to overcome the inter-particle potential holding the particles in the condensed liquid state. However, at the gas-liquid interface, the kinetic energy of the liquid particles is sufficient for a fraction of the particles to escape the inter-particle potential and enter the gas phase. In a closed, single-component system where a gas-liquid interface exists, the loss of particles from the liquid to the vapor phase is accompanied by gas particles colliding with the liquid surface, becoming

trapped by the liquid phase. When the system is in vapor-liquid equilibrium (VLE), the transfer of particles from the liquid to the gas is balanced by the transfer of particles from the gas to the liquid, resulting in zero net mass transfer between the two phases. The pressure in the vapor phase above the liquid surface in a system under these conditions is termed the vapor pressure, which is a fundamental property of liquids related to the strength of their inter-particle potential. In this conception of the liquid state, the liquid and gas phases resemble one another, in that they are both regarded as disordered and isotropic states of matter, differing only in density, i.e. average distances between particles.[109, 110, 111, 112]

Liquids are classified as a fluid state of matter along with gases, in that they continuously deform in response to an external shear stress applied to the material, i.e. they flow. Liquids are largely considered to be nearly incompressible, i.e. their volume remains almost constant when exposed to pressure changes; a feature that distinguishes them from gases, which expand or contract in response to changes in pressure. Real liquids are not truly incompressible, but their volume changes in response to a differential change in pressure are typically so small as to be negligible. The flow properties of liquids are determined by their ability to resist deformation caused by an applied stress at a given rate. This property of resistance to flow is defined as the viscosity, η , of the liquid.[113] This property can be used to distinguish between the solid and the liquid state. The difference between the crystalline solid and the amorphous liquid is determined by the internal arrangement of the constituent atoms or molecules. However, in the case of glasses, or amorphous solids, there is no point at which the structure of the material drastically changes during the transition from the liquid to the glass. However, the viscosity increases by more than 15 orders of magnitude between the high temperature liquid and the glassy state.[114, 115, 116, 117, 118] That is to say, in terms of the arrangement of their constituent particles, the glass is indistinguishable from the liquid. And yet, the glassy state behaves like a solid in response to applied stress even though it structurally resembles the liquid from which it was formed.

Liquids, by virtue of their status as the intermediary equilibrium state of matter, are exceedingly rare in the universe. In most environments beyond Earth's atmosphere, matter will either vaporize or freeze when exposed to low pressure and extremely cold temperatures. From our perspective on Earth, however, liquids are abundant, with water covering over

70% of the planet’s surface and falling from the sky quite regularly. We take for granted the relative scarcity of liquids in the universe and the uniqueness of our planet where liquids are stable and plentiful. We even have a saying; something about water being everywhere. Of course, our biology requires that we always have access to water, so one could say that, were it not for the liquid-rich environment in which we exist, we would simply not. Liquids overall have many fascinating and useful properties. Perhaps the most crucial for the existence of all life everywhere is the ability to dissolve a variety of different substances. The solvent behavior of liquids is important, not just for biological functions, but for many chemical processes as well. Liquid matter is found in, or integral to, virtually every aspect of technology and industry. The applications of these materials are practically limitless. And yet, at the fundamental level, liquids remain the least well-understood among the common phases of matter. But why is that the case?

2.1.2 Liquid Structure

Liquids of all types, including atomic, molecular, metallic, and ionic, are generally regarded as disordered and isotropic phases that are condensed such that interparticle distances are on the order of the particle sizes.[109, 111] The short distances between particles in the liquid phase mean that the structure and properties of the liquid will depend on intermolecular forces related to the chemical and electronic structures of the constituent particles, including van der Waals interactions, Coulombic interactions, and hydrogen bonding. The simplest model of a liquid, the hard sphere model, is defined by a single repulsive interaction that approximates the overlap of valence electron states. This strong repulsive force manifests at short distances, defined by the particle diameter. The strength of intermolecular forces and their spatial influence can be described by a pair potential showing the potential energy, $u(r)$, between two particles as a function of their separation distance, r . Pair potentials contains contributions from short-range repulsive forces as well as attractive forces with a longer range of influence, such as electrostatic interactions.[109, 110, 111, 112] In real liquid systems, the interplay between these two types of intermolecular forces give rise to the overall structure and properties of the liquid. The simplest version of a pair potential that includes both attractive and repulsive contributions is given by a repulsive, hard sphere potential with the

addition of an attractive, square well potential which provides the necessary cohesive energy to stabilize the liquid, defined by:

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (2.1)$$

where $u(r)$ is the potential energy of interaction, r is the distance separating the two particles, and σ is the repulsive diameter or range in units of length.[112] In real systems, the exact form of the pair potential will vary depending on the constituent particles that comprise the system.[112] Another commonly-employed pair potential to describe simple liquids is the well-known Lennard-Jones (LJ) potential, given by:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.2)$$

where σ , again, gives the repulsive diameter and ϵ is the depth of the minimum in potential energy.[112] The first term in the LJ potential corresponds to short-range repulsion arising from overlap of electronic shells, while the second terms describes the attractive van der Waals interaction arising from induced dipole-dipole interactions caused by distortions in the electronic structure around an atom in the presence of other atoms.[109, 112] In liquids where ions are present, the Coulomb interaction must be accounted for with a pair potential incorporating electrostatic contributions. A common form for the pair potential describing Coulombic interactions between ions is the Tosi-Fumi potential, given by the equation:

$$u(r_{ij}) = A_{ij}e^{-r_{ij}/a_{ij}} + \frac{q_i q_j}{r_{ij}} \quad (2.3)$$

where r_{ij} is the separation distance between ions of charge q_i and q_j , with A_{ij} and a_{ij} parameterizing the electronic repulsive contribution, termed the Born-Mayer approximation.[112] An attractive van der Waals term can be included in this potential, depending on the system. The use of a pair potential to describe the liquid state is a simplified approach based on the assumptions of homogeneity and isotropy of the liquid to construct an effective two-body

potential by explicitly ignoring specific many-body interactions in order to make the problem tractable.[109, 112]

In general, for simple liquids, the structure arising from the combination of short-range repulsion and long-range attraction can be characterized by a single correlation length manifesting in the structure factor, $S(q)$, as a single peak at q values between about $1 \text{ \AA}^{-1}$ and $2.5 \text{ \AA}^{-1}$ for small organic molecular liquids, with much weaker correlations decaying at higher q values (see the examples shown in Figure 2.1).[4, 119, 120, 121, 122] Liquids in the bulk possess global translational and rotational symmetry. This is evident from the typical X-ray diffraction pattern for a pure, simple liquid, be it water or mercury, showing a diffuse halo or ring at a scattering angle related to the correlation length or interparticle distances within the liquid. Naturally, the correlation length will vary depending on the size and geometry of the liquid particles. Depending on the types of atoms present and how they are arranged in a molecular form, different intermolecular forces will be present. Their relative strength and directionality will determine how a localized cluster of molecules in the liquid will arrange. By moving from the simplest liquid model composed of spherically symmetric particles to more complex forms and interactions, we move from the single peak in the structure factor to an asymmetric feature that may be composed of numerous overlapping peaks or even separate, well-defined peaks total two or more. Whatever it is we see in the X-ray diffraction pattern of a liquid corresponds to the local arrangement of the molecules extending over a few molecular distances at most. At longer distances, the arrangement of the molecules is completely random and disordered. Since liquids are a fluid state of matter, the positions of the molecules and their orientations are in constant flux. The local arrangement of molecules defined by molecular geometry and specific interactions will always reemerge from the fluctuations and rearrangements that churn the system towards disorder. That is because there is a particular set of local configurations that define the equilibrium liquid structure. It is this set of configurations that produces the unique interference pattern that emerges on the detector. The limited range of the forces that define the equilibrium structures combined with the randomizing effect of fluctuations influence how broad and diffuse the features of the diffraction pattern will be. This is what defines the structure of a liquid, the set of localized configurations at equilibrium and the random fluctuations that

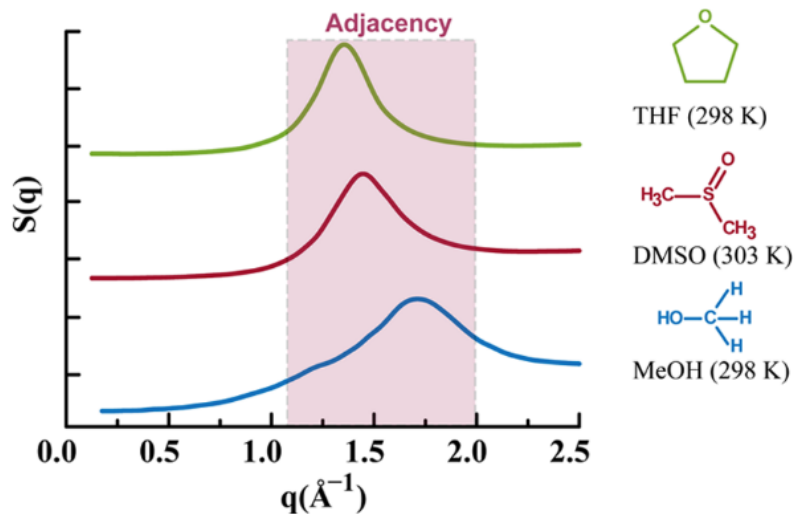


Figure 2.1: Computationally derived $S(q)$ data for a few small organic molecular solvents. Reprinted (adapted) with permission from [4]. Copyright 2015 American Chemical Society.

disrupt them. The dynamics and properties of the liquid state at the macroscopic scale stem from these local structures. The difficulty inherent in understanding the liquid state lies in the interpretation of one from the other, macroscopic properties from microscopic structure.[123]

2.1.3 Dynamics in the liquid state and the dynamic glass transition

The molecules in a liquid are not fixed relative to one another. They are in constant flux, free to move, to rearrange and reorient. In a liquid at equilibrium, the particles in the system will fluctuate, moving around and colliding in accordance with the average kinetic energy of the particles corresponding to the thermal energy contained in the system at a given temperature. This phenomena is known as Brownian motion, where the particles move in a random path in their local region with no preferential direction, while the total linear and angular momentum of the fluid remains zero over time. The fluctuation-dissipation theorem of statistical mechanics states that the macroscopic response of a system to a small, external perturbation within the linear response regime occurs by the same molecular mechanism responsible for the random, thermal fluctuations that manifest at equilibrium. From this correspondence, the structural relaxation time of the system is defined as the time required for the system to return to its equilibrium state following an external perturbation. Since the process that governs the relaxation from the perturbed state back to the equilibrium state corresponds to the same process by which the particles spontaneously fluctuate at equilibrium due to stochastic thermal motion, the structural relaxation time is an observable quantity that describes the dynamics of the system on the molecular level at a given temperature.[117, 124]

In the liquid state, the temperature of the system corresponds to the rate of thermal fluctuations of the system. In the high temperature limit, the particles fluctuate locally at a rate corresponding to a relaxation time of about 10^{-13} s.[117, 124] As the temperature is decreased, the fluctuations become slower and the relaxation times become longer. Localized vibrational motions of the particles in the liquid slow down with decreasing temperature

according to an Arrhenius-type dependence with a single activation energy where the logarithm of the relaxation time for the corresponding local motion depends linearly on inverse temperature.[117, 124] These localized motions are referred to as secondary or β -relaxations. Due to the condensed nature of the liquid state, the molecules do not reorient independently from each other; to some extent, the molecules relax cooperatively with the neighboring molecules. A central concept in the dynamics of liquids and the dynamic glass transition is this cooperative motion on the molecular level governing the structural relaxation of the system. A consequence of the cooperativity of molecular reorientation is the non-Arrhenius temperature dependence of the structural or α -relaxation time of the liquid. In the dynamic glass transition, the structural relaxation time, τ_α , of the liquid increases strongly with decreasing temperature, T , approximately following the empirical Vogel-Fulcher-Tammann (VFT) equation, given by:

$$\tau_\alpha(T) = \tau_\infty \exp \left[\frac{DT_0}{T - T_0} \right] \quad (2.4)$$

where τ_∞ is the high temperature limiting relaxation time ($\approx 10^{-13}$ s), D is a constant, and T_0 is the Vogel temperature, sometimes called the ideal glass transition temperature.[117, 125, 126, 127] Glass-forming liquids are often classified by the degree to which they deviate from Arrhenius behavior, termed the fragility of the liquid, with systems that strongly deviate from Arrhenius behavior classified as fragile and systems with close to Arrhenius behavior classified as strong.[128, 129, 130, 131, 132, 133]

The dynamic glass transition is defined by the continuous slowing-down of the structural relaxation of the liquid encapsulated by the non-Arrhenius behavior.[124] However, the final, glassy state of the system in the process of vitrification is structurally indistinguishable from the supercooled liquid from which it formed.[134] The glassy state is defined by its solid-like response at normal timescales.[124] When the liquid is cooled far enough in the dynamic glass transition, the relaxation time of the system becomes longer than the timescale on which we observe its response to a perturbation. At that point, it is in a non-ergodic state because the system has insufficient time to explore its configurational phase space and the timescale required for it to relax back to equilibrium far exceeds the practicality of experimental

observation.[134] For all intents and purposes, it is frozen into a solid, although, on the molecular level, the particles of the system are arranged in a disordered, amorphous state practically identical to the liquid from which it formed. Because the transition from liquid-like behavior to solid-like behavior occurs continuously as the dynamics slow with decreasing temperature, a calorimetric glass transition temperature, T_g , is assigned by convention as the temperature at which the structural relaxation time reaches a value of 100 s.[134] Thus, the dynamics of the liquid span 15 orders of magnitude in the process of vitrification. Defining T_g in this manner, we find that T_0 from the VFT equation is typically around 40 K lower than T_g . [117, 124]

The situation describing the dynamic glass transition seems simple enough to digest. The molecular motions in the liquid are cooperative to some extent and so the dynamics slow continuously to a point where the relaxation time of the system becomes too long to measure by any practical means. The resulting state of the material behaves like a solid rather than a liquid so we call it a glass. However, the glass problem is more complicated than it appears. It remains a mystery why the dynamics slow so dramatically spanning 15 decades and the origin of the cooperative motion is not well-understood from a theoretical perspective. The particles in the liquid are arranged in a disordered manner and their motion is dictated by stochastic laws. Thus far, every attempt to theoretically describe the phenomena of vitrification from the liquid state on the molecular level from first principles has been flawed in one way or another. The VFT equation frequently employed to fit experimental dynamic data is a very good empirical model that describes what we see rather well in most cases, but it has no firm theoretical foundation despite numerous attempts to find one.[126, 127, 135, 136, 137, 138] Extrapolating the α -relaxation time below T_g using the VFT equation, we find that it apparently diverges at T_0 , a fact that is difficult to support using physical arguments.[5, 139, 140, 141, 142, 143] To further confound the situation regarding vitrification, the so-called Kauzmann paradox would need to be accounted for by any successful theory of the glass transition. The paradox, first raised by Walter Kauzmann in 1948[144], concerns the excess entropy of the supercooled liquid over the crystalline solid. As the liquid is supercooled, the difference in entropy between the liquid and the crystal phases decreases. By extrapolating the heat capacity of the supercooled liquid to temperatures below T_g , ones

finds a finite temperature at which the difference in entropy between the liquid and the crystal becomes zero, the eponymous Kauzmann temperature, T_K . The paradox arises from the fact that further extrapolation to temperatures below T_K suggests the entropy of the liquid would become lower than that of the crystal, a situation that, if it was realized in an actual experiment, would be paradoxical resulting in a crisis in physics with far-reaching consequences. The Kauzmann paradox has engendered copious debate and literature in an effort to resolve it, lest it becomes real. In actuality, the chances of experimentally confronting the crisis suggested by Kauzmann are infinitesimally remote, as the cooling rate required to measure the heat capacity of the equilibrated liquid far below T_g , let alone below T_K would correspond to geological or, quite possibly, cosmological timescales.[124]

Despite the fact that the Kauzmann paradox has never been realized in an actual liquid, and doing so is quite likely impossible, it presents a conundrum that one is obliged to address in attempting to solve the glass problem. In the second half of the 20th century, numerous theoretical frameworks were proposed to account for the phenomena of the vitrification process along with various schemes to resolve the entropy crisis.[114, 132, 145, 146, 147, 148, 149, 150, 151] None of the theories amount to a satisfactory description of all of the experimental results regarding the dynamics of the liquid state on the way to becoming a glass. A few are noteworthy in their ability to neatly account for some subset of the experimental data while offering insight into the complexity of the problem from a molecular perspective.

First, we mention the various energy landscape models, which broadly describe the metastable states of the supercooled liquid in terms of local minima in a complex, spatially-varying, fluctuating potential energy landscape with the dynamic arrest at T_g corresponding to a locally minimal configuration being energetically cut-off from neighboring minimal states preventing the system from exploring the surrounding landscape to achieve the lowest possible energy configuration.[152, 153, 154, 155, 156] Next, we have the Adam-Gibbs model, which accounts for the continuous slowing-down of the dynamics of the system with the concept of expanding cooperatively rearranging regions, defined as the minimal region capable of adopting a new configuration independent of the surrounding regions.[157] In this model, it is assumed that the boundaries of the cooperative regions expand as

the liquid is supercooled such that the number of liquid particles that react collectively increases as the system approaches T_g . Donth developed a method based on temperature fluctuations, δT , of the collective behavior at T_g to calculate the volume of the cooperatively rearranging regions from the step change in the heat capacity at T_g and the width of the glass transition.[158, 159, 160] The concept of cooperative regions has garnered lasting appeal to this day.[161, 162, 163] In addition, it offers an intuitive interpretation for the evidence of dynamic heterogeneity, whereby the dynamics of the supercooled liquid state can vary spatially by multiple orders of magnitude between regions of the material separated by mere nanometers.[164, 165] Although it should be noted that the Adam-Gibbs model does not directly address or explain the problem of dynamic heterogeneity, which is a complex puzzle in its own right that has attracted a substantial amount of attention resulting in a number of models devoted to explaining the mechanism by which these heterogeneities emerge.[151, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174]

Another approach, that has been expanded on and modified over the years since its inception, is the free volume theory.[66, 175, 176, 177] In its early form, the free volume approach assumed each liquid particle occupied its own local volume, with the excess volume over some critical volume amounting to the local “free” volume. For molecular transport to occur, a molecule has to jump over a discrete distance corresponding to the size of the molecule, which is only allowed if the free volume available between the two sites before and after the jump exceeds some minimum volume on the order of the molecular volume. Additionally, the rearrangement of free volume has no energy cost. The exchange of free volume and molecular rearrangement follows Boltzmann statistics normalized by the total free volume of the system. This framework results in a VFT-like dependence for the structural relaxation time. However, because this simple approach assumed only the jump mechanism for molecular rearrangement, it describes all dynamic quantities by the same temperature dependence. The extended framework of the free volume theory, developed by Cohen and Grest[176], distinguished between two types of volume elements, solid-like and liquid-like cells, and introduced percolation theory to describe the gradual development of communal entropy in the amorphous phase in order to account for thermodynamic behavior in addition to dynamic behavior. In their model, they imposed a sharp demarcation

between their liquid-like and solid-like cells, in addition to only allowing exchange of free volume among liquid-like cells in a cluster. With the set of assumptions employed in this approach, the model predicts a first-order phase transition for the liquid-glass transition in the limit of an infinitely slow cooling rate, with the characteristic temperature of the first-order transition occurring below the calorimetric glass transition, T_g , where the supercooled liquid falls out of metastable equilibrium forming the amorphous solid (glass) phase when an experimentally feasible cooling rate is applied. Their theory predicts the equilibrium liquid-glass transition to occur at a temperature greater than or equal the Kauzmann temperature, thus dodging the entropy crisis by introducing the hypothetical “ideal” glass state. Mathematically, the theory as developed by Cohen and Grest is a variation on the two-state model of Strässler and Kittel[178] from which Tanaka’s two order parameter model of the liquid state is derived.[167, 179, 180, 181, 182] This mathematical similarity accounts for the fact that this version of the free volume theory predicts a first-order transition for the liquid-glass transition. This type of theory that endeavors to resolve the Kauzmann paradox via a thermodynamic phase transition to an ideal glass state nearly arrives at the concept of polyamorphism. However, they achieve their thermodynamic transition by imposing unrealistic constraints on the dynamic evolution of the system. Despite the fact that the physical interpretation of the glass transition offered by the Cohen-Grest theory is unsubstantiated at best, and at worst, impossible to verify experimentally, the theory yields equations that can describe empirical data above T_g , but, like the VFT equation obtained from the earlier free volume theory, the theoretical basis for the equations is oversimplified and lacking physical insight.

Finally, we will briefly mention the mode-coupling theory (MCT) of the glass transition, which describes the dynamics in a liquid system using a hydrodynamic approach. The basis of the MCT is the generalized non-linear oscillator equation for the normalized density correlation function, $\Phi(t)$. [114, 117, 124, 139, 140, 183, 184, 185] The time evolution of the density correlation function is modeled as a damped harmonic oscillator with an additional term containing a memory function. The memory function effectively accounts for the effects of correlated motion, which become significant at higher density corresponding to the condensed liquid state. The dynamics associated with the type of correlated motion

described by the MCT are referred to as the “cage effect,” which is summarized by two timescales.[186] At shorter times, a particle is said to be enclosed by the cage formed by the neighboring particles. In this regime, the correlated motion of the particle in the cage incurs a steep frictional cost. This type of motion, sometimes referred to as cage rattling motion, is localized and corresponds to the secondary β -relaxation. At longer times, the cage dissolves due to diffusion of the particles from which it is formed, freeing the trapped particle and reducing the frictional load. This diffusive motive involving the freeing of the trapped particle corresponds to the structural α -relaxation. The form of the memory function is not prescribed in the theory, so an ansatz is required to obtain a solution. A simple approach is to employ a Taylor-expansion of the memory function in terms of the density correlation function, which yields a result that resembles the relaxation process of the dynamic glass transition. The structural relaxation time obtained from this idealized version of the MCT has a non-Arrhenius temperature dependence that diverges at a critical temperature, T_c , corresponding to the transition from an ergodic to a non-ergodic state. The critical temperature of the MCT is higher than both the Vogel temperature and the calorimetric glass transition temperature ($T_c > T_g > T_0$). This feature was appealing to researchers who hoped to reframe the problem of the glass transition around a temperature that was fixed for the system corresponding to a physical quantity that could be directly measured by experiments. The critical behavior of the structural relaxation time given by the MCT was found to agree reasonably well with the dynamic crossover observed in a number of molecular glass-formers. The focus on the empirically-derived dynamic crossover temperature, found to be close to T_c for a number of glass-formers that exhibit a fragile-to-strong crossover in their dynamics, would allow a description of the dynamic glass transition without relying on a convention to define the glass transition temperature and avoids the Kauzmann paradox by predicting a transition to a non-ergodic state well above T_K . Unfortunately, dynamic crossover behavior is not observed prominently in all glass-forming systems, so this application of the MCT is limited. Additionally, a number of results from the MCT do not agree with experimental observations. Modified versions of the MCT have been explored[187, 188, 189], however the general approach of the model

appears to be invalid and insufficient to describe the universal features of the dynamic glass transition.[114, 190]

In practice, when analyzing experimental dynamic data, many researchers rely on the widely-applicable VFT equation, preferring a model-free approach to parameterize the dynamic glass transition. The parameters of the VFT equation can be used to quantify characteristics of the glass transition, including the calorimetric glass transition temperature, fragility, and the Vogel temperature. Model-free analysis of dynamic crossover behavior can be performed using derivative methods.[115, 117, 125, 191, 192] Additionally, the connection of the Adam-Gibbs model to the VFT equation makes it possible to compare dynamic quantities measured by dielectric or mechanical spectroscopy, for example, directly with calorimetric data measured by differential scanning calorimetry. Even though the Adam-Gibbs model does not fully succeed in explaining the dynamic glass transition, it has shown limited validity in describing certain data sets and offers a simple picture that accounts for the role of cooperative motion in the dynamic glass transition.

No theory attempting to explain the glass transition has yet achieved success in accounting for all observed phenomena or resolving all open questions. The glass transition is among the greatest unsolved problems in condensed matter physics. There are some who are working currently to develop a framework that can account for vitrification as well as polyamorphic behavior by relying on a two-state description of liquid matter.[123, 124, 181, 182, 193, 194, 195, 196] This idea is intriguing, but it remains unresolved whether the two-state description is generally applicable to all liquids or if it is only valid in a subset of systems. On this note, we conclude our review of the dynamic glass transition and let the mystery be.

2.1.4 Liquid-liquid transition and the phenomenological two order parameter model

Having discussed some of the key features that define the liquid state in general and peered into some of the complexities that make a general theory of the liquid state difficult to construct, we now turn our discussion to the liquid-liquid transition (LLT). This strange and

elusive phenomenon is the central topic of this dissertation. For those who are unfamiliar with the concept, it may sound fanciful, or even impossible, for more than one liquid phase to exist in a single component system. It seems counterintuitive only because we are accustomed to imagining a liquid as a homogeneous medium composed of molecules in a completely disordered and isotropic arrangement on the microscopic level. However, this conception is oversimplified. A liquid is never entirely homogeneous nor completely disordered nor even truly isotropic on the local level where individual molecules can be discerned.[112, 190] From the perspective of a single molecule, its state is defined in relation to the neighboring molecules that surround it. In order to conceptualize the LLT, we only need to assume that the state of the molecule in relation to its neighbors can switch between two fundamentally distinct ways of arranging the set of molecules in question, one where the molecules minimize the average distances between their neighbors and another where the molecules adopt a locally symmetric configuration with a preferred orientation of the molecules by taking advantage of specific interactions between neighboring molecules. If we allow this local switching between distinct states defined by two different ways of achieving a locally minimal energy configuration, then all we need to have an LLT is a way to drive the switching between local states in the system such that the liquid goes from having an abundance of one state to having more of the other. The composition of the liquid does not change, and the bulk liquids are both homogeneous, disordered, and isotropic, but the local states of the molecules have changed in a definite way, which has implications for the bulk properties of the liquid.

A liquid-liquid transition can be defined as a first-order phase transition from one liquid state to another liquid state of the same composition. The existence of the LLT was first hypothesized based on computational studies of liquid water suggesting that water’s anomalous properties in the supercooled metastable liquid state originate from a second critical point, similar to but other than the liquid-gas critical point.[197] Since the existence of the second critical point, termed the liquid-liquid critical point (LLCP), was first conjectured for the case of water, researchers began looking for evidence of LLT in other systems as well. In the 30 years following the conception of the LLCP as the source of water’s anomalous behavior, numerous examples of single-component liquid systems that

apparently undergo LLT have been identified in the literature, ranging from simple atomic liquids, like phosphorus[23, 24, 198], silicon[20, 21], carbon[76], and sulfur[82], to molecular liquids, including triphenyl phosphite (TPP)[25, 26, 27, 28, 29, 86, 124, 199, 200, 201], *n*-butanol[84], and D-mannitol.[87, 124, 202] Despite the substantial and growing body of literature supporting the existence of LLT in real liquid systems, along with model systems suggesting a generic mechanism for the manifestation of LLT behavior[8, 10, 11, 12, 13, 77, 85, 150, 203, 204], the field remains plagued by controversy on the basis that the LLT in pure water exists in the so-called “no man’s land” region of the phase diagram making unambiguous experimental observation of LLT nearly impossible due to homogeneous crystal formation in real water under the conditions where the LLT is to be found.[5, 205]

In an effort to provide a theoretical foundation for LLT phenomena, Tanaka introduced the two order parameter (TOP) model of the liquid state as a framework to understand the anomalous properties of liquids ascribed to the existence of the LLCP.[14, 179, 180, 190, 206, 207, 208] In the TOP model, the liquid state is fully specified by two scalar order parameters, density ρ and the fraction of locally favored structures ψ . The density order parameter, ρ , naturally describes the liquid-gas transition and is the single order parameter given in the classical theory of the liquid state. The second order parameter, ψ , is introduced to account for local structural ordering in the liquid arising from many-body interactions. In this conception, two competing types of ordering emerge in the local arrangement of constituent particles. The distinction between the two types of local ordering is defined in terms of possible states in the underlying liquid structure. The TOP model distinguishes between two types of liquid states, ρ -states associated with the density order parameter and ψ -states associated with locally favored structures (LFS). The two-state description of liquid matter forms the basis for the formulation of the TOP model. The two states are defined by energy levels corresponding to the local configuration of liquid particles. The higher energy ρ -states are associated with the “*normal liquid structures*” (NLS) described by the pairwise interactions governed by the density order parameter ρ . The lower energy ψ -states are related to the LFS connected to the order parameter ψ defined as the fraction of LFS. Figure 2.2 shows a schematic depiction of the two state description of liquid matter. Each of these states are defined by three parameters, namely their energy E_i , volume v_i , and

degeneracy g_i , where $i = \rho$ or ψ . The phenomenological two-state description of the liquid state, which forms the basis for Tanaka's TOP model, was originally developed by Strässler and Kittel[178], in which a system having two energy levels of the type represented in Figure 2.2 can be shown to undergo a phase transition of the first or second order depending on the parameters used to specify the system.

In the two-state description of the liquid state, locally favored structures are spontaneously generated and destroyed in a sea of normal liquid structures. Assuming a finite lifetime for the LFS, the order parameter ψ can be defined as the equilibrium fraction of LFS, that is the fraction of particles in the ψ -state (ground state). We can parameterize the system in terms of the differences in the energy (ΔE), specific volume (Δv), and entropy ($\Delta \sigma$) of the ρ - and ψ -states, given by Equations 2.5, 2.6, and 2.7, respectively.[5, 14]

$$\Delta E = E_\rho - E_\psi \quad (2.5)$$

$$\Delta v = v_\rho - v_\psi \quad (2.6)$$

$$\Delta \sigma = k_B \ln \frac{g_\rho}{g_\psi} \quad (2.7)$$

where k_B is the Boltzmann constant. The change in free energy associated with the formation of LFS can then be written as:

$$\Delta G = \Delta E - T\Delta \sigma + \Delta v P \quad (2.8)$$

where T and P are the temperature and pressure of the system, fully specifying the thermodynamic state for the single-component liquid.

We can express the relevant part of the mean-field free energy of the liquid which describes the LLT as a function of ψ , given by the equation:

$$f(\psi) = f_\rho - \Delta E \psi - \Delta v P \psi + J \psi (1 - \psi) + k_B T \left(\psi \ln \frac{\psi}{g_\psi} + (1 - \psi) \ln \frac{1 - \psi}{g_\rho} \right) \quad (2.9)$$

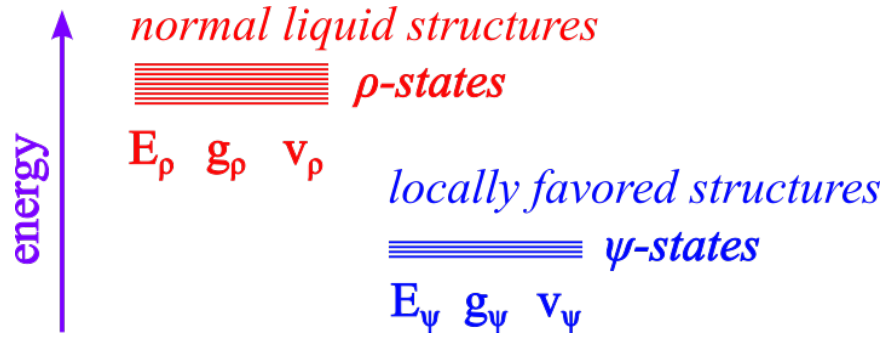


Figure 2.2: Schematic representation of a two-state liquid. The excited state (higher energy) corresponds to the normal liquid structures (NSL) characterized by energy E_ρ , volume v_ρ , and degeneracy g_ρ . The ground state (lower energy) corresponds to locally favored structures characterized by energy E_ψ , volume v_ψ , and degeneracy g_ψ .

where f_ρ is the free energy corresponding to the NLS (ρ -states) and J represents the cooperativity of the formation of LFS.[5, 14] The value of ψ at equilibrium is defined by $\delta f(\psi)/\delta\psi = 0$. At the liquid-liquid critical point, the following conditions involving the derivative of the free energy with respect to the order parameter ψ governing the LLT must be satisfied:

$$f'_\psi(\psi_c) = f''_\psi(\psi_c) = f^{(3)}_\psi(\psi_c) = 0; f^{(4)}_\psi(\psi_c) > 0 \quad (2.10)$$

with ψ_c being the equilibrium value of ψ at the critical point. From Equation 2.9, we obtain the critical fraction of LFS, ψ_c , the critical temperature, T_c , and the critical pressure, P_c , given by Equations 2.11, 2.12, and 2.13, respectively.

$$\psi_c = 1/2 \quad (2.11)$$

$$T_c = J/2k_B \quad (2.12)$$

$$P_c = (-\Delta E + T_c\Delta\sigma)/\Delta v \quad (2.13)$$

It is clear that the only conditions that must be satisfied for the existence of the LLT are the two-state feature and a non-zero J for the cooperative formation of LFS. The first-order LLT is determined by two points in the 2D ρ - ψ plane of the free energy of the liquid with the following conditions on the values of ψ at the points labeled 1 and 2:

$$f_\psi(\psi_1) = f_\psi(\psi_2); f'_\psi(\psi_1) = f'_\psi(\psi_2) = 0; f''_\psi(\psi_1), f''_\psi(\psi_2) > 0 \quad (2.14)$$

The pressure dependence of the transition temperature, $T_t(P)$, describes a line on the T - P phase diagram given in terms of the parameters of the two-state feature:

$$T_t(P) = (\Delta E + P\Delta v)/\Delta\sigma \quad (2.15)$$

At all points on this line, we have $\Delta G = 0$ and $\psi = \psi_c = 1/2$. The first-order LLT only occurs for $T_t < T_c$. When $T_t > T_c$, $T_t(P)$ gives the so-called Widom line.[5, 14]

The top panel in Figure 2.3 shows a graphical depiction of the T - ψ phase diagram for a system with LLT.[5] Due to the scalar nature of the order parameter ψ , the LLT is a transition of the same type as the liquid-gas transition, in that it does not involve the breaking of either translational or rotational symmetry. As a consequence, the LLT, like the liquid-gas transition controlled by ρ , should belong to the 3D Ising universality class.[29, 209, 210, 211] By way of analogy, we can imagine the LLT as a phase transition between a ψ -gas and a ψ -liquid controlled by the fraction of LFS given by the order parameter ψ , in the same way that the transition between the normal gas and the normal liquid is controlled by the density ρ . Changes in the density between the two liquid states, liquid I and liquid II, arise as a consequence of the coupling between ρ and ψ , represented by the free-energy surface of the ρ - ψ plane depicted in the bottom panel of Figure 2.3.[5]

Figure 2.4 shows a representation of the P - T phase diagram for a liquid with LLT in the vicinity of the LLCPP. The positive slope of the coexistence line reflects the case where the LFS are denser than the NLS, i.e. $\Delta v > 0$. This scenario is seen in the cases of the molecular liquids, TPP[26, 209] and *n*-butanol.[84] This is likely the case for the ionic liquids in this study as well, as demonstrated by the evidence laid out in Chapters 4, 5, and 6 below. In the situation depicted in Figure 2.4, we have ΔE , Δv , and $\Delta \sigma > 0$. In this case the LLT corresponds to the transition between the less dense high-temperature liquid state (HTLS or Liquid I) and the denser low-temperature liquid state (LTLS or liquid II). The LLT is also accompanied by a change in the dynamics of the liquid reflected by the fragility of the HTLS and LTLS. At temperatures above T_c , the extension of the LLT coexistence line, where $\psi = \psi_c = 1/2$, gives the Widom line corresponding to thermodynamic and structural anomalies in the liquid properties in the absence of a first-order transition. Beyond the critical regime, this line is sometimes referred to as the Schottky line. Static anomalies are predicted to arise at higher temperatures than dynamic anomalies, due to the hierarchical nature of the two-state model. This is based on the fact that dynamic properties are not determined locally, but depend on the interaction of particles in the surrounding liquid. Thus, the dynamic behavior of a two-state liquid depends on the spatially coarse-grained order parameter $\psi^D \leq \psi$, in general. So the line where $\psi = 1/2$ gives the “static Schottky line,” while the line where $\psi^D = 1/2$ gives the “dynamic Schottky line.”[5] In systems with

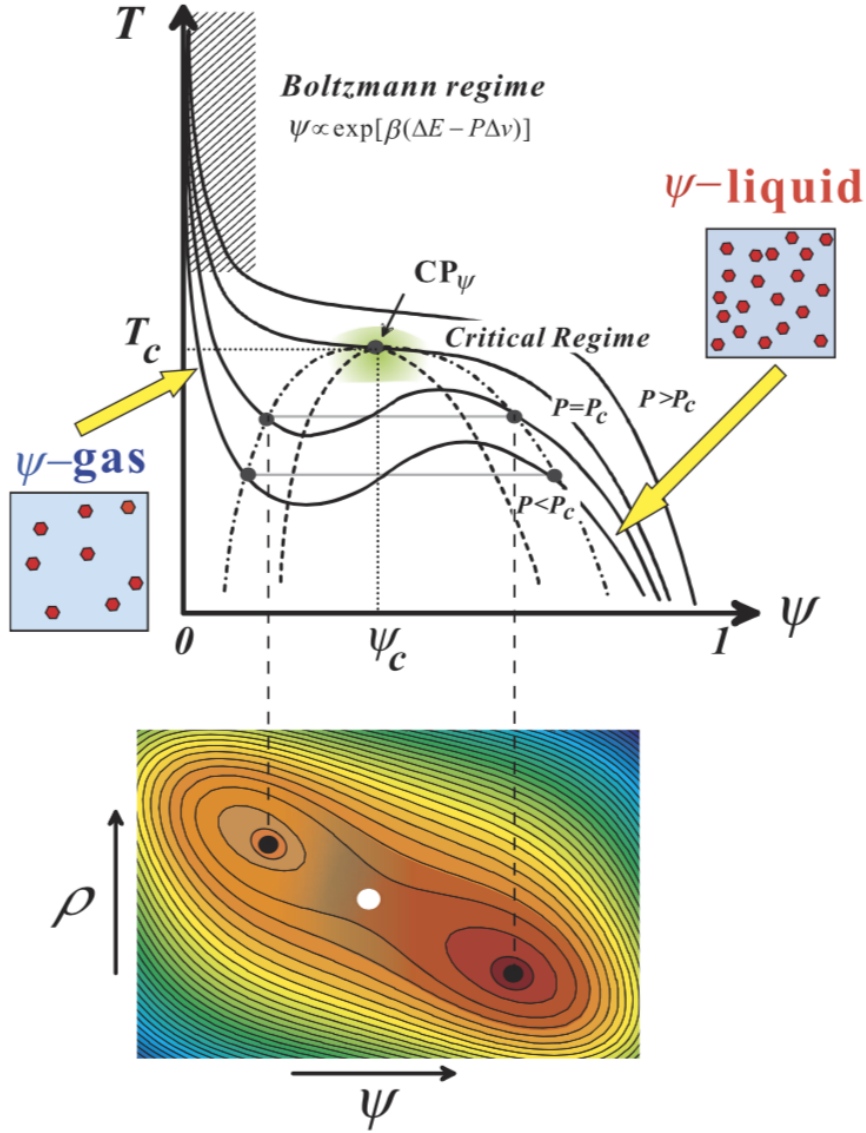


Figure 2.3: Prototypical phase diagram of a two-state liquid near the liquid-liquid critical point (LLCP). The top panel shows the phase diagram in the T - ψ plane at constant volume. The bottom panel shows the free-energy surface of LLT in the ρ - ψ plane. Reprinted from [5], with the permission of AIP Publishing.

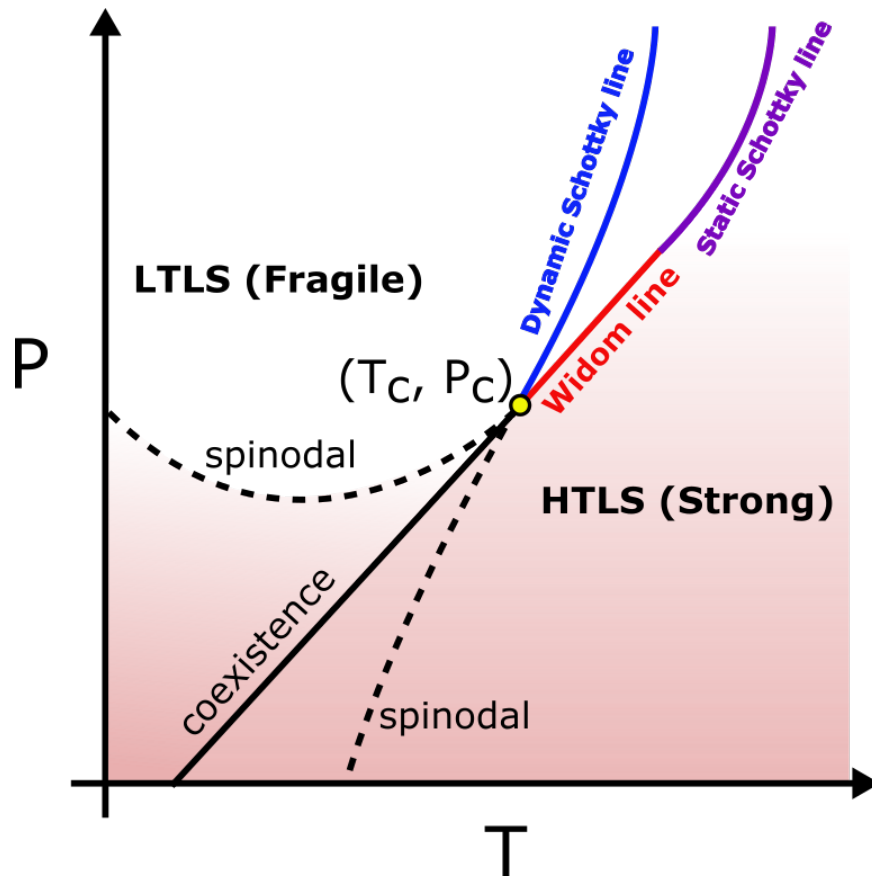


Figure 2.4: Prototypical $P - T$ phase diagram of a two-state liquid near the liquid-liquid critical point (LLCP).

criticality, these two lines should intersect at the LLCP, offering a means to systematically identify the location of the critical point.

2.1.5 Examples of liquid-liquid transition in real liquid systems

Numerous examples of LLT behavior have been identified in the literature for a range of liquid systems including pure atomic systems[20, 21, 76, 77, 82], molecular systems[18, 26, 29, 84, 86, 87, 88, 202, 212, 213, 214], oxides[211, 215], and multi-component atomic systems like metallic liquids[78, 81, 216] and chalcogenides[217, 218, 219]. A few of these examples will be presented in the following subsections. A related, but distinct, set of phenomena is the critical-like behavior of multi-component systems, or mixtures, describing liquid-liquid phase separation of the components of the mixture. Such behavior is well-studied in ionic solutions involving salts dissolved in solvents, including water and organic liquids[220, 221, 222, 223, 224, 225]. However, an example of LLT in a pure ionic liquid could not be found in the literature prior to the case of trihexyltetradecylphosphonium borohydride ($\text{P}_{666,14}\text{BH}_4$)[6], which is included in the present work, having been published in March 2021 by yours truly and coworkers.

Atomic Systems

Among the more recent examples of LLT in a pure atomic system is that of sulfur. In an article by Henry *et al.*[82] published in 2020, experimental evidence showing a density discontinuity in liquid sulfur at the LLT line was reported. Furthermore, they demonstrated that the LLT line in sulfur terminates at a second critical point (LLCP) in the equilibrium liquid state, making it the first experimental identification of the LLCP. They found the LLCP for sulfur to lie around $T_c = 1100\text{ K}-1200\text{ K}$ and $P_c = 2.1\text{ GPa}-2.2\text{ GPa}$. The LLT line for sulfur has a positive slope in the T - P phase diagram, suggesting $\Delta v > 0$, similar to the case of TPP.[26, 209] The case for LLT in sulfur appears to be supported by incontrovertible experimental evidence, but this finding is very recent and further research to understand the nature of LLT in sulfur is necessary.

A number of other pure atomic liquids that have been investigated on the basis of a possible LLT remain rife with controversy with the existence of the first-order LLT in these systems still being hotly debated. Controversial examples of LLT in atomic systems include the cases of carbon[76, 79] and phosphorus.[23, 24] In the carbon case, the proposed LLT manifests in the local coordination configuration of the atoms, which can have two-, three-, or four-fold coordination states.[5] It has been established that the coordination number of liquid carbon increases with increasing pressure, but studies have been unable to conclusively show these changes transpire via a first-order LLT with at least one account describing a gradual and continuous change from three-fold coordinated carbon to a diamond-like liquid structure, suggesting another mechanism entirely.[226] The case for phosphorus is a curious one. The initial study that reported it found that a first-order polyamorphic transition manifests in the equilibrium state, rather than in the supercooled state below the melting point, and it was therefore possible to study the coexistence of the two phases directly using X-ray scattering methods.[23] The evidence of a first-order transition is clear, but it is accompanied by a density change too large for LLT.[5] The controversial assignment of a first-order LLT in phosphorus arises from the fact that the transition occurs above the liquid-gas critical point, arising as a transformation between a dense molecular fluid and a polymeric liquid state.[24] Fundamentally, the classification of the transition observed in phosphorus hinges on establishing whether the relevant order parameter in this case is the scalar parameter associated with LLT or the type of order parameter associated with the classical λ -transition characterizing the self-avoiding walk of polymers.[5]

Water

Water is the most abundant liquid on the planet and is necessary for all life as we know it. It exhibits an unusual number of anomalous properties, many of which have been known for centuries. And yet, despite the omnipresence of this critical substance, efforts to unravel the mysterious origins of water’s peculiar properties remained largely unsuccessful in the history of science, even as the sophistication of measurements techniques and our understanding of the atomic substructure of chemical substances matured, especially following the quantum revolution of the early 20th century.

The hypothesis that water’s anomalous properties originate from the existence of a second critical point similar to the liquid-gas critical point was proposed based on a computational study put forth by Poole *et al.* in the early 1990s.[197] Controversy around the idea of LLT exploded into debate concerning whether the second critical point was merely a feature of the model used to perform the calculations or if it was, in fact, a property of real water. The difficulty in settling this debate stems from the fact that the proposed liquid-liquid critical point (LLCP) is to be found in the “no man’s land” region of water’s phase diagram, where homogeneous crystal nucleation obfuscates experimental access to the bulk liquid properties where the two phases, referred to as the high-density liquid (HDL) and low-density liquid (LDL), are predicted to coexist.[5, 124]

Efforts to experimentally confirm LLT in water include ultra-fast pump-probe techniques to examine the transition in the bulk liquid using X-rays prior to the onset of crystal nucleation[227], as well as attempts to link behavior far from the critical point to Widom line crossing and inferring the existence of two-state behavior based on changes observed in certain dynamic and thermodynamic properties.[13, 18, 214, 228, 229] Recently, Shi and coworkers[230] reported verification via X-ray diffraction of bimodality in the distribution of molecular orientations, a fingerprint of the two-state feature in water’s liquid structure, supporting the validity of the LLT hypothesis.

Triphenyl Phosphite

Triphenyl phosphite (TPP) is the earliest example of an organic molecular liquid demonstrating LLT behavior found in the literature. To date, very few other compelling cases of LLT in organic molecular liquids have even been identified. As a result, TPP has become the *de facto* model system for research into the mechanisms and origins of LLT behavior in liquids in general, partially owing to the relative ease with which it can be supercooled. The low temperature phase of TPP was first identified as an amorphous solid differing from both the normal glass and the crystalline form, and was dubbed the glacial phase.[25, 199]

Since this discovery, it was found that the glacial phase of TPP could be obtained as a second, metastable liquid phase by quenching the high temperature equilibrium liquid to a low temperature in the supercooled regime and annealing above T_g , resulting in LLT

from the normal liquid to a second liquid phase with distinct local ordering.[26] The low-temperature polyamorphic phase behavior of TPP became a testing ground for theories of the LLT and fueled speculation of the LLT being a general feature of the liquid state.[84] One consequence of the theory developed to explain LLT is the idea that the local ordering responsible for the low-temperature liquid phase would either resemble a crystal polymorph, enhancing the tendency toward crystallization, or exhibit symmetries incongruent with the crystal structure, leading to enhanced frustration and better glass forming abilities. The discovery of a second crystal polymorph in TPP suggested a link between local order in the low-temperature liquid and an equilibrium crystal structure[30, 231, 232], although the frustration scenario is still considered a viable explanation for glass-forming behavior.[233]

The two-order parameter model of the LLT has been extensively tested using the case of TPP.[27, 28, 209] The reversibility and first-order nature of the LLT has been investigated with two possible mechanisms for the transition being observed, where, depending on the annealing temperature at the onset of the transition, it can proceed either via nucleation and growth or spinodal decomposition.[200, 201, 234] One of the most critical tests of the TOP model is the identification of the order parameter governing the LLT in TPP, which was found to align with the concept of locally favored structures as a distinct state in the local ordering of the liquid, in contrast with the normal liquid structures, supporting the hypothesis of a two-state description underlying the LLT behavior in the molecular liquid, TPP.[29, 86, 235] The LLT in TPP represents a case where the evidence for two liquid phases of a single-component molecular liquid is incontrovertible. The extensive experimental studies devoted to this system have made validation of the TOP model as a suitable theoretical framework with which to explain LLT possible, lending credence to the generic nature of the two-state description of the liquid state that forms the basis of the TOP model, where two-state behavior is a prerequisite for the existence of LLT.[5, 14]

Interestingly, recent experiments into the formation of an ultra-stable glass through physical vapor deposition onto a low-temperature substrate for the TPP system resulted in the formation of the ordinary glass phase regardless of the temperature of the substrate.[236] This process of creating ultra-stable glass films is thought to rely on a similar set of underlying principles as the LLT[124, 237, 238, 239], so the result was unexpected. It was suggested

that the preferred structure of the free surface determines which polyamorphic phase will form in the as-deposited thin films.[236]

2.2 Ionic Liquids

Ionic liquids (ILs) are typically classified as salts that are liquid at or near room temperature. The low melting points of these materials is generally ascribed to delocalization of the charge on the constituent ions of the liquid, as well as asymmetries in the size and shape of the cations and anions that lead to inefficient packing which frustrates crystal formation. Typical ILs possess organic cations paired with anions ranging from simple halides to large, organic bases or even organo-metallic complexes. Common anions found in ionic liquids include chloride, bromide, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, triflate, carboxylates, sulfonates, dicyanamide, and thiocyanate.[35, 57, 66, 165, 240] Anions containing metal centers, such as iron or lanthanide elements, impart magnetic properties to the resulting IL, forming what are known as magnetic ionic liquids (MILs), which have potential applications in the areas of analytical chemistry and separation/extraction processes.[42, 47, 97, 98, 241, 242, 243, 244, 245, 246, 247, 248, 249] The possible variations of the cation and anion structures lead an innumerable quantity of different ILs that could be created. Some of the most common cations used in ionic liquid synthesis are imidazolium, pyrrolidinium, piperidinium, triazolium, tetraalkylammonium, and tetraalkylphosphonium.[31, 35, 57, 66, 250] Each of the types of cations listed here possess a side group that can be modified to change the properties of the resulting IL. In many cases, the side groups are alkyl substituents, whose length can be changed to tune the amphiphilic qualities of the cation, although substituents containing ether linkages are also common. The general properties shared by ILs in general, combined with the tunability of their cation and anion structures, make them suitable for a diverse array of potential applications including electrochemical energy storage[36, 37, 38, 39, 40], catalysis[55, 56, 57, 58, 59], extractions[63, 64], separations[41, 42, 43, 44, 45, 46, 47, 48, 61], biomass processing[49, 50, 51, 52, 53, 54], nanoparticle synthesis[58, 251, 252], tribological and heat

transfer fluids[65, 108, 253, 254], and electrospray propellants[255, 256, 257, 258, 259], to name a few.

2.2.1 Structure of Ionic Liquids

Ionic liquids are organic salts that are liquid at room temperature. As such, they are defined not only by intermolecular forces arising from repulsive exclusion and attractive cohesion, but also from charge alternation constraints. Ionic liquids are unique among liquids in general in their structural features. Since ionic liquids are composed of individual cations and anions, they possess a hierarchical structure governed by multiple correlation lengths.[68, 165, 260, 261] At the shortest lengths, adjacent ions encounter a minimum approach distance limited by ionic size and geometry stemming from steric effects and repulsion of electronic orbitals. At some intermediate length scale, ionic liquids are arranged according to charge alternation arising from constraints of net neutrality. Finally, at the longest length scales of organization identified in ionic liquids, a feature of polarity alternation is present in ionic liquids that contain long alkyl chains in either their cation or anion structure, the former being the most commonly studied. These structural features that manifest in ILs, corresponding to the three regions of the static structure factor, $S(q)$, highlighted in Figure 2.5, arise due to physical constraints on the system, and therefore relate to dynamic and thermodynamic properties of the system.

Even the simplest ionic liquids display alternating patterns in their structure on the sub-nanoscale. The constraint of local electroneutrality results in alternation between the positive and negative parts of the ionic liquid. When alkylated substituents are present on the cation, the formation of a non-polar domain where the alkyl chains reside can result. This is due to the fact that the positive and negative charges on the cations and anions, respectively, interact very strongly via the Coulombic potential. Since the neutral alkyl side groups do not interact strongly with the charged groups, they tend to be excluded from the regions occupied by the ionic groups. This behavior has been called the solvophobic effect, where molecular components with different solvent properties become spatially segregated from one another.

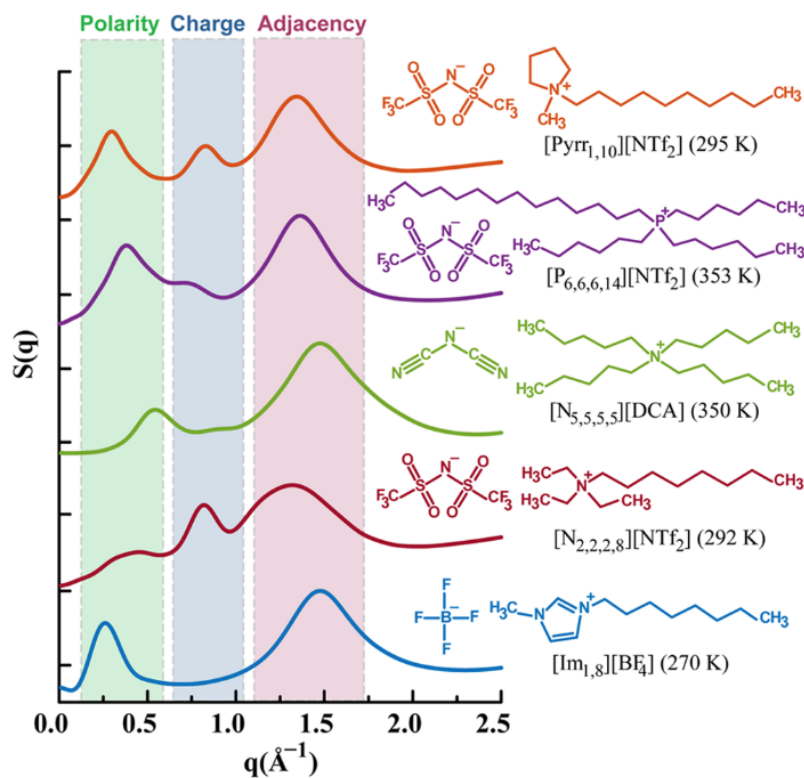


Figure 2.5: Computationally derived $S(q)$ data for a variety of ionic liquids. Reprinted (adapted) with permission from [4]. Copyright 2015 American Chemical Society.

Ionic liquids can form a number of different morphologies in their polarity alternation structure depending on the number and length of the alkyl substituents present on the cations or anions, as well as on the relative sizes of the polar and non-polar parts of the ILs.[4, 101] Most commonly, it is the cations that contain alkyl side chains. The resulting polarity alternation structure can be experimentally observed using X-ray diffraction methods, where the separation between regions of high charge density by the non-polar domains occupied by the alkyl chains results in a sharp diffraction peak at low values of q , often referred to as the first sharp diffraction peak (FSDP) or pre-peak. In homologous series of imidazolium-based ILs with the same anion, where the length of a single alkyl chain is varied, the FSDP has been observed to increase in intensity and shift to lower q values as the side chain length is increased.[262, 263, 264, 265, 266] A similar effect has been observed in the case of 1-alkyl-1-methylpyrrolidinium-based ILs.[267, 268, 269, 270]

Studies which focus on the role of the alkyl chain length present on one of the ions in an IL, typically on the cation, point to a composition-dependent percolation transition in the nanostructured morphology of the liquids corresponding to the polarity alternation level in the hierarchical structure.[4, 101] When the alkyl chains are short, segregation of the chains is found to be restricted to isolated islands of low charge density in a sea of strongly interacting cations and anions which form a continuous polar network. As the lengths of the alkyl side chains are increased, the sizes of the non-polar domains grow, and beyond a certain percolation limit that depends on the relative size of polar network formed by the charged groups, the morphology of the non-polar domains transitions from a dispersed phase to a second continuous network that permeates the polar network of high charge density.

The variation in the nanostructure of ILs as a function alkyl side chain length in the manner described above has been extensively studied in the 1-alkyl-3-methylimidazolium family of ILs, making use of both computational and experimental approaches to arrive at these conclusions.[101, 262, 263, 264, 265, 271, 272, 273, 274, 275, 276] In ILs of this type, another percolation transition has been identified as the length of the alkyl chain is further increased to lengths exceeding 14 carbon atoms. Not only do the resulting materials exhibit higher melting temperatures, they tend to form liquid crystal mesophases of the smectic variety.[266, 277, 278, 279, 280, 281, 282, 283] Examples of liquid crystal mesophases

formed in IL systems, termed ionic liquid crystals, are interesting in their own right and understanding how to control their formation and properties is the focus of considerable concerted efforts for use in a number of potential applications. But the details of ionic liquid crystal properties fall outside the scope of the topic at hand, so further discussion of these systems will be limited.

The morphology of nanostructured ionic liquids has been further subdivided into filamentous or globular sub-types, depending on the number of nearest neighbors, or the average ion coordination number, allowed in a given IL, which affects the branching of the polar network.[101] Cations with a single long alkyl substituent, such as 1-alkyl-3-methylimidazolium and 1-alkyl-1-methylpyrrolidinium, are capable of forming nearest-neighbor pairs with many (> 2) counter-ions simultaneously, which typifies the globular morphology sub-types. In contrast, tetraalkylammonium[284, 285, 286] and tetraalkylphosphonium[100, 103, 105, 287] cations, having four carbon chain substituents that hinder the ability of the central cation to interact with numerous counter-ions simultaneously, form non-branching sequences of alternating charges, resulting in thread-like structures in the polar network of ILs based on these cation types typical of the filamentous sub-type. In ILs containing these cation types, the relative lengths of the four alkyl chains will ultimately determine the morphology of the polar network. It has been shown that triethylalkylphosphonium-based ILs, having three alkyl tails only 2 carbons long, will display the globular-type morphology, while tributylalkylphosphonium-based ILs, with three of the alkyl tails being 4 carbon atoms long, will exhibit the filamentous sub-type.[287] Further extension of the alkyl chains on the tetraalkylphosphonium cation typically results in a filamentous polar network in ILs based on this cation, the most well-studied example of which are the trihexyltetradecylphosphonium-based IL systems.[100, 102, 103, 104, 106, 288] The filamentous structure found in ILs bearing the trihexyltetradecylphosphonium ($P_{666,14}$) cation is schematically represented in Figure 2.6, with characteristic length scales indicated by the double arrows indicating polarity alternation, charge alternation, and ion adjacency corresponding to the first, second, and third features in the static structure factor, $S(q)$, respectively, in ascending order of peak position on the q -axis. Although temperature-dependent studies of IL structure are uncommon, investigations of this nature have been

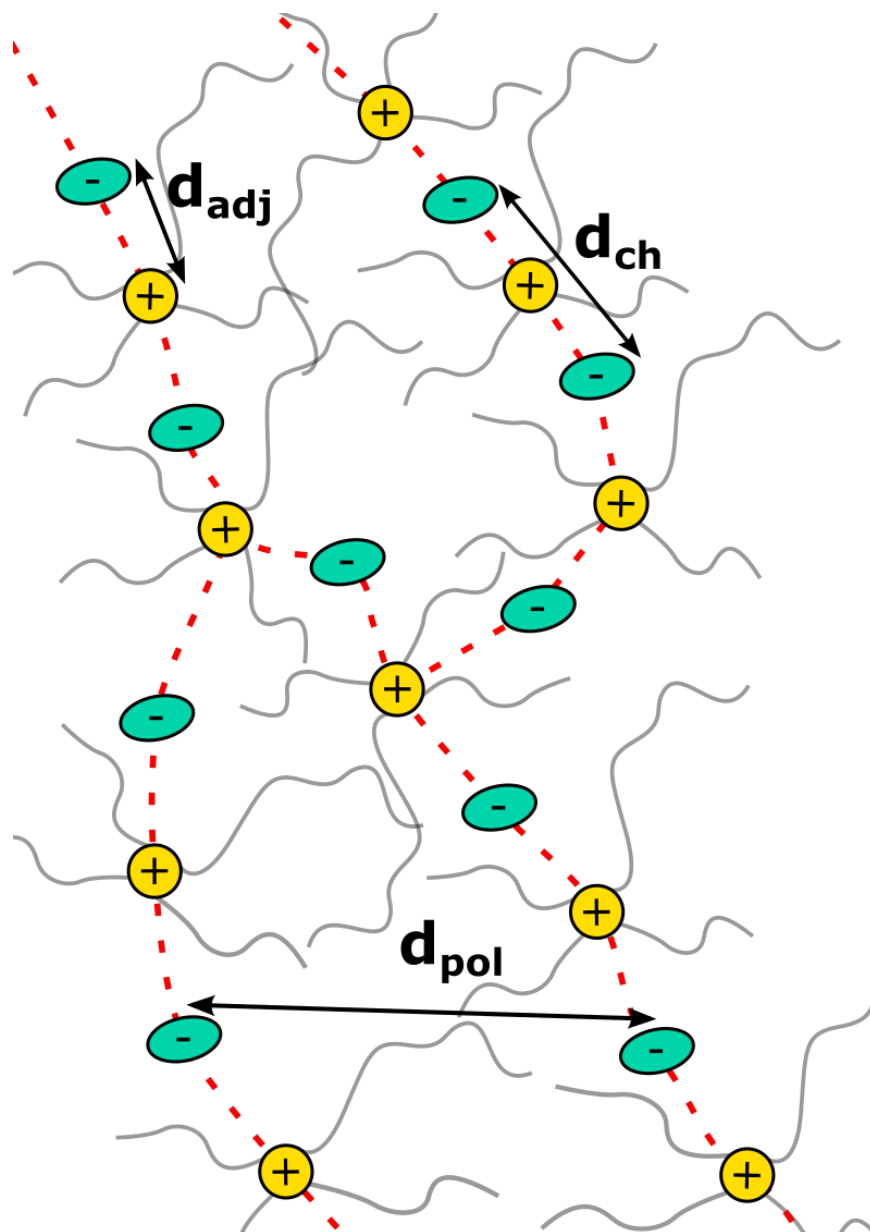


Figure 2.6: Schematic representation of the structure of a $P_{666,14}$ -based ionic liquid in the high temperature liquid state (HTLS). The polar charge network is described as a 3-D percolated network composed of alternating positive and negative ions forming filamentous structures or strands. The strands are separated by the non-polar regions composed of the 14-carbon chains and decorated by the 6-carbon chains. The resulting polarity alternation structure is described as a bicontinuous network of alternating polar and non-polar domains or a sponge-like morphology.

undertaken. Most prescient for the topic of this dissertation is a study combining X-ray scattering and computational techniques to elucidate the effect of temperature on the structure of P_{666,14}-based ILs. [102, 103] The researchers highlight what appears to be anomalous behavior in the pre-peak of $S(q)$ for the P_{666,14} cation paired with the bis(trifluoromethylsulfonyl)imide (TFSI) anion, suggestive of competing packing interactions related to the polar and apolar sub-components of the polarity alternation structure governing the intensity of the pre-peak.[103] These studies do not cover a wide enough temperature range to uncover the LLT, which manifests much closer to the T_g of these systems, but this counter-intuitive result in the temperature dependence of the structure offers a clue to the presence of an underlying two-state feature in the local ordering of the ions in the P_{666,14}-family of ILs.

2.2.2 Dynamics and Charge Transport in Ionic Liquids

In addition to solvent properties of ILs, which are known to be largely influenced by the liquid structure on the nanoscale, the intrinsic ionic conductivity of these substances is an important property for their potential use in a variety of applications. Since ionic liquids are pure electrolytes, composed entirely of cations and anions, they exhibit high ionic conductivity, making them materials of interest for a number of electrochemical technologies for energy storage, analytical chemistry, and separation/deposition processes, to name a few. Ionic conductivity results from the transport of free, mobile charge carriers in a material. The charge carriers in an IL are the cations and anions, which also comprise the structural units of the fluid. As a result, the structural relaxation is coupled to charge transport in room temperature ionic liquids over a wide range of temperatures. However, this may not be the case for all ILs at all temperatures.

The connection between structural relaxation and charge transport in ILs can be studied using dielectric spectroscopy, which is capable of yielding accurate measurements of relaxation times and dc ionic conductivity. However, separating the independent contributions from structural relaxation and charge transport requires careful analysis. Another approach is to use dielectric measurements to determine dc ionic conductivity

combined with other experimental techniques capable of determining structural relaxation times such as dynamic mechanical spectroscopy or dynamic light scattering.

Similar to other glass-forming liquids, ILs exhibit non-Arrhenius behavior in the temperature dependence of their dynamic properties following a typical VFT-like dependence. The various dynamic properties relevant to the understanding of charge transport in ILs include dc ionic conductivity, σ_0 , and the self-diffusion coefficient, D . The dynamic glass transition in ILs can be characterized by the structural relaxation times, τ_α and viscosity, η . Viscosity and structural relaxation are linked in the dynamic glass transition according to Maxwell's relation, $\eta \propto \tau_\alpha$.^[289, 290] This suggests a means by which one could test the coupling of charge transport in ILs to the dynamic glass transition by comparing timescales corresponding to the onset of dc ionic conductivity from dielectric measurements to viscosity data. In the classical theory of liquids, the diffusion of molecules in the liquid can be related to the timescale of the structural relaxation of the liquid medium by the inverse proportionality defined by the Stokes-Einstein relation, $D \propto \frac{1}{\tau_\alpha}$.^[289, 290, 291, 292] Another relation of significance for the case of ILs is the Nernst-Einstein equation relating σ_0 and D , given by:

$$\sigma_0 = n \frac{q^2 D}{kT} \quad (2.16)$$

where n is the number density of free ions, q is the charge on the ions, k is the Boltzmann constant, and T is the temperature.^[289, 290, 291, 292] We can rewrite this equation, replacing D with a term proportional to the timescale of ion diffusion, and we get the Einstein-Smoluchowski equation:

$$\sigma_0 = n \frac{q^2 \lambda^2 \omega_c}{6kT} \quad (2.17)$$

where λ is the characteristic diffusion length and ω_c is the characteristic rate of ion diffusion related to the onset of dc conductivity.^[289, 290, 291]

The relations between the various dynamic quantities relevant to charge transport and glassy dynamics have been tested for a wide array of different ILs using a combination of experimental methods including dielectric spectroscopy, dynamic mechanical spectroscopy, dynamic light scattering, and pulsed field gradient nuclear magnetic resonance. Remarkably, these relations hold for many of the IL systems that have been studied, which suggests the

mechanism of charge transport in ILs is a diffusion process mediated by the dynamic glass transition, and therefore the fragility of the liquid is an important quantity in determining the charge transport properties in ILs.[287, 289, 290, 293, 294, 295, 296, 297, 298, 299, 300] The dynamics of ILs vary considerably with changes in the cation and anion structures. Changing the type of anion while keeping the cation structure constant can result in differences in dynamic properties spanning in excess of 6 decades approaching T_g . However, variation is present in the values of T_g as determined by differential scanning calorimetry as well. When dynamic quantities are normalized by T_g , they are found to coincide across the various anion structures, further revealing the universal nature of the dynamic glass transition and charge transport in ILs.[289, 296, 300, 301]

The number density of free ions, n , present in both the Nernst-Einstein and Einstein-Smoluchowski equations plays an important role in the dc ionic conductivity. It turns out that the diffusion coefficient, D , contains all of the non-Arrhenius behavior contributing to the VFT-like temperature dependence of σ_0 . The temperature dependence of n has been found to follow an Arrhenius activation law. This factor is determined by the formation and dissociation of ion pairs in the liquid. It is important to recognize that only free, dissociated ions can contribute to the dc ionic conductivity of a pure ionic liquid and in general, the number of free ions in ionic liquids is less than the total number of ions. The fraction of free ions is typically found to vary from about 0.5 to 0.8.[72] Determining the degree of ion dissociation in an IL is crucial for developing technologies based on the electrolytic properties of ILs.[71, 72, 302]

Beyond the dynamics of the glass transition and charge transport, slow relaxation behavior has been found in ionic liquids bearing long alkyl chains, indicating these slow dynamics originate from the nanostructured morphology of the polarity alternation structure.[287, 298, 299, 303, 304] The evidence for slow dynamics associated with the ionic liquid nanostructure suggests the dielectric manifestation of this phenomenon is the result of interfacial polarization of the polar-apolar domain boundaries and it is only observed in ILs with a globular-type morphology of the polar network.[287]

2.2.3 Phase Behavior of Ionic Liquids

Any liquid that is cooled below its melting temperature will ultimately follow one of two possible paths. One possibility is that it will crystallize into the solid state. However, the formation of the crystalline phase is a kinetic transformation that generally proceeds in two steps, nucleation and growth. Due to the time required for the liquid to transform into the crystalline solid, most liquids are able to be cooled fast enough to remain in a metastable, supercooled liquid state. As the temperature of the liquid is decreased below the melting point, the kinetic processes necessary for the formation of stable crystals become slower. When a liquid is cooled at a critical rate to avoid the formation of stable crystals, it will ultimately form a glass at some temperature where the dynamic motion of the constituent particles slows to the point that the structural relaxation time of the system exceeds the experimental timescale. There are many examples in the literature of ionic liquids showing glass-forming ability with relative ease.[92, 305, 306, 307] Even still, ILs exhibit the full spectrum of supercooling behaviors, from excellent glass-forming ability to crystallization kinetics fast enough to render supercooling to the glass a technical challenge.[308, 309, 310] The intermediate behavior of cold crystallization is a common observation in many IL systems. This phenomenon describes the case where the system, starting from above the melting point, will supercool to a glassy state at nominal cooling rates, but upon reheating from the glass to the liquid, the system spontaneously crystallizes at a temperature above T_g , but below T_m . Further heating results in the solid melting back to the liquid state at T_m .

In addition to the glassy and crystalline forms obtained by cooling ionic liquids, other examples of phase behavior in ionic liquid systems reported in the literature include crystal polymorphic behavior[308, 311], ionic liquid crystal mesophases[266, 277, 278, 279, 280, 281, 282, 283], and liquid-liquid phase separation in binary mixtures of ILs with other solvents.[220, 221, 222, 224, 225] Prior to the undertaking of the work reported in this dissertation, part of which was published focusing on the trihexyltetradecylphosphonium borohydride ($P_{666,14} BH_4$) case[6], no examples had been given in the literature of LLT in a pure IL system.

2.2.4 Ionic liquids as candidates for studying liquid-liquid transition

Liquid-liquid transitions are a general feature of liquids that possess a two-state description of their local structure. It has been hypothesized and demonstrated both experimentally and by computational methods that even the simplest liquids can be described using the two-state model, where both low-symmetry normal liquid structures and locally preferred structures coexist. In the cases of monatomic and certain metallic liquids that can be described by a spherically symmetric potential, the LFS exhibit icosahedral symmetry.[150, 179, 208, 312, 313, 314, 315] Molecular liquids have also been shown to align with a two-state description with LLT being a consequence of this feature. The case of ionic liquids should, in principle, be no different. However, for larger and more complex molecular structures, determining the appropriate descriptor for the LFS is not a trivial task. Nevertheless, it is reasonable to assume that a two-state description can be applied to complex liquids, including ILs[71, 316], and therefore we can expect that cases of LLT in ILs should exist. It is prudent to ask, why, then, has a case of LLT in an IL not been found previously? The simple answer is no one thought to look. But then we find ourselves with the question of what we should be looking for.

First of all, since many examples of LLT in the literature occur somewhere in the supercooled liquid state below T_m , it is reasonable to assume that a case of LLT in an IL system would manifest in the supercooled regime as well. To avoid the ambiguities that would arise in extracting evidence of LLT from data obscured by incipient crystallization, we should prefer ILs with excellent glass-forming ability. Second, with foreknowledge concerning particular morphological sub-types of various common IL systems, we can rationalize which systems are most likely to manifest LLT. We are also able to rule out certain IL systems that have been extensively studied down to the glass transition temperature, as it is unlikely LLT would have gone unnoticed in such cases. Regarding the morphology required for a potential candidate for LLT in an IL system, we can only speculate. However, if we take a filamentous-type IL, we could rationalize a possible anion pairing where, at a reduced temperature, the sequential arrangement of ions could become increasingly condensed and

branched, taking on more of a globular-type arrangement in the polar network. If such a change could manifest at a reduced temperature through a first-order transition, it would represent a case of LLT in a pure IL system. This line of reasoning suggests we should consider $P_{666,14}$ -based ILs paired with small, non-coordinating anions, which would increase the likelihood of multiple anion associations with a central cation. This particular choice is further justified by the anomalous behavior already observed in the temperature dependence of the structure of $P_{666,14}$ -based ILs originating from competing interactions associated with the polar and apolar sub-components, lending credence to the hypothesis of an underlying two-state feature that may be lurking in cation-anion interactions in ILs. The rationale for the choice of IL to look for the LLT described here is meant to clarify why we have chosen the specific set of $P_{666,14}$ -based ILs studied in this dissertation. The Venn diagram shown in Figure 2.7 is meant to represent how three subsets of liquid matter, namely glass-formers (GF), ionic liquids (ILs), and polyamorphic systems (LLT), might intersect. The six $P_{666,14}$ -based ionic liquids chosen for this study (see Figure 4.1 in Chapter 4 for details) are represented by the regions occupied by the stars on the diagram. Five of the six show all three of the attributes on the diagram, with the remaining sample, which is lacking LLT behavior, serving as a comparative example of normal glass-forming behavior in an IL.

A quote from Angell found in a monograph from a book published in 2012 on the subject of supercooled liquids and glasses[140] reveals that the conspicuous lack of studies regarding the existence of LLT in pure ILs did not go unnoticed. He states, “What is needed, now, is a study of a fragile ionic liquid with a phase transition similar to that of triphenyl phosphite...”[140] He, additionally, expressed his opinion that such a study “should...be regarded as a matter of some urgency.”[140] The set of experiments described in the following chapters of this dissertation represent the long-awaited study prescribed by Angell almost a decade ago.

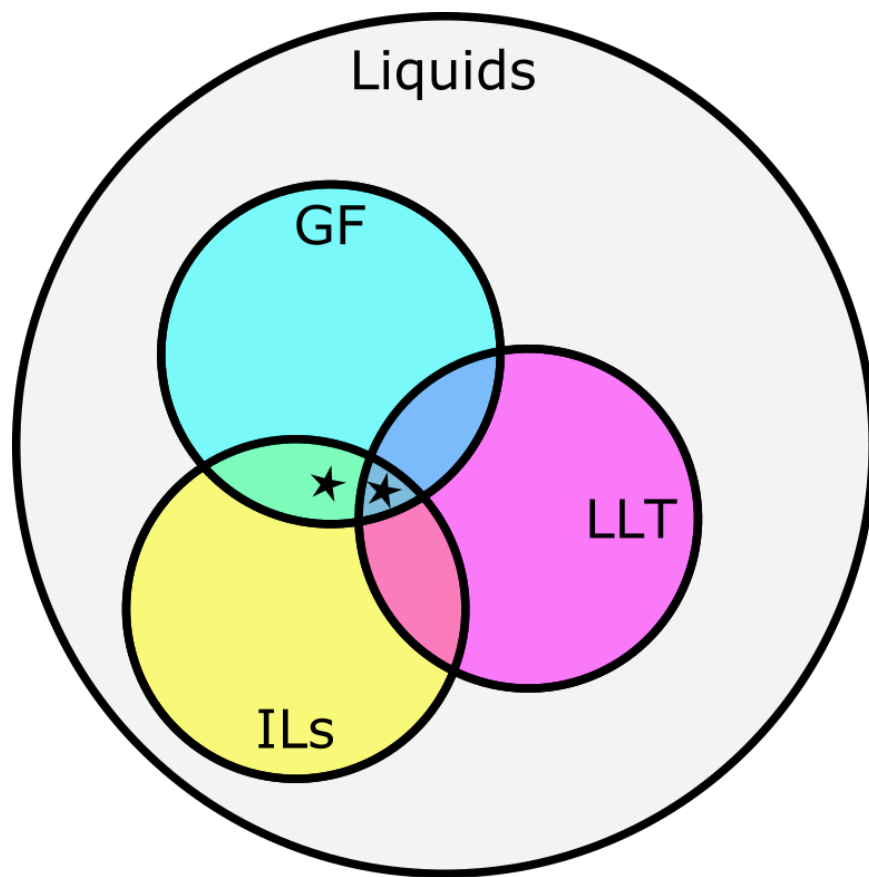


Figure 2.7: The intersection of three subsets of liquid matter, glass-formers (GF), liquids with a first order liquid-liquid transition (LLT), and ionic liquids (ILs), forming the basis for the present work.

Chapter 3

Experimental Methods

In this chapter, the experimental techniques employed in this research and the physical principles upon which they are founded are discussed. These methods include broadband dielectric spectroscopy (Section 3.1), wide-angle X-ray scattering (Section 3.2), Raman spectroscopy (Section 3.3), and differential scanning calorimetry (Section 3.4). Broadband dielectric spectroscopy is the primary experimental tool in this work as it is capable of providing accurate measurements of transport and dielectric properties yielding information concerning dynamics from local molecular fluctuations, the structural relaxation, ion transport, and mesoscopically correlated regions, as well as macroscopic properties including the dc ionic conductivity and the static dielectric permittivity. The dielectric measurements are complimented by differential scanning calorimetry, which provides information related to dynamics in addition to thermodynamic properties related to phase transitions. Wide-angle X-ray scattering is used to examine the local structure and organization of the ionic liquids in this study and provide insight into the relation between dynamic and macroscopic properties and the local structure in these systems. Raman spectroscopy is employed to probe the local conformational order of the alkyl tails on the tetraalkylphosphonium cation, which augments the structural information obtained via wide-angle X-ray scattering.

3.1 Broadband Dielectric Spectroscopy

Dielectric spectroscopy is a powerful experimental technique that has been used to study polarization phenomena for over a century. It has its historical roots in the scientific discoveries of Henry Cavendish.[317, 318] Much of Cavendish’s research went unpublished during his lifetime. Nevertheless, we know of many of his accomplishments thanks to James Clerk Maxwell, who edited a considerable swath of Cavendish’s original manuscripts and made them publicly accessible for the first time in 1879.[317, 318] Key among Cavendish’s findings was his observation that the capacity of a condenser (an early term for a capacitor) depended on the material used in its construction as well as being proportional to the surface area of the foil electrodes and inversely proportional to the thickness separating the conducting foil. These concepts were later developed by Michael Faraday, who defined the property of a dielectric material or insulator as its specific inductive capacity.[318] In modern terminology, this property is the relative dielectric permittivity, ϵ . From these early investigations on the dielectric properties of matter, it was the seminal work of Peter Debye that would lay the theoretical groundwork for the molecular interpretation of dielectric spectra.[319, 320, 321, 322, 323] Debye, for whom the unit of the dipole moment is named, published his theory of dielectrics in a static electric field in 1912 followed by a treatment for the case of a sinusoidal, time-varying electric field in 1913.[319, 323] These two papers form the basis for modern molecular approaches to dielectric spectroscopy. The theoretical approach he used will be described later on in this section.

3.1.1 Theoretical foundations

The theoretical foundation of dielectric spectroscopy is summarized in Maxwell’s unifying set of equations, which relate the electric field ($\mathbf{E}$) and magnetic flux density ($\mathbf{B}$) to the source terms, total charge density (ρ) and total current density ($\mathbf{J}$).[117, 324]

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \tag{3.1}$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3.2)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (3.3)$$

$$\nabla \times \mathbf{B} = \mu_0 \left(\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \quad (3.4)$$

These equations, written in SI units, include the fundamental constants, ε_0 and μ_0 , referred to as the permittivity of free space and the permeability of free space, respectively, with $\varepsilon_0 \mu_0 = \frac{1}{c^2}$ where c is the speed of light in vacuum. The form of Maxwell's equation given above is sometimes referred to as the differential formulation or “Maxwell's equation in vacuum.” To reformulate the equations to describe the behavior of the electric and magnetic fields in bulk matter, auxiliary fields, the dielectric displacement ($\mathbf{D}$) and the magnetizing field ($\mathbf{H}$), are introduced to account for the influence of bound charges and currents in the material medium. Thus, the dielectric displacement, $\mathbf{D}$, is defined as:

$$\mathbf{D} \equiv \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon^* \varepsilon_0 \mathbf{E} \quad (3.5)$$

where $\mathbf{P}$ is the polarization of the material and ε^* is the complex dielectric permittivity function. Note this definition is only valid in the linear regime at correspondingly small electric field strengths. The polarization, $\mathbf{P}$, is the portion of the dielectric displacement that results from the response of the material to an external electric field. For small electric field strengths, the polarization, $\mathbf{P}$, is linearly related to the external field by the relation:

$$\mathbf{P} = \varepsilon_0 \chi^* \mathbf{E} = \varepsilon_0 (\varepsilon^* - 1) \mathbf{E} \quad (3.6)$$

where χ^* is the complex dielectric susceptibility of the material.[\[117, 324\]](#)

In general, ε^* is time or, inversely, frequency dependent owing to time dependent phenomena that occur within a dielectric medium. A number of types of time dependent processes occur in ordinary matter, which is composed of atoms and molecules, which, in

turn, are composed of negatively charged electrons and positively charged nuclei. At high frequencies in the optical range of the electromagnetic spectrum, atomic and molecular vibrations dominate the dielectric response, giving rise to resonance phenomena. At the lower, sub-optical frequencies, relaxation phenomena manifest due to fluctuations of molecular dipoles. If the material under investigation contains mobile charge carriers such as ions, electrons, or holes, diffusion of these charges will result in conductive or dissipative contributions to the response of the material to an applied external electric field. Essentially, these internal dynamic processes give rise to a difference between the time dependence of the external electric field, $\mathbf{E}(t)$, and time dependence of the resulting polarization response function, $\mathbf{P}(t)$.^[117]

Fundamentally, dielectric spectroscopy is concerned with understanding the polarization response of materials in the presence of an applied periodic electric field, $\mathbf{E}(t) = \mathbf{E}_0 \exp(-i\omega t)$. This is achieved by measuring the complex dielectric permittivity:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad (3.7)$$

where $\varepsilon'(\omega)$ is the real part of the complex dielectric function accounting for the storage of energy from the electric field, $\varepsilon''(\omega)$ is the imaginary part of the complex dielectric function accounting for energy dissipated by the material, ω is the radial frequency (in units of $[\text{rad}\cdot\text{s}^{-1}]$ with $\omega = 2\pi\nu$ where ν is the frequency in $[\text{Hz}]$), and $i = \sqrt{-1}$. Based on Maxwell's equations (Equations 3.1-3.4), the complex dielectric function is related to the complex index of refraction:

$$\varepsilon^*(\omega) = (n^*(\omega))^2 \quad (3.8)$$

where $n^*(\omega) = n'(\omega) + in''(\omega)$, $n'(\omega)$ is the real part of the complex index of refraction, and $n''(\omega)$ is the imaginary part of the complex index of refraction, suggesting that dielectric spectroscopy is essentially an extension of optical spectroscopy into sub-optical frequencies.^[117]

In regard to the motion of charges within a material, Ohm's law relates the current density, $\mathbf{J}$, to the electric field, $\mathbf{E}$, by the following equation, defined in the linear regime as:

$$\mathbf{J} = \sigma^* \mathbf{E} \quad (3.9)$$

where $\sigma^*(\omega)$ is the complex conductivity function with $\sigma^*(\omega) = \sigma'(\omega) + \sigma''(\omega)$ and $\sigma'(\omega)$ and $\sigma''(\omega)$ corresponding to the real and imaginary parts, respectively. Based on Maxwell's equations (Equations 3.1-3.4) and the definition of dielectric displacement (Equation 3.5), the derivative of the dielectric displacement with respect to time is equivalent to a current density, meaning that the relation:

$$\sigma^*(\omega) = i\omega\varepsilon_0\varepsilon^*(\omega) \quad (3.10)$$

holds by definition. This relation implies that $\sigma'(\omega) = \varepsilon_0\omega\varepsilon''(\omega)$ and $\sigma''(\omega) = \varepsilon_0\omega\varepsilon'(\omega)$. Thus, $\sigma^*(\omega)$ and $\varepsilon^*(\omega)$ contain equivalent information.[\[117\]](#)

3.1.2 Measuring the frequency dependent complex dielectric function

In the broad frequency range spanning 10^{-6} Hz to 10^{12} Hz, the complex dielectric function, $\varepsilon^*(\omega)$, can be measured by combining various measurement systems. In the high frequency range from 10^7 Hz- 10^{12} Hz, the complex dielectric function can be determined from reflection or transmission measurements of the complex propagation factor. These measurements require waveguide or cavity based instruments using network analysis or quasi-optical approaches. In the lower frequency range, 10^{-6} Hz- 10^7 Hz, a lumped circuit method can be employed by considering the sample as a parallel or series circuit of an ideal capacitor and an ohmic resistor.[\[117\]](#) This is the frequency domain of the dielectric measurements reported in Chapter 5.

The dielectric measurements in this work were performed in the frequency range of 10^{-1} Hz- 10^7 Hz using a Novocontrol High Resolution Dielectric Alpha Analyzer with a Quatro liquid nitrogen temperature control system with ± 0.1 K temperature stability. The samples

for these measurements were first dried under vacuum ($< 10^{-6}$ bar) at 340K for 24 hours prior to loading into the sample measurement chamber in the cryostat. The sample capacitors were prepared by filling the gap between two gold-plated brass electrodes, 20 mm in diameter, with the ionic liquids using Teflon spacers approximately 150 μ m thick to maintain a uniform distance between the electrodes. Once the samples were placed in the cryostat, they were annealed at 340K for 2 hours to ensure the liquids were uniformly distributed within the capacitor cell and thermally equilibrated by determining that the measured responses of the samples were not changing over time. After the stability of the samples was confirmed, isothermal measurements were performed by sweeping the frequency of the applied electric field from 10^7 Hz to 10^{-1} Hz with 10 data points per decade. This was done in 5K increments on cooling from 340K down to 150K and on reheating back to 340K to ensure thermal reproducibility. The same procedure was performed on a second, independently-prepared sample to check the uniformity of the results.

A schematic representation of the experimental arrangement for performing the dielectric measurements, corresponding to the Novocontrol High Resolution Dielectric Alpha Analyzer employed, is shown in Figure 3.1. In these experiments, the lower part of the sample holder, containing the upper and lower electrodes, the sample, and the thermocouple, is placed inside of the cryostat and connected externally to the analyzer, which generates the alternating signal and records the amplitude and phase of the applied voltage and the current response.

In this arrangement, the complex dielectric function of the sample can be measured in the frequency range from 10^{-6} Hz to 10^7 Hz in the following manner. The sample, in between the two metal electrodes, forms a simple, parallel-plate capacitor which is connected to the analyzer in a two-wire configuration. The signal generator is used to apply a frequency-dependent voltage, $U^*(\omega)$, to the sample capacitor and the current response of the sample, $I^*(\omega)$, is measured by the analyzer. The complex impedance, $Z^*(\omega)$, is determined by the ratio of the applied voltage to the current response, which is then inversely related to the complex capacitance, $C^*(\omega)$, according to the relations:

$$Z^*(\omega) = \frac{U^*(\omega)}{I^*(\omega)} = \frac{1}{i\omega C^*(\omega)} \quad (3.11)$$

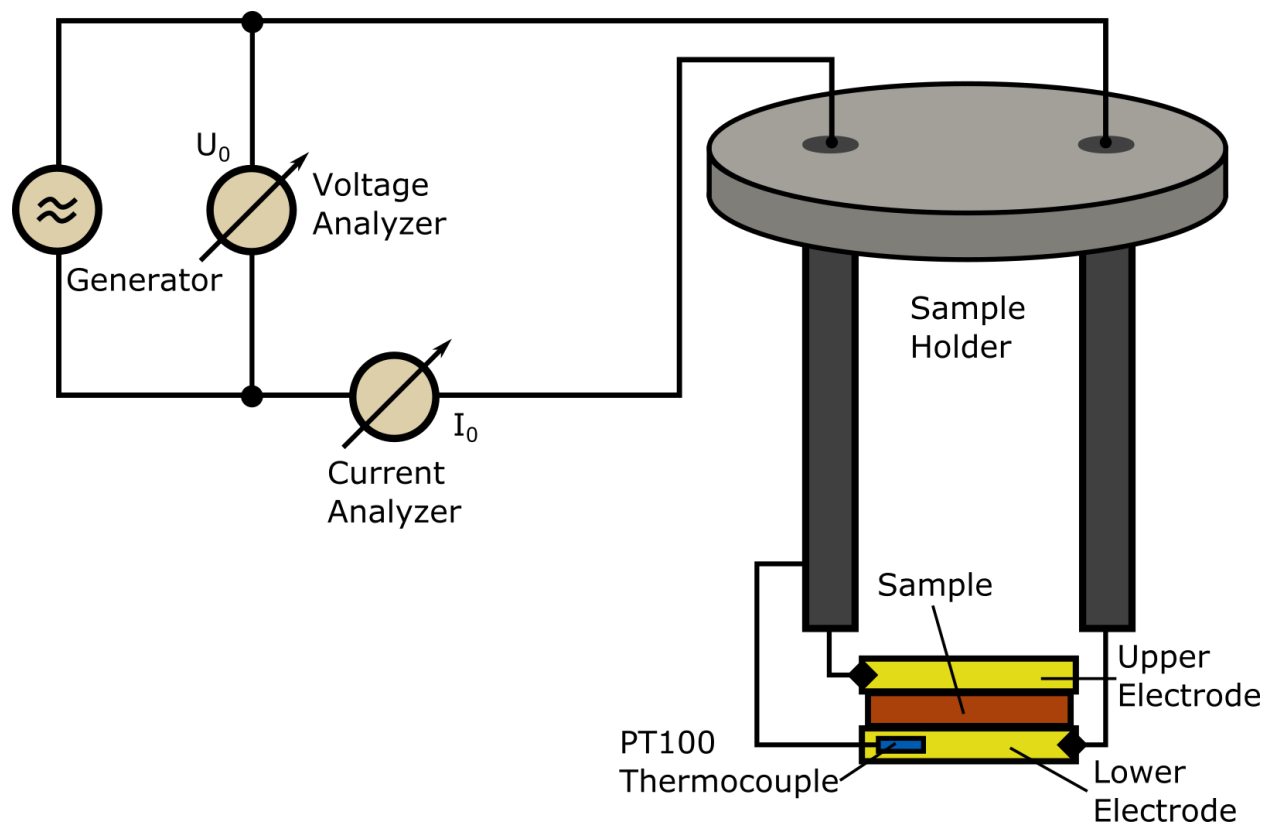


Figure 3.1: Schematic diagram of the dielectric measurement cell

where ω is the radial frequency of the applied voltage in rad/s, and i is the imaginary unit. The complex dielectric function, $\varepsilon^*(\omega)$, of the capacitor containing the sample under investigation is defined as:

$$\varepsilon^*(\omega) = \frac{C^*(\omega)}{C_0} = \frac{I^*(\omega)}{i\omega U^*(\omega)C_0} \quad (3.12)$$

where C_0 is the capacitance of the empty capacitor arrangement determined by the geometry of the electrode set-up and the vacuum permittivity, ε_0 . Modern dielectric equipment can deliver measurements of $\varepsilon^*(\omega)$ with an accuracy surpassing 10^{-4} in $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$. [117]

This technique allows us to experimentally access the complex dielectric function of a material across a very broad frequency range over a wide range of temperatures. In order to make use of this data, we must first understand how the polarization response of the material on the molecular level contributes to the measured behavior of the complex dielectric function. The remaining sections will provide a review of the static case and the time dependent polarization response, respectively.

3.1.3 The stationary case

In general, a sample material can be viewed as being composed of microscopic dipoles corresponding to the molecules (or particles) that make up the system. The macroscopic polarization, $\mathbf{P}$, is determined by the individual dipole moments, $\mathbf{p}_i$, of the constituent molecules within a given volume V of the material by:

$$\mathbf{P} = \frac{1}{V} \sum \mathbf{p}_i \quad (3.13)$$

The simplest example of a dipole corresponds to two charges, $+q$ and $-q$, equal in magnitude with opposite signs, separated by a distance, $\mathbf{d}$, resulting in a dipole moment of $\mathbf{p} = q\mathbf{d}$. The dipoles composing the system can be of a permanent or induced nature. Permanent dipoles in molecules arises when there exists a net separation of positive and negative charges in the chemical structure of the molecule. Induced dipoles, on the other hand, result from the distorting effects of the local electric field, $\mathbf{E}_{Loc}$, on neutral arrangements of charge, such as the electronic cloud surrounding an atomic nucleus. In the linear regime, the induced dipole

moment is proportional to the local electric field as:

$$\mathbf{p} = \alpha \mathbf{E}_{Loc} \quad (3.14)$$

where α is the polarizability of the atom or molecule. Induced dipole effects can be lumped together to give an induced polarization, $\mathbf{P}_\alpha$. Similarly, we can account for the polarization response from the orientation of permanent dipoles in a single term, $\mathbf{P}_\mu$. Thus, the total polarization $\mathbf{P}$, which is related to the electric field $\mathbf{E}$ by the permittivity ε of the material, is decomposed into two terms of differing molecular origins given by:

$$\mathbf{P} = \mathbf{P}_\mu + \mathbf{P}_\alpha = \varepsilon_0 (\varepsilon - 1) \mathbf{E} \quad (3.15)$$

The polarization due to induced dipoles can be further defined as:

$$\mathbf{P}_\alpha = \sum_k n_k \alpha_k (\mathbf{E}_i)_k \quad (3.16)$$

where n_k is the number density of molecules of type k , α_k is the polarizability of the molecules, and $\mathbf{E}_i$ is the local electric field. We can also define the orientational polarization as:

$$\mathbf{P}_\mu = \sum_k n_k \bar{\boldsymbol{\mu}}_k \quad (3.17)$$

where n_k is the number density of dipoles of type k , and $\bar{\boldsymbol{\mu}}_k$ is the average dipole moment of dipoles of type k in the system. For systems containing only one type of dipole, this expression can be simplified by removing the summation.[\[117\]](#)

Theoretical statistical mechanics demonstrates that the factors contributing to the average value of the dipole moment are the interactions between neighboring dipoles and the strength of the electric field in the location of the dipole. The scenario under consideration can be simplified even further by assuming the interactions between neighboring dipoles are negligible and that the local electric field strength is equal to that of the applied external electric field. In this case, the mean value of the dipole moment is determined by the energy of interaction between the dipoles and the electric field having a tendency to orient the

dipoles parallel to the external field counterbalanced by the randomizing effect of thermal fluctuations. The interaction energy, U , for an isolated dipole in an external electric field is given by:

$$U = -\boldsymbol{\mu} \cdot \mathbf{E}_d = -|\boldsymbol{\mu}| |\mathbf{E}_d| \cos \theta \quad (3.18)$$

where θ is the angle between the dipole moment vectors, μ , and the electric field, $\mathbf{E}_d$. The average dipole orientation can then be determined using Boltzmann statistics given by:

$$\langle \cos \theta \rangle = \frac{\int_0^\pi \exp \left[\frac{\mu E_d \cos \theta}{k_B T} \right] 2\pi \sin \theta \cos \theta d\theta}{\int_0^\pi \exp \left[\frac{\mu E_d \cos \theta}{k_B T} \right] 2\pi \sin \theta d\theta} = \frac{1}{a} \frac{\int_{-a}^a e^x x dx}{\int_{-a}^a e^x dx} = \coth a - \frac{1}{a} = L(a) \quad (3.19)$$

where T is the temperature in K, and k_B is the Boltzmann constant. Using the substitutions:

$$x = \frac{\mu E_d \cos \theta}{k_B T} \quad (3.20)$$

and

$$a = \frac{\mu E_d}{k_B T} \quad (3.21)$$

the integration can be carried out, resulting in the average dipole orientation being given by the Langevin function, $L(a)$. If we plot $L(a)$, as in Figure 3.2, we see that the average dipole orientation can be approximately described by a linear dependence for small values of a .^[117]

This approximation, written as:

$$L(a) \approx \frac{1}{3}a \quad (3.22)$$

holds for electric field strengths much less than 10^6 Vm^{-1} . Under the assumptions outlined above and the approximation for low field strengths, the mean value of the dipole moment for a collection of non-interacting dipoles in an external, directing electric field subject to randomizing fluctuations originating from the thermal energy of the system can be written as:

$$\bar{\boldsymbol{\mu}} = \mu \langle \cos \theta \rangle \approx \frac{\mu^2}{3k_B T} \mathbf{E}_d \quad (3.23)$$

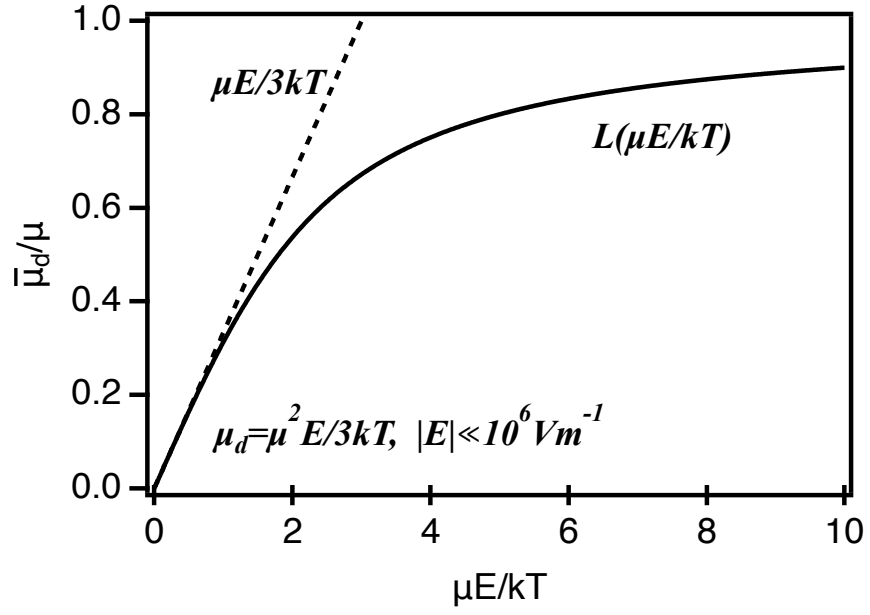


Figure 3.2: Plot of the Langevin function. $\bar{\mu}_d/\mu$ as a function of $\mu E/k_B T$ (solid line). The dashed line gives the linear approximation for low field strength.

where μ is the magnitude of the permanent dipole moment of the molecules.[117]

This result, combined with the expressions in Equations 3.15, 3.16, and 3.17, yields the following form for the total polarization response of a material to an external electric field:

$$\mathbf{P} = \mathbf{P}_\mu + \mathbf{P}_\alpha = \varepsilon_0 (\varepsilon - 1) \mathbf{E} = \sum_k n_k \left[\alpha_k (\mathbf{E}_i)_k + \frac{\mu_k^2}{3k_B T} (\mathbf{E}_d)_k \right] \quad (3.24)$$

where sum is taken over k types of molecules in the system. For a system with a single type of molecule with number density n , permanent dipole moment μ , and polarizability α , this expression can be simplified by removing the summation.

We are left with an equation that relates the static dielectric permittivity ε (sometimes called the dielectric constant), which we can measure in a dielectric experiment, to the microscopic properties of the molecules comprising the system, i.e. n , α , and μ , taking into account the randomizing effect of thermal energy on the orientation of permanent dipoles in response to an applied electric field. However, we are also left with three different electric field terms in this expression. The external electric field $\mathbf{E}$ is the applied field used to measure the dielectric constant of the sample. This is the macroscopic field determined by the design of the experimental conditions. The other two fields, $\mathbf{E}_i$ and $\mathbf{E}_d$, are both local fields, which are not equal to the macroscopic field in general. The local inducing electric field, $\mathbf{E}_i$, acts to induce dipole moments in polarizable groups by distorting the electrons around the atomic nuclei or displacing atoms from their equilibrium positions in molecules or crystals. The effects of induced polarization take place on a timescale on the order of 10^{-12} s, much faster than orientational polarization and other polarization phenomena such as charge transport and space-charge polarization. Due to differing timescales of various polarization phenomena, the static case we are considering here corresponds to the conditions at infinite time after the application of the external electric field $\mathbf{E}$ such that all microscopic contributions to the macroscopic polarization are in equilibrium. The contribution coming from orientational polarization of the permanent dipoles in the system depends on the local directing electric field, $\mathbf{E}_d$. We are left with the question as to how we should determine or define the local electric fields, $\mathbf{E}_i$ and $\mathbf{E}_d$.

In one approach, introduced by Peter Debye, the inducing and directing fields are assumed to be equal to each other and to the Lorentz field, $\mathbf{E}_l$, given by the expression:

$$\mathbf{E}_l = \mathbf{E}_i = \mathbf{E}_d = \mathbf{E} + \frac{(\varepsilon + 2)}{3} \mathbf{E} \quad (3.25)$$

The Lorentz field is itself derived by considering a spherical cavity inside a homogeneously polarized material with dielectric constant ε . An applied outer electric field polarizes the surface of the spherical boundary separating the homogeneous dielectric medium from the vacuum of the cavity. Thus, the internal electric field of the spherical cavity is determined from the contributions of the outer electric field and the polarized surface of the dielectric, yielding the expression in Equation 3.25. If we replace the local electric field terms in Equation 3.24 with the Lorentz field, we obtain:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{n}{3\varepsilon_0} \left(\alpha + \frac{\mu^2}{3k_B T} \right) \quad (3.26)$$

which is the famous Debye formula relating static dielectric permittivity ε to number density n , polarizability α , molecular dipole moment μ , and temperature T .^[117]

Considering the case of non-polar dielectrics, with no permanent dipoles, Debye's formula can be simplified to:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{n\alpha}{3\varepsilon_0} \quad (3.27)$$

referred to as the Clausius-Mossotti formula. This result can also be applied to polar materials in the high frequency limit, hence the designation of ε_∞ as the high frequency limiting value of the real part of the complex dielectric function.^[117]

For polar molecules in the gas phase or dilute solutions of polar molecules in a non-polar solvent, the Debye formula gives accurate estimates for the values of the molecular dipole moment μ or the static dielectric permittivity ε . However, for polar liquids, this simple approach fails due to the failure of the Lorentz cavity approach to accurately describe the effective local electric field around a polar molecule. An extension of Debye's theory introduced by Onsager accounts for the additional polarization arising from the reaction of the surrounding dielectric medium to a point dipole placed at the center of the Lorentz

cavity.[325, 326] This gives a more accurate estimate for the local electric field, the so-called reaction field ($\mathbf{F}$), expressed as derived by Onsager as:

$$\mathbf{F} = \left(1 + \frac{\varepsilon_\infty(\varepsilon_s - 1)}{2\varepsilon_s + \varepsilon_\infty}\right) \mathbf{E} + \frac{2(\varepsilon_s - 1)}{2\varepsilon_s + 1} \frac{\boldsymbol{\mu}}{\alpha} \quad (3.28)$$

where ε_s is the low frequency limit of the real part of the complex dielectric function, ε_∞ is the high frequency limit of the real part of the complex dielectric function, $\mathbf{E}$ is the external electric field, $\boldsymbol{\mu}$ is the molecular dipole moment vector of the dipole placed inside the spherical cavity, and α is the polarizability of the molecular.[325, 326] The resulting Onsager equation is given by:

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{n\mu^2}{9\varepsilon_0 k_B T} \quad (3.29)$$

where ε_s is the low frequency limit of the real part of the complex dielectric function, ε_∞ is the high frequency limit of the real part of the complex dielectric function, n is the molecular number density, μ is the molecular dipole moment, T is the absolute temperature, ε_0 is the vacuum permittivity, and k_B is the Boltzmann constant.[117, 325, 326] The Onsager approach yields accurate predictions for ε_s or, alternatively, μ for many pure, polar liquids so long as interactions between neighboring dipolar molecules are negligible, meaning the orientation of a dipole does not influence the orientation of its neighbors. When this is not the case, as in so-called “associating” liquids which exhibit directional or anisotropic intermolecular interactions such as hydrogen bonding, the Onsager equation fails to provide accurate predictions of the molecular dipole moment μ or, alternatively, the static dielectric permittivity ε_s .[117, 327, 328, 329]

To account for the influence of neighboring dipoles on the local dipole orientation, a correction factor was introduced by Kirkwood and Fröhlich, g_k , which describes the degree of correlation between neighboring dipoles. The Kirkwood-Fröhlich form of the Onsager equation is written as:

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{n\mu^2}{9\varepsilon_0 k T} g_k \quad (3.30)$$

In the case of $g_k > 1$, the dipoles prefer to align parallel to their neighbors, resulting in higher values for ε_s than those predicted from the Onsager approach in Equation 3.29. When $g_k < 1$,

the dipoles align anti-parallel to their neighbors, resulting in a lower value for ε_s compared to the predictions of the Onsager equation. Of course, if $g_k = 1$ the Onsager result is recovered and the dipoles in the system have zero tendency to preferentially align with their neighbors. [117, 327, 328, 329]

The dipole correlation factor, g_k , is defined in terms of the local coordination environment around the molecules in the system as:

$$g_k = 1 + z \langle \cos \gamma \rangle \quad (3.31)$$

where z is the average number of nearest neighbor dipoles and γ is the angle of orientation between neighboring dipole moments. In this way, the influence of local structural ordering can be seen to have an effect on the dielectric properties of polar liquids. [117, 327, 328, 329]

3.1.4 Time dependent dielectric relaxation

Until now, we have focused our attention on describing the polarization phenomena of dielectric materials in the static case corresponding to placing the system in an external dc electric field for a sufficiently long time that the equilibrium polarized state is developed. Now let us consider what happens in a dielectric when the external electric field is suddenly turned off. As soon as the external field is removed, the system begins to relax to a new equilibrium as the energy stored in the polarized state is dissipated by the thermal motion of molecules and the polarization diminishes. By measuring the time dependence of the polarization, information about the dynamics of the system at the molecular level can be obtained. In the regime of small electric field strengths under consideration, the polarization response depends linearly on the external electric field. Thus, the theory of dielectric relaxation phenomena is a particular case of linear response theory. Thus, the polarization response to a step change in the applied electric field strength is given by:

$$\mathbf{P}(t) = \mathbf{P}_\infty + \varepsilon_0 \int_{-\infty}^t \varepsilon(t - t') \frac{d\mathbf{E}(t')}{dt'} dt' \quad (3.32)$$

where the contributions from induced polarization are lumped together in the term $\mathbf{P}_\infty$. In this equation, $\varepsilon(t)$ is the time dependent dielectric function, which can be directly determined by measuring the time dependent response to a step-like change in the applied electric field strength. Due to the conditions of linearity and causality upon which the linear polarization response is formulated in Equation 3.32, we can consider the response of the system under the application of a stationary periodic disturbance, i.e. an alternating electric field of the form:

$$\mathbf{E}(t)(\omega) = \mathbf{E}_0 \exp(-i\omega t) \quad (3.33)$$

where ω is the angular frequency of the periodic disturbance in rad/s. Thus, Equation 3.32 can be transformed into the following expression:

$$\mathbf{P}(t)(\omega) = \varepsilon_0(\varepsilon^*(\omega) - 1)\mathbf{E}_0 \exp(-i\omega t) \quad (3.34)$$

where $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is the complex dielectric function. The real part of the complex dielectric function, $\varepsilon'(\omega)$, is related to the energy from the electric field that is stored reversibly by the system during the period of the oscillation, while the imaginary part of the complex dielectric function accounts for the dissipation of energy by the system. The complex dielectric function is related to the time dependent dielectric function by the expression:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty - \int_0^\infty \frac{d\varepsilon(t)}{dt} \exp(-i\omega t) dt \quad (3.35)$$

which is defined as a one-sided Fourier transform, or equivalently, a Laplace transform with an imaginary argument. By virtue of the fact that the complex dielectric function is given by a one-sided Fourier transform of a causal function, the real and imaginary parts of $\varepsilon^*(\omega)$ are related by the Kramers/Kronig relations, meaning that $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ contain equivalent information. This relation forms the basis for the derivative representation of the imaginary part of the complex dielectric function, defined as $\varepsilon''_{der} = (-\pi/2) [\partial\varepsilon'/\partial \ln(\omega)]$, which gives an approximation of $\varepsilon''(\omega)$ using $\varepsilon'(\omega)$ data. This approximation proves to be a valuable tool in analyzing dielectric data of systems with a significant contribution from dc conductivity including ionic liquids and other ion-conducting materials. The contribution

from dc conductivity appears in the real part of the complex conductivity function $\sigma'(\omega)$ as a frequency-independent plateau over a frequency range covering multiple (typically ~ 4) orders of magnitude between the frequency corresponding to the hopping rate of charge carriers and the frequency corresponding to the full development of electrode polarization effects caused by the blocking and accumulation of charge carriers at the metallic electrode interfaces. Based on the relation given in Equation 3.10, a strong contribution from dc conductivity appears in the imaginary part of the complex dielectric function $\varepsilon''(\omega)$ as a dispersion that increases inversely in ω , overshadowing any underlying dipolar relaxation processes that occur at or below the onset frequency of long-range charge transport. In contrast, the contribution from dc conductivity to the real part of the complex dielectric function $\varepsilon'(\omega)$ is small, so the derivative representation is useful in uncovering dipolar relaxation processes obscured by dc conductivity in $\varepsilon''(\omega)$ data.[117]

Thus far, we have only considered the macroscopic response of the system to a small (linear) disturbance. In order to connect what we measure in a dielectric experiment to the microscopic behavior of the system, we need a theoretical framework that explains how processes on the molecular level give rise to the macroscopic response observed by dielectric spectroscopy. In the framework of the linear response theory, the polarization $\mathbf{P}(t)$ of a dielectric material is the response function $y(t)$ corresponding to a disturbance function $x(t)$ defined by the application of an external electric field $\mathbf{E}(t)$. Therefore, since polarization is an intensive thermodynamic quantity defined in Equation 3.6 as a dipole moment density, $\varepsilon^*(\omega)$ is a generalized compliance $J^*(\omega)$, which is useful when comparing the results from dielectric spectroscopy to other types of relaxation measurements, e.g. mechanical or calorimetric techniques. At the same time, because polarization is a thermodynamic property describing the macroscopic state of the system, it is necessarily an average quantity, where as the stochastic nature of thermal motion on the molecular level causes the system to fluctuate around the mean value. The Fluctuation-Dissipation Theorem states that the macroscopic response of a system in the linear regime to an outer disturbance arises from the same molecular mechanism that causes the system to stochastically fluctuate about its mean value. If we write the fluctuation of the polarization at a time t as $\Delta P(t)$, we can define the

normalized correlation function $\Phi(\tau)$ for the stationary state as:

$$\Phi(\tau) = \frac{\langle \Delta P(\tau) \rangle \langle \Delta P(0) \rangle}{\langle \Delta P^2 \rangle} \quad (3.36)$$

where τ represents the variable in time. In the simplest approach to describe time dependent relaxation behavior in a dielectric material, we assume that the polarization changes in proportion to its value at time t , described by the ordinary differential equation:

$$\frac{d\mathbf{P}(t)}{dt} = -\frac{1}{\tau_D} \mathbf{P}(t) \quad (3.37)$$

where τ_D is the characteristic relaxation time of the system. This yields a correlation function that decays exponentially in time according to:

$$\Phi(\tau) = \exp \left[-\frac{t}{\tau_D} \right] \quad (3.38)$$

The complex dielectric function $\varepsilon^*(\omega)$ as determined by the exponential correlation, given by:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon \int_0^\infty \exp(-i\omega t) \left[-\frac{d\phi(t)}{dt} \right] dt = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau_D} \quad (3.39)$$

is referred to as the Debye relaxation, where $\omega = 2\pi f$ is the oscillating frequency of the external periodic electric field, $\Delta\varepsilon$ is the dielectric strength, ε_∞ is the high frequency limiting value of the real part of the complex dielectric function, and τ_D is characteristic relaxation time of dipolar reorientation. The Debye formulation describes a relaxation process with a single relaxation time. However, it turns out that most molecular relaxations display a broad distribution of relaxation times. In the time domain, processes with a distribution of relaxation times can be described using various stretched exponential correlating functions. The empirical function introduced by Kohlrausch, Williams, and Watts, referred as the KWW function, has been used to describe many cases of non-Debye relaxation behavior.^[117, 130, 164, 330, 331, 332, 333, 334] The KWW function is given by:

$$\Phi(\tau) = \exp \left[-\left(\frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right] \quad (3.40)$$

where τ_{KWW} is the characteristic relaxation time and β_{KWW} is the stretching parameter which takes values between 0 and 1 leading to asymmetric broadening at short times. In the frequency domain, modifications to the Debye relaxation model have been introduced to describe empirical results showing non-Debye behavior. The most general of these empirical formulas is given by the Havriliak-Negami (HN) function written as:

$$\varepsilon_{HN}^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left(1 + (i\omega\tau_{HN})^{\beta}\right)^{\gamma}} \quad (3.41)$$

where τ_{HN} is the characteristic time of the HN function, β ($0 < \beta \leq 1$) is the symmetric shape parameter, and γ ($0 < \beta\gamma \leq 1$) is the asymmetric shape parameter. It should be noted that the characteristic time of the HN function, $\tau_{HN} = 1/\omega_{HN}$, does not correspond to the frequency of maximum loss at the peak maximum in $\varepsilon''(\omega)$. In general, the frequency of maximum loss, which is taken to be the characteristic relaxation rate, ω_{max} , depends on the shape parameters, β and γ by the expression:

$$\omega_{max} = \frac{1}{\tau_{HN}} \left[\sin \frac{\beta\pi}{(2+2\gamma)} \right]^{1/\beta} \left[\sin \frac{\beta\gamma\pi}{(2+2\gamma)} \right]^{-1/\beta} \quad (3.42)$$

From the HN function, the empirical Cole-Cole (CC) function is obtained when γ is set equal to 1. Similarly, setting β equal to 1 yields the Cole-Davidson (CD) function. The HN model can be used to describe dipolar relaxation phenomena in a vast number of materials.^[117]

In addition to relaxations originating from the reorientation of molecular dipoles, ion-conducting systems such as ionic liquids exhibit contributions from the diffusion of charge carriers to their dielectric spectra. As mentioned previously, dc ionic conductivity due to the long-range motion of ionic species in the material appears as a frequency independent plateau in the real part of the complex conductivity function $\sigma'(\omega)$. The plateau value of σ' gives the dc ionic conductivity, σ_0 . The characteristics of the charge transport phenomena observed in $\sigma'(\omega)$ are well-described in the theoretical framework introduced by Dyre. This approach considers an isolated ion in a randomly varying potential energy landscape in which, in order for the ion to move, it must overcome or hop over randomly distributed, spatially varying potential energy barriers. The onset of dc ionic conductivity is characterized by the

timescale, τ_e , which corresponds to the average time it takes the ion to overcome the largest barrier and percolate through the system. This formulation is termed the Random Barrier Model (RBM).[335, 336] By the use of appropriate assumptions, including the continuous time random walk approximation, an analytical expression for the complex dielectric function corresponding to this mode of charge transport can be given, shown here as:

$$\varepsilon_{RBM}^*(\omega) = \frac{\sigma_0}{i\omega\varepsilon_0} \frac{i\omega\tau_e}{\ln(1 + i\omega\tau_e)} \quad (3.43)$$

depending only on the free parameters σ_0 and τ_e . [335] Since the theory upon which this formula is based considers the motion of an isolated ion with the surrounding molecules replaced by the spatially-varying energy landscape, the charge transport process described by the RBM is typically accompanied by dipolar-type relaxation resulting from the rearrangement of the molecules in the vicinity of a mobile ion following a successful hopping event.[337] An improved model of ion conduction via the hopping mechanism was introduced by Schröder and Dyre in 2008[338], in which they consider the role of the percolating cluster and the percolation threshold in the determination of the activation energy for dc ionic conductivity in the limit of extreme disorder. This approach using percolation theory to provide an accurate model of universal ac conductivity in disordered systems yields a detailed physical description of the phenomenon. They also concluded that the earlier iteration of the RBM, given by Equation 3.43, is capable of providing accurate analytical results, so long as the system under investigation is extremely disordered. Suffice to say, the approximate form of the RBM given by Equation 3.43 can be employed to analyze charge transport in ionic liquid systems without incurring significant error from the inaccuracies of the model.[339]

The systems under investigation in the present work all belong to the trihexyltetradecylphosphonium class of ionic liquids. Dielectric spectra showing typical ionic liquid behavior is often well-described by the combination of the RBM to account for charge transport and the HN function to describe the structural relaxation of the molecular dipole units comprising the system. In the case of ionic liquids in general, the cations and anions are mobile and therefore can both contribute to the dc ionic conductivity. However, strong, attractive Coulombic interactions between ions of opposite charge impose large energy

barriers impeding ion motion, meaning the motion of cations and anions cannot be considered to occur independently of each other. For this reason, every successful ion hopping event is accompanied by the cooperative rearrangement of the surrounding ions. By way of explaining the coupling between ion hopping motion and the rearrangement of the surrounding ions, consider the simple example of 4 ions, 2 cations and 2 anions, initially arranged in an alternating linear fashion, say starting with an anion (A1), followed by a cation (C1), then the second anion (A2), then the second cation (C2). Now imagine the second anion, A2, were to hop from its initial position between the two cations, C1 and C2, to a new position at the end of the line. The new arrangement is then A1, C1, C2, A2 with a void region left between C1 and C2. The tendency of the ions surrounding the void is to fill the gap, but the like charges of the 2 cations repel each other. To simultaneously fill the space left by the hopping anion and minimize the interaction potential between neighboring ions, the first 2 ions, A1 and C1, will behave collectively by acting as a single dipole that reorients or flips following the hopping event. The final arrangement of the ions following the hopping event and the accompanying rearrangement will be C1, A1, C2, A2. One could argue that the same result could be achieved if the first hopping event is followed by a second hopping event involving A1 hopping to the position formerly occupied by A2. This would also represent a valid sequence in this simplified scenario. The necessary distinction is made between ion motion in the form of a percolating conduction path through the material and ion motion that takes place locally to balance the electrostatic forces exerted by the remaining ions.

Thus, the ability of the ions to find percolated paths that traverse the system is intricately linked to the local rearrangement of ions acting to restore and maintain balance in the forces imposed by the interactions between neighboring ions. Since these two types of motion are coupled in typical ionic liquids in which the only mechanism of charge transport is the ion hopping motion, they occur at roughly the same timescale, with the ion hopping motion proceeding at a slightly faster rate due to the fact that the charge network in such systems typically form a continuously percolating, well-connected, three-dimensional cluster on which conducting paths abound. Since the local reorientation of dipoles occurs often as a reaction to a hopping event, these events proceed at a slightly slower rate on average. Due to the mobility of the ions in an ionic liquid, the dominant process in the dielectric spectra is the

dc ionic conductivity. Therefore, these systems can be classified as lossy materials since the tendency of the ion motions is to dissipate the energy of the electric field by using it to transport charges across the sample as opposed to using it to store energy in the orientation of the dipole moments. Despite their lossy nature, ionic liquids still show a modest ability to store the energy of the electric field in the arrangement and orientation of dipoles. Due to the coupling between the ion conduction and the rearrangement of dipoles and their similar characteristic timescales, the dipolar relaxation is not observable in the imaginary part of the complex dielectric function $\varepsilon''(\omega)$ due to the overshadowing contribution from dc ionic conductivity. Nevertheless, we can observe the dipolar relaxation in $\varepsilon'(\omega)$, since dc ionic conductivity contributes only weakly in this representation. In this instance, we can make use of the approximation based on the Kramers/Kronig relations given by the derivative representation, $\varepsilon''_{der} = (-\pi/2) [\partial\varepsilon'/\partial \ln(\omega)]$, to uncover the loss peak associated with the reorientation of dipoles.[117] This representation also proves useful in uncovering slower relaxation processes that can arise in ionic liquids attributed to mesoscale organization in the liquid structure.[287, 299, 303] For a graphical representation of the dielectric spectra of ionic liquids described here, refer to Figure 5.1 in Chapter 5.

3.2 Wide-angle X-ray Scattering

The discovery of X-rays is credited to Wilhelm Röntgen, who first noted this “new kind of ray” while experimenting with electrical discharge tubes. On December 28, 1895, he published his first manuscript on what he referred to as X-rays to designate the phenomenon as an unknown type of radiation.[340] Röntgen recognized the medical applications of his discovery early on, which he demonstrated by making photographic images of his wife’s hand using X-rays revealing the internal skeletal structure. However, the application of X-rays to study the internal structures of matter would not be developed until 1912 in the work of Max von Laue on the diffraction of X-rays by crystalline matter.[321, 323, 341, 342] This work confirmed that X-rays are, in fact, a type of electromagnetic radiation as described by Maxwell’s theory of electricity and magnetism (see Equations 3.1-3.4). The following year, Lawrence and William Henry Bragg proposed an interpretation of X-ray diffraction

in terms of the reflection of waves from different crystalline planes.[323, 341, 343] They observed intense peaks in diffraction patterns for certain wavelengths and incident angles of the radiation and interpreted these findings as a result of constructive interference when the difference in path length of reflected X-rays from different crystal planes is equal to an integer multiple of the wavelength. Bragg's law is given by:

$$n\lambda = 2d \sin \theta \quad (3.44)$$

where λ is the wavelength, d is the spacing between crystalline planes, θ is the incident angle, and n is an integer.[343] Bragg's law identified for the first time the relation between the scattering of X-rays and the internal structure of matter.[344] As the theory of X-ray scattering progressed and improvements were made to the instrumentation, X-ray scattering techniques were developed to study not only crystalline solids, but liquids, gases, amorphous solids, polymers, and complex materials as well. Pioneering work on the application of X-ray scattering techniques to study non-crystalline matter resulted from the research of Peter Debye, whose work laid the foundations of the theory and application of dielectric spectroscopy to the study of materials was highlighted previously in Section 3.1. Debye's earliest contributions to the field of X-ray scattering included the introduction and quantitative description of thermal effects on the scattering amplitude in 1914 and the atomic scattering factor in 1915.[323] It was also in 1915 that Debye first wrote down his assertion that all matter, regardless of its thermodynamic state, is never in a completely disordered and random arrangement, and thus all forms of matter, not just perfectly crystalline materials, should show X-ray diffraction patterns to some degree corresponding to the internal structure of the material, even in the gaseous state.[323] He further concluded that in disordered systems such as gases, liquids, and amorphous solids, the diffraction intensity with respect to diffraction angle would show broad maxima and minima, in contrast to the sharp, narrow peaks appearing in the diffraction patterns of crystalline solids.[321, 323] Thus began an intense period of experimental efforts to quantitatively describe the diffraction of X-rays by disordered materials. In one of the early experiments along this line of research, Debye along with Scherrer (1916) measured a finely powdered sample of lithium fluoride, expecting

the diffraction of the X-rays by the randomly oriented, nearly microscopic particles to show broad features. Instead, they observed the unanticipated result of sharply defined, bright spots resembling the diffraction pattern for a crystal lattice. They were able to explain their results as being due to the intersection of scattered beams from randomly oriented crystals and demonstrated for the first time the valuable technique of X-ray powder diffraction.[323]

It would take almost a whole decade (1925) before Debye published his refined arguments concerning the interpretation of X-ray diffraction in disordered states of matter relating to the structure of the atoms or molecules.[323] In this work, he reiterated his assertion that certain configurations of atoms or molecules would be more probable than others, regardless of state, and information related to these configurations should be found in the analysis of the scattering intensity. X-ray scattering experiments on liquids showed a number of broad, diffuse rings, which Debye referred to as “outer” and “inner” interferences. He ascribed the “outer” rings to interference caused by intermolecular scattering sources, while the “inner” were assigned to scattering between atoms on the same molecule. It is not generally the case that the halos observed upon exposure of liquid matter to X-rays can be distinguished in this manner, but Debye’s reasoning led him to the conclusion that upon dilution, the “outer” contributions should vanish as the intermolecular distances increase by orders of magnitude on going from the liquid state to that of the dilute gas. He determined that in the absence of an intermolecular source of scattering, the scattered intensity of a dilute gas should only contain information concerning the structure of the molecules, i.e. the arrangement and distances between atoms in the chemical structure. To provide a mathematical foundation for this work, Debye developed the well-known formula for the scattering intensity, written here for a molecule containing n atoms in the dilute gas state given by:

$$I = \sum_{i=1}^n \sum_{j=1}^n f_i f_j \frac{\sin x_{ij}}{x_{ij}} \quad (3.45)$$

where f_i is the atomic form factor of atom i and x_{ij} is proportional to the distance l_{ij} between atoms i and j given by:

$$x_{ij} = 4\pi l_{ij} \frac{\sin \theta}{\lambda} \quad (3.46)$$

Here, λ is the wavelength of the incident X-ray beam and the 2θ is the scattering angle. The summation is taken to include the case where $i = j$.^[323]

Around the same time that he was working on the use of X-rays to determine molecular structure in gaseous systems, Debye was conducting experiments to understand the internal structure of liquid matter based on X-ray analysis. X-ray scattering from liquid matter was known to contain contributions from both intra- and intermolecular origins in superposition. The reasoning was, if one could separate the two sources of interference then one could obtain information concerning the structure of the liquid. To test this hypothesis, monatomic liquid mercury was used. Separation of the two types of contributions for this system could be accomplished and analysis based on the earlier method of Zernicke and Prins could be carried out to obtain a distribution function related to the probability of the particles in the liquid being separated by some distance.^[321, 323] The results for mercury showed that molecules in the liquid tend to arrange in a preferentially ordered configuration on the local scale bearing some symmetry resembling a quasi-crystalline state. The short-range ordering observed in the liquid state was referred to as “clustering”, a concept Debye also employed in his theory of electrolytes and the critical state. This “clustering” behavior in the local liquid structure bears some resemblance to the concept of the coordination environment in liquid matter while simultaneously foreshadowing the idea of locally favored structures in the liquid state described by short-range ordering bearing crystal-like motifs as distinct from the normal liquid structures where this type of order is lacking.

With the groundwork laid by the work of pioneers including Wilhlem Röntgen, Max von Laue, Lawrence and William Henry Bragg, and Peter Debye among many others, we turn our attention in the following sections to the modern techniques of X-ray scattering and their application to the study of the structure of liquids, glasses, and other soft matter.

3.2.1 Principles of X-ray scattering experiments

Modern X-ray scattering techniques for studying structures of amorphous, semi-crystalline, and heterogeneous materials typically employ a $\text{CuK}\alpha$ X-ray source with a wavelength of 1.54 Å. The typical spacing between atoms or molecules in crystals and liquids is on the order of a few angstroms, so the scattering angles of the radiation from a $\text{CuK}\alpha$ source is

large, hence the term wide-angle X-ray scattering. Larger structures, like those found in colloids, emulsions, self-assembled block copolymers, and biological matter, on the order of tens of nanometers, are studied using small-angle X-ray scattering since these structures scatter the incident X-rays at smaller angles. In principle, however, these techniques are the same and experiments covering the small- and wide-angle ranges can be performed on the same instrument.[109]

The typical X-ray scattering instrumentation is shown schematically in Figure 3.3. This schematic shows the basic set-up of the Xenocs Xeuss 3.0 SAXS instrument at the Joint Institute for Advanced Materials (JIAM) at the University of Tennessee, which was used to perform the wide-angle X-ray scattering measurements presented in Chapter 4.

In a typical X-ray scattering experiment, a collimated X-ray beam of wavelength λ is directed at a sample with the momentum vector of the incident beam defined as $\mathbf{k}_i$. When the incident X-rays strike the sample, some of the radiation is transmitted while a portion of the radiation is scattered with a momentum vector of $\mathbf{k}_s$. The difference between the scattering momentum vector and the incident momentum vector defines the scattering wavevector, q , in reciprocal space defined by the wavelength of the X-rays and the scattering angle, 2θ . [341]

$$\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i = \frac{4\pi}{\lambda} \sin \theta \quad (3.47)$$

According to the conditions for constructive interference in the scattering intensity, stated in Bragg's law, peaks that appear in the scattering profile at a particular value of q correspond to real-space distances of correlated (periodic) structures, d , defined by the relation[287]:

$$q = \frac{2\pi}{d} \quad (3.48)$$

Thus, information regarding the static structure of the material can be obtained via X-ray scattering experiments as described herein.

The ionic liquid samples studied in this work were dried under vacuum ($< 10^{-6}$ bar) at 340K for 24 hours prior to preparation for wide-angle X-ray scattering measurements. Each liquid was then loaded into a fused silica capillary tube with 1.5mm outside diameter and 0.01mm wall thickness. The capillary tube was sealed with a clear epoxy prior to the meas-

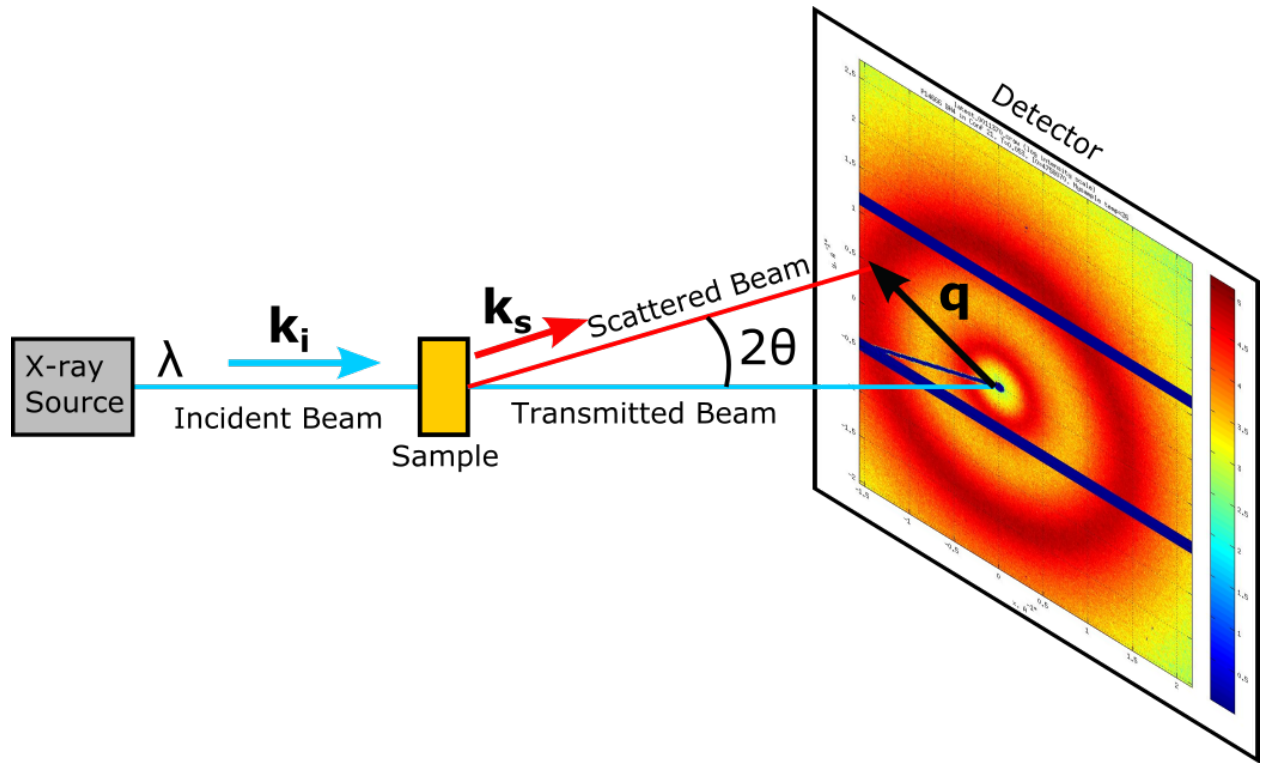


Figure 3.3: Schematic diagram of the wide-angle X-ray scattering measurements. Here, λ is the wavelength of the X-rays, $\mathbf{k}_i$ is the incident momentum vector, $\mathbf{k}_s$ is the momentum vector of the scattered X-rays, 2θ is the scattering angle, and $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$ is the scattering wavevector.

urement. The sample temperature was controlled with a Linkam HFSX350 stage to within $\pm 0.1\text{K}$ using liquid nitrogen as a coolant. The scattering intensity, $I(q)$, was measured under vacuum in the q -range from 0.13 to $3.9\text{ \AA}^{-1}$. Each sample was initially measured at room temperature and then cooled down below the T_g of the sample at 10K/min . The samples were held at the set temperature for 60s before collecting data over a 120s integration time. Measurements were taken at a series of temperatures upon heating the sample from below T_g back to room temperature.[6]

3.2.2 Theory of X-ray scattering in liquids

The portion of the electromagnetic spectrum encompassing all radiation with wavelength λ ranging from about 10 pm to 10 nm is classified as the domain of X-rays. The range of wavelengths defining the X-ray regime is on the order of typical interatomic and intermolecular distances in chemical bonds, crystal lattices, liquids, glasses, and other forms of matter. This makes X-rays well-suited to studying structure in a vast number of materials on the microscopic level. X-ray radiation directed at a sample is primarily scattered by the electronic shell surrounding the atomic nuclei. If the electron density within a region of the sample is given by $\rho(\mathbf{x})$, the scattering intensity in reciprocal space as a function of the wavevector, $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$, is given by the Fourier transform:[341]

$$I(\mathbf{q}) = \int \rho(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}} d\mathbf{x} \quad (3.49)$$

In a typical small- or wide-angle X-ray scattering experimental set-up to study structural characteristics in soft condensed matter, the scattering of the radiation by the electron density in the material is elastic, meaning there is no energy exchanged during the scattering event and the incident photon energy is equal to the scattered photon energy. In the elastic case, only the direction of propagation of the radiation is altered in the scattering event corresponding to a transfer of momentum. In addition, the scattering intensity measured in these experiments corresponds to the total coherent intensity $I_{coh}(q)$. The coherent scattering condition requires that the relative phases of the radiation scattered from different regions

of the sample remain unaltered leading to constructive and destructive interference in the total scattering intensity.

The relevant structural information collected in an X-ray scattering experiment is contained the structure factor, $S(q)$, which can be computed from the total coherent scattering intensity, $I_{coh}(q)$, by the equation:[\[4\]](#)

$$S(q) = \frac{I_{coh}(q) - \sum_i x_i f_i^2(q)}{\left[\sum_i x_i f_i(q) \right]^2} \quad (3.50)$$

where q is the magnitude of the scattering wavevector related to the momentum transfer, x_i is the mole fraction of atoms of type i and f_i is atomic form factor for atoms of type i . The structure factor can be readily computed from molecular dynamics simulation data for a given system in a number of ways. The methods for obtaining $S(q)$ from simulations can be divided into two types of methods, by either computing a sum in real space involving the Fourier transform of each atomic pair radial distribution function $g_{ij}(r)$ or by direct computation in reciprocal space. $S(q)$ determined experimentally using Equation [3.50](#) can be directly compared to results obtained from simulation data. The combination of experimental and computational results can provide crucial insights regarding structure in disordered materials that would be otherwise unobtainable by only employing one technique or the other. Experimental results provide computational researchers with model-free information about the systems they are studying in order to check the accuracy and predictive capabilities of their models and inform them how to improve and refine their models. On the other side, computational studies provide experimentalists with insight into how the structural components of the system, i.e. pair-wise atomic correlations, contribute to the features of the total structure factor.

In the case of liquids, some degree of short-range order is expected to contribute to the static structure factor while at long distances, the system appears isotropic. This type of short-range ordering found in the bulk, isotropic liquid state can be expressed in real space as a radial distribution function, $g(r)$, describing the deviation from ideal uniformity in the local distribution of particles in the liquid. For liquids, since the particles can interact with

each other only in their local neighborhood extending at most a few molecular distance, $g(r)$ relates to the probability of finding a particle at a distance r from a particle at the origin. Since the interaction between particles goes to zero at long distances, $g(r)$ decays to unity at large r . The radial distribution function of a liquid has the general form of a damped, spatially-varying periodic function in r . The radial distribution function ($g(r)$) of a liquid can be calculated from structure factor ($S(q)$) data obtained experimentally by the following equation:[112]

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty q[S(q) - 1] \sin(qr) dq \quad (3.51)$$

where ρ_0 is the atomic number density of the liquid. The relation between $g(r)$ and $S(q)$ is defined by the Fourier transform. Since the distance r between a particle at the origin and its closest neighbor can never be smaller than the minimum approach distance defined by the particle sizes, $g(r)$ must be identically zero for distances r smaller than the minimum approach distance between the particles. Above this distance, there is a broad peak in $g(r)$ corresponding to the probability of particles occupying a range of distances in direct proximity to the particle at the origin. By analogy to the concept for crystals, we can define a coordination number, n_1 , for particles in a liquid representing the number of nearest neighbor particles occupying the first coordination shell. By defining the first shell as the region from r_0 corresponding to the minimum approach of the particles to r_1 cut off at the first local minimum in $g(r)$, the coordination number for the liquid can be defined as:[112]

$$n_1 = 4\pi\rho_0 \int_{r_0}^{r_1} g(r)r^2 dr \quad (3.52)$$

representing the area under the first peak in $g(r)$. Higher order coordination numbers can be defined by integrating subsequent peaks in $g(r)$. The average coordination number for particles in a liquid defined in this way is a useful quantity to identify changes in the local liquid structure.

3.3 Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique that uses a monochromatic light source to induce molecular vibrations, phonon modes and other excitations in a sample. The principle of Raman spectroscopy is based on the inelastic scattering of the incident radiation, where the energy of the scattered photons is shifted by an amount equal to the difference in energy between the excited vibrational state and the initial unexcited (ground) state. This type of inelastic scattering, resulting from absorption of photonic energy by the electronic parts of the molecules promoting them to a higher energy, virtual state and the subsequent emission of a photon differing in energy from the initial excitation is termed Raman scattering. The final state of a molecule following a Raman scattering event is in a different vibrational-rotational-electronic state from the initial state and the energy difference between the initial and final states is accounted for by the Raman shift of the photonic energy. This is distinguished from the elastic scattering resulting from absorption and emission of photons of equal energy, referred to as Rayleigh scattering, in which the initial and final states of the molecules are identical. A schematic view of the principle of Raman spectroscopy is given by Figure 3.4. The set-up depicted in this diagram represents the back scattering configuration corresponding to the Raman measurements reported in this work in Section 3.3.

The Raman measurements were made using the Horiba LabRAM HR Evolution confocal Raman microscope with a 532nm excitation laser at 50% power using a 50x LWD objective. Data collection was taken over three 15s accumulations filtered by a grating of 1800 lines per mm to achieve 0.5cm^{-1} resolution. The sample was first dried under vacuum ($< 10^{-6}$ bar) at 340K for 24 hours. A drop of the sample was then loaded into a Linkam THMS600 temperature stage with silica windows to control the temperature to within $\pm 0.1\text{K}$ using liquid nitrogen as the coolant, and the sample thickness was maintained at approximately $150\mu\text{m}$ using Teflon spacers. The samples were measured in the temperature range from 183K to 253K on cooling at 5K/min and heating at 10K/min pausing at each temperature for the duration of the measurement. Variations between the data obtained on cooling and heating were minimal, indicating thermal reproducibility of the results.[6]

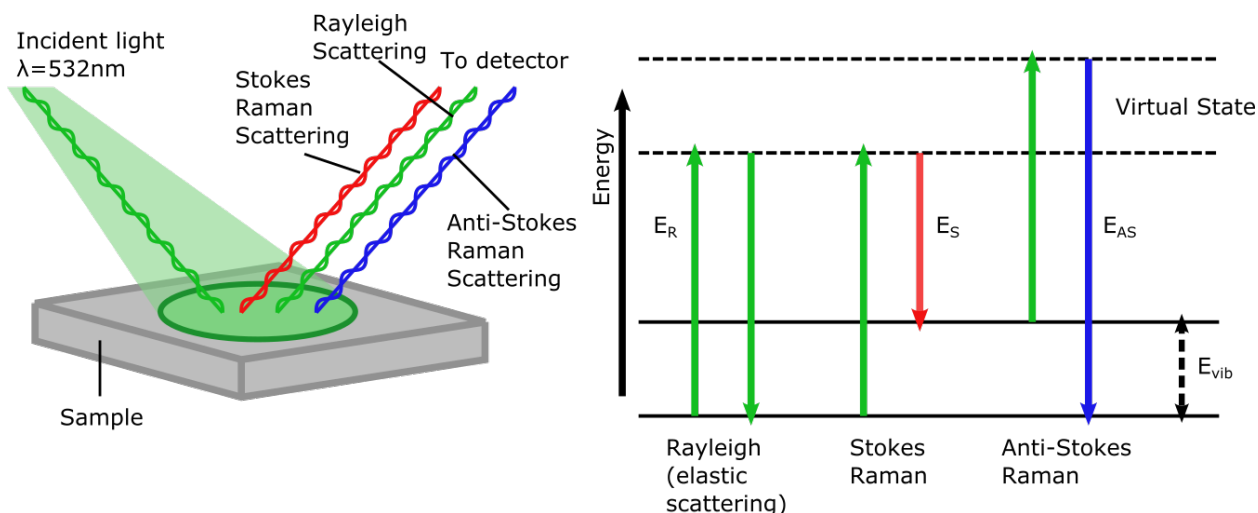


Figure 3.4: Schematic diagram of the principle of Raman spectroscopy. Here, E_{vib} represents the energy difference between two vibrational states. E_R corresponds to the energy of the incident radiation in the process of Rayleigh scattering, where the initial and final energy states of the molecule are the same. E_S refers to the red-shifted Stokes radiation, resulting from excitation of the molecule by the incident beam from its initial state to a higher-energy virtual state and the subsequent relaxation to the higher vibrational state. E_{AS} refers to the blue-shifted anti-Stokes radiation, resulting from excitation of the molecule by the incident beam from a higher vibrational state to a higher-energy virtual state and the subsequent relaxation to a lower vibrational state. The magnitude of the Raman shift in both Stokes and anti-Stokes scattering is equal to the energy difference between the initial and final vibrational states of the molecule, E_{vib} .

3.4 Differential Scanning Calorimetry

Calorimetry, as a field of science, is the sets of techniques used to measure heat flow into and out of a system in order to study thermodynamic changes associated with physical processes such as crystallization, melting, mixing, vaporization, vitrification, etc., as well as chemical processes, namely chemical reactions. Differential scanning calorimetry (DSC) is a specific thermal analysis technique used to accurately study heat flow that was first developed in 1962.[345] Since its invention, DSC has become the most widely used thermal analysis method employed in a broad range of research areas. The reason it has become so ubiquitous is that it delivers rapid and accurate measurements of heat flow and heat capacity changes associated with phase transitions and other physical and chemical processes.

The basic premise of DSC is to measure the amount of heat absorbed or released by the sample and the reference in order to change the temperature of the system (or hold it constant as in isothermal measurements) over a period of time. Essentially, energy is transferred between the system, including the sample, the reference, and the temperature sensors, and the external environment, which includes the rest of the apparatus surrounding the sample chamber, in order to affect a temperature path defined over a period of time. Since physical and chemical processes that occur within the temperature path will either consume (endothermic) or generate (exothermic) excess heat within the sample, the heat flow signal measured by DSC provides thermodynamic and kinetic information about the processes occurring in the sample. While this premise is the basis for all DSC techniques, we will focus our discussion on the operating principles and capabilities of the heat flux type of DSC using a disk-type sample holder environment to exchange heat between the sample and the surroundings.[134]

In heat flux DSC, heat is exchanged between the sample and its surroundings via a specified heat conduction path with a known thermal resistance. The amount of heat transferred between the sample and its surroundings is well-defined by the thermal circuit and as such, it can be measured accurately and rapidly by monitoring specific quantities in the heat conduction path. The key component of the thermal circuit is the sample chamber

where the heat exchange between sample and surroundings takes place. A schematic diagram of the sample chamber for a typical disk-type, heat flux DSC is given in Figure 3.5.

In this set-up heat flows from the furnace surrounding the sample chamber to the sample and reference crucibles by passing through the disk which acts as a solid support for the crucibles and as a conductor in the exchange of heat. Temperature sensors for the reference and the sample are integrated directly into the disk with the sample, the reference, and their associated temperature sensors arranged symmetrically with respect to the center of the disk in a precise way so the heat path is the same for both the sample and the reference. Fourier's law of heat conduction defines the driving force for heat flow as the difference in temperature. By measuring the temperature of the sample and the reference simultaneously, the heat flow to the sample can be deduced from the difference in heat flow into the sample chamber as a whole and into the reference itself.

Using Fourier's law, we can define the DSC signal, Φ , which is proportional to the heat flow rate to the sample in $\text{J g}^{-1} \text{s}^{-1}$, as:[134]

$$\Phi = \Phi_S - \Phi_R = \frac{T_S - T_R}{R_{th}} = \frac{\Delta T}{R_{th}} \quad (3.53)$$

where Φ_S and Φ_R are the heat flux to the sample and the reference, respectively. The difference between the heat fluxes is proportional to the temperature difference between that of the sample, T_S , and that of the reference, T_R , by the thermal resistance, R_{th} , of the sensor. The temperature differential is measured using two thermocouples, whose sensitivity S is defined as the ratio between the thermoelectric voltage signal V to the temperature difference ΔT . Thus, we can define the heat flux as:

$$\Phi = \frac{\Delta T}{R_{th}} = \frac{V}{R_{th}S} \quad (3.54)$$

Relating this heat flux to the actual heat flow rate into or out of the sample, Φ_{true} requires proper calibration of the instrument.

DSC calibration is carried out by two independent steps to determine the proportionality K_Φ between the measured heat flow Φ and the true heat flow Φ_{true} as well as the proportion-

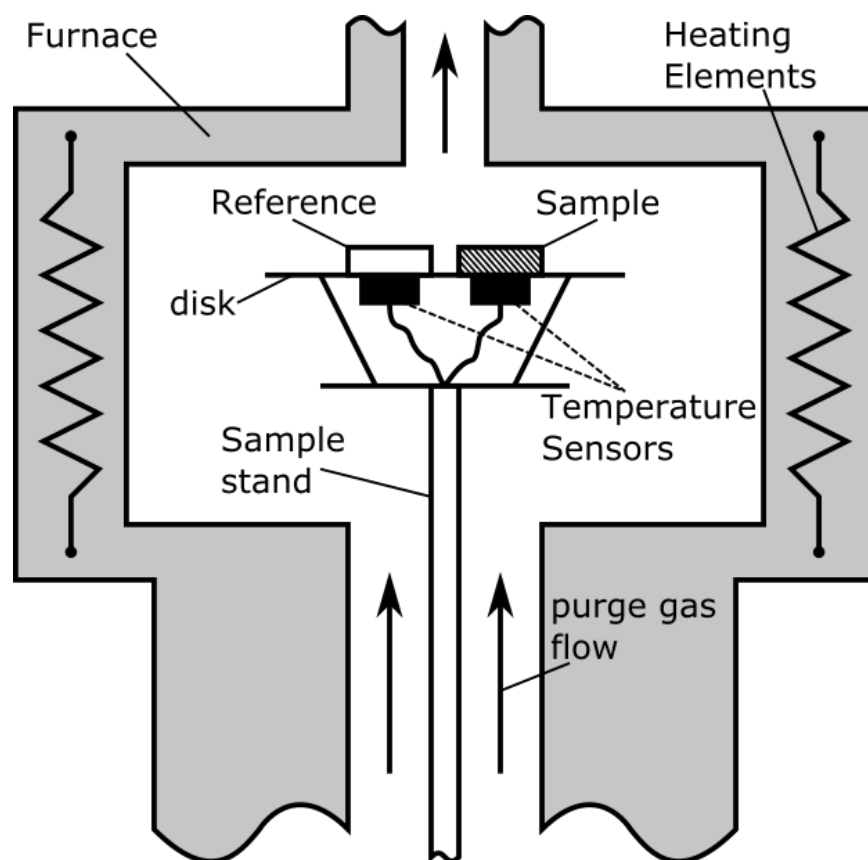


Figure 3.5: Schematic diagram of the heat-flow differential scanning calorimetry measurement cell

ality K_Q between the measured heat exchanged Q_{meas} and the actual heat exchanged Q_{true} . The determination of K_Φ is performed by measuring the heat flow to a sample of known heat capacity C_p subject to a constant scan rate $q = dT/dt$. Then the actual heat flow rate is $\Phi_{true} = C_p \cdot q = K_\Phi \Phi$ giving K_Φ as:

$$K_\Phi(T) = \frac{C_p(T)q}{\Phi_S(T) - \Phi_R(T)} \quad (3.55)$$

The calibration for the amount of heat exchanged is accomplished by comparing the signal from a sample with a known heat of transition to a baseline signal obtained by measuring two empty crucibles of the same type. Integrating over the transition peak of the standard sample gives Q_{true} , which can be defined as:

$$Q_{true} = K_Q Q_{meas} = K_Q \int (\Phi[T(t)] - \Phi_{bl}[T(t)])dt \quad (3.56)$$

Once the calibrations are performed to determine K_Φ and K_Q , the actual heat flow rate and quantity of heat exchanged can be computed from the measured signal for a sample of unknown heat capacity.

DSC is a useful tool in the study of ionic liquids because it can provide information about phase changes taking place with the liquid and concerning the calorimetric glass transition observed in a variety of ionic liquid systems. The process of a liquid transforming into a crystalline solid (crystallization or freezing), or the reverse of a solid transforming to a liquid (melting) is a first-order thermodynamic transition, meaning a certain quantity of heat per amount of substance is consumed (endothermic process) to convert from the more-ordered crystal to the less-ordered liquid on melting with an equivalent amount of heat generated (exothermic process) during the reverse process. The signature of this type of transition appears in the DSC signal plotted as specific heat flow rate Q as a function of temperature T as a peak whose width in temperature for a given scan rate dT/dt is related to the kinetics of the transition with the integrated peak area giving the enthalpy change associated with the transition. The temperature at which this transition occurs for a pure substance is defined as the melting temperature, T_m . Since the process of crystal formation from the liquid state proceeds in two steps, nucleation whereby stable clusters of molecules form with the requisite

symmetries characteristic of the periodic crystal structure and crystal growth in which the size of the nucleated clusters increases as molecules from the liquid phase precipitate on the surface of the growing crystal. Both of these steps occur over a certain timescale dependent on the temperature, pressure, and composition of the system. Formation of stable clusters of a critical size via nucleation occurs on a timescale dictated by the size and frequency of fluctuations in the system. The process of crystal growth proceeds after critical stable nuclei have formed. The growth mechanism is a dynamic process occurring at equilibrium involving the deposition of molecules from the liquid phase onto the crystal surface in conjunction with the dissolution of molecules from the crystal phase back into the liquid. The relative rate of deposition to dissolution determines the direction and the kinetics of the transformation. A well-designed DSC experiment defined by moving the system under investigation along a prescribed temperature path by cooling or heating the sample at some constant scan rate $q = dT/dt$ can be used to determine the melting point T_m , the enthalpy of melting ΔH_m , and information related to the kinetics of the solid-liquid phase transition.

Since crystallization is an activated process, the rate of crystal formation depends strongly on the temperature of the crystallizing system, in our case, the pure liquid form. Therefore, if one were to cool the liquid below T_m faster than the nucleation rate of stable cluster formation, the molecules would not have enough time to rearrange to form crystalline regions of critical size to overcome the activation barrier and the entire system will remain in the metastable, supercooled liquid state. Given enough time, the supercooled liquid eventually transitions to the equilibrium crystal phase. However, if the system is cooled further before it has time to crystallize, it reaches a point where the timescale of the relaxation dynamics associated with the liquid state exceeds the observational timescale of the experiment and the liquid becomes “frozen” in a nonequilibrium, nonergodic solid-like state lacking the long-range, periodic order of the crystal. The phenomena associated with the dynamic arrest of the supercooled liquid is known as the dynamic glass transition, with the glassy state defined by a solid-like response at short timescales, that is nevertheless in a nonequilibrium state that continuously relaxes toward the liquid state on very long timescales. The point at which the relaxation timescale exceeds the observational timescale given by the constant scan rate q determines the calorimetric glass transition temperature, T_g . As a supercooled liquid is

cooled at a rate sufficient to approach T_g before crystallization sets in, a step-like decrease in the heat capacity of the substance is observed as the material becomes frozen in the glassy state. The drop in C_p is associated with the reduction in the number of microscopic configurations accessible by the system. The value of T_g varies depending on the scan rate. By convention, a standardized method of determining T_g is defined by measuring the increase in heat capacity upon reheating the sample at a rate of 10K/min which had been previously cooled to the glassy state at a high enough rate to avoid crystal formation. The point at which T_g is defined corresponds to the inflection point in the C_p curve during the upscan, which appears as a maximum in the derivative of the heat flow with respect to temperature.

While crystallization/melting phenomena and the glass transition are just two examples out of many physical and chemical processes that can be studied using DSC, they are generally the most commonly observed in the ionic liquid family of materials. In addition, certain systems exhibit polymorphic behavior defined by a first-order phase transition from one crystal structure to another, i.e. a solid-solid transition. By analogy, another type of phase behavior known as polyamorphism involves a first-order phase transition from one amorphous (noncrystalline) phase to another. The liquid-liquid transition (LLT) is a type of polyamorphic transition between two liquid states, which in theory would appear as a reversible enthalpic peak in the DSC signal similar to the liquid-solid and solid-solid transition peaks. For a system that undergoes LLT in the supercooled liquid state, the feature would appear between T_m and T_g when the system is cooled fast enough to avoid crystal formation.

Chapter 4

Structural aspects of the liquid-liquid transition in ionic liquids

In this chapter, the temperature dependence of the structural features of ionic liquids as reported by wide-angle X-ray scattering is investigated covering the temperature range from 300K to below T_g . In order to elucidate the structural changes that occur at the liquid-liquid transition, refer to Section 2.2 for a discussion on the hierarchical nature of ionic liquid structure. In the first section of this chapter (Section 4.1), the experimental results from WAXS on the set of ILs studied are reported and a discussion of the structural changes that occur at the LLT is given. The next section (Section 4.2) deals with the conformational order of the alkyl chains present on the $P_{666,14}$ cation as reported by Raman spectroscopy. It is determined, for the case of the borohydride anion, that the alkyl chains become increasingly dominated by the trans-conformer corresponding to the expansion of the apolar region of the liquid structure. This chapter concludes (Section 4.3) with a summary of the results presented from WAXS and Raman studies, along with a discussion of the implications for the existence of a LLT in $P_{666,14}$ -based ILs.

4.1 Temperature dependent X-ray scattering of ionic liquids

In general, a liquid-liquid transition, similarly to other types of phases transitions, is expected to manifest a discontinuous structural reorganization at the transition temperature where the high temperature liquid state (HTLS) and the low temperature liquid state (LTLS) coexist. Above this characteristic temperature, T_{LL} , the HTLS is stable and behaves as the normal, high-temperature, equilibrated liquid. Below T_{LL} , the LTLS becomes stable and manifests distinct properties compared to the normal HTLS, which have been attributed to the dominance of locally favored states described by the generic bond orientation order parameter of Tanaka’s two order parameter model[5]. In an effort to characterize the structural reorganization that manifests in the LLT of $P_{666,14}$ -based ILs, temperature dependent wide-angle X-ray scattering studies were carried out for the six ILs shown in Figure 4.1.

The ILs in this study are members of the particular class or family of ILs that bear the $[P_{666,14}]^+$ cation, and as such they all exhibit the tri-fold hierarchical structure defined by the structure factors shown in Figure 2.5. This class of ILs is often described as exhibiting a filamentous morphology[101] where the cations and anions are arranged in an alternating fashion in polar strands forming a branched, connected charge network. The strands or filaments of the charge network are separated from each other by the long alkyl tails attached to the central phosphonium cation. The three regions in the structure factor correspond to the correlation lengths that define this type of charge network. The highest q feature, between about 1 and $1.75 \text{ \AA}^{-1}$, corresponds to ion adjacency and defines the correlation length associated with nearest neighbor ions. In the intermediate q region, from about 0.5 to $1 \text{ \AA}^{-1}$, charge alternation correlations dominate. The correlation length associated with this region describes the distance separating ions of the same charge. This feature can sometimes appear as a weak shoulder or be absent from the structure factor resulting from cancellation of positive and negative contributions of correlations between ions of the same charge and opposite charge respectively.[4] The lowest q feature, around 0.2 to $0.5 \text{ \AA}^{-1}$ in the structure factor, is attributed to polar alternation contributions being defined by the distance separating polar regions across the apolar, alkyl-rich domains. These three regions

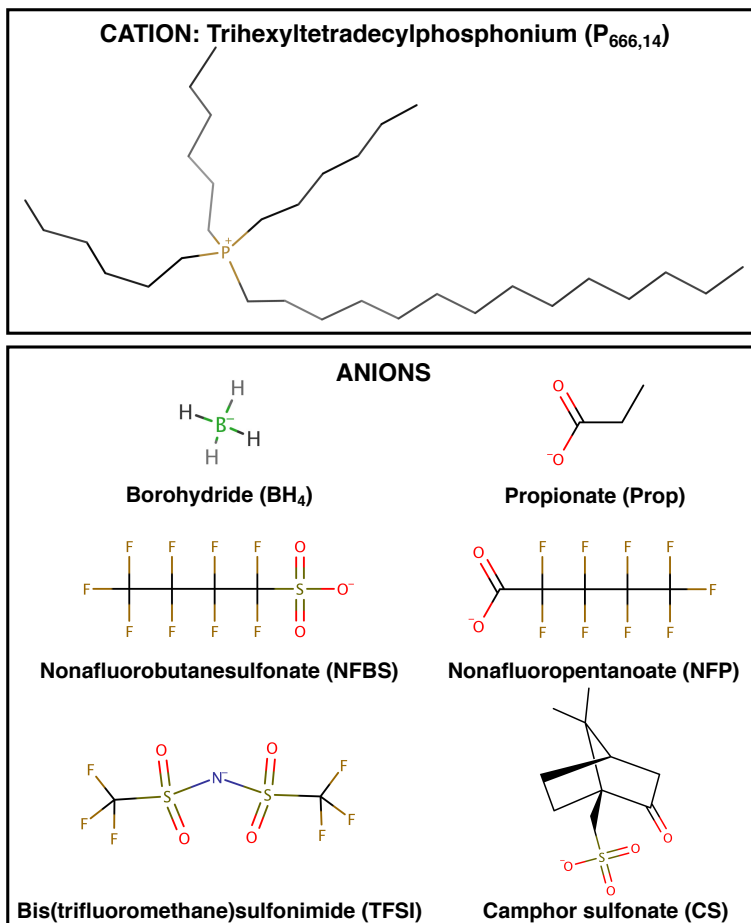


Figure 4.1: Chemical structure of the trihexyltetradecylphosphonium ($P_{666,14}$) cation and the six anions comprising the ionic liquid systems studied. The anions are (left column from top to bottom) borohydride (BH_4), nonafluorobutanesulfonate (NFBS), bis(trifluoromethane)sulfonimide (TFSI), (right column top to bottom) propionate (Prop), nonafluoropentanoate (NFP), and camphor sulfonate (CS).

can be identified in the experimental structure factor, $S(q)$, of the $P_{666,14}$ -containing ILs. What is of interest here is the identification of temperature dependent changes in $S(q)$.

Figure 4.2A shows the structure factor measured for the borohydride (BH_4) sample across the temperature range spanning from room temperature to below the glass transition of the material. The $S(q)$ data at each temperature are vertically offset for clarity. Notably, the ion adjacency peak shifts to progressively higher q values with decreasing temperature. This behavior is evidence of increased packing density of the ions as the liquid is cooled. Interestingly, the low q peak associated with the alternation of polar and apolar structures shifts to lower q values as the temperature of the sample is decreased. Additionally, the charge alternation feature is largely absent in the BH_4 sample except as a weak shoulder apparent only at low temperatures.

This general temperature dependence of $S(q)$ is similarly borne out in the case of the propionate (Prop) anion, shown in Figure 4.3A. Here, the polarity alternation peak appears around $0.3 \text{ \AA}^{-1}$ shifting to slightly lower q with decreasing temperature. As in the case of BH_4 , the charge alternation structure appears as a shoulder around $0.4 \text{ \AA}^{-1}$, only becoming prominent at low temperatures. The feature corresponding to ion adjacency shows up around $1.3 \text{ \AA}^{-1}$, again shifting to higher values of q as the sample is cooled.

The cases of the BH_4 and Prop samples indeed show the same general trends. In order of the sizes of the anions, these two are the smallest. Proceeding then to the next size up, the nonafluoropentanoate (NFP) and nonafluorobutanesulfonate (NFBS) samples, a distinct difference in structure as reported by wide-angle X-ray scattering is observed. Figure 4.4A shows the measured $S(q)$ data at various temperatures for the NFP sample. In a similar manner to the BH_4 and Prop samples, the polarity alternation peak is observed around $0.3 \text{ \AA}^{-1}$ shifting to slightly lower q at lower temperatures, while the ion adjacency peak around $1.3 \text{ \AA}^{-1}$ shifts to slightly higher q with decreasing temperature. The distinction from the cases of the smaller anions is immediately obvious in the prominence of the charge alternation structure, here appearing as a shoulder around just above $0.5 \text{ \AA}^{-1}$. This may appear to be simply due to the larger size of the anion contributing to a larger charge alternation distance, but that would contradict the fact that this shoulder is observed at higher q in the NFP case

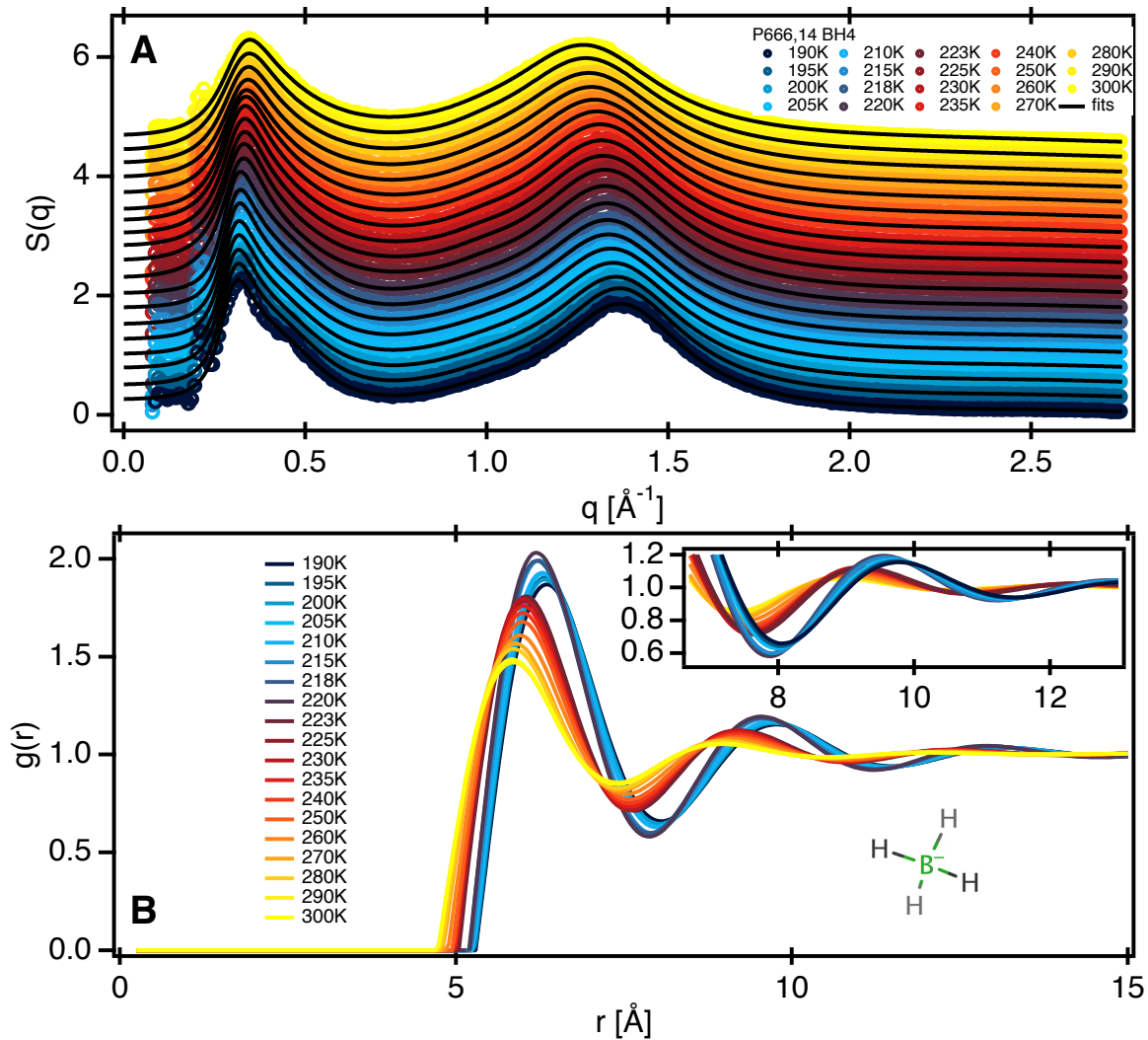


Figure 4.2: Temperature dependence of structural data. (A) Structure factor, $S(q)$, of [P_{666,14}]⁺[BH₄]⁻ at various temperatures. (B) Radial distribution function, $g(r)$, of [P_{666,14}]⁺[BH₄]⁻ at various temperatures calculated from fits to $S(q)$ data.

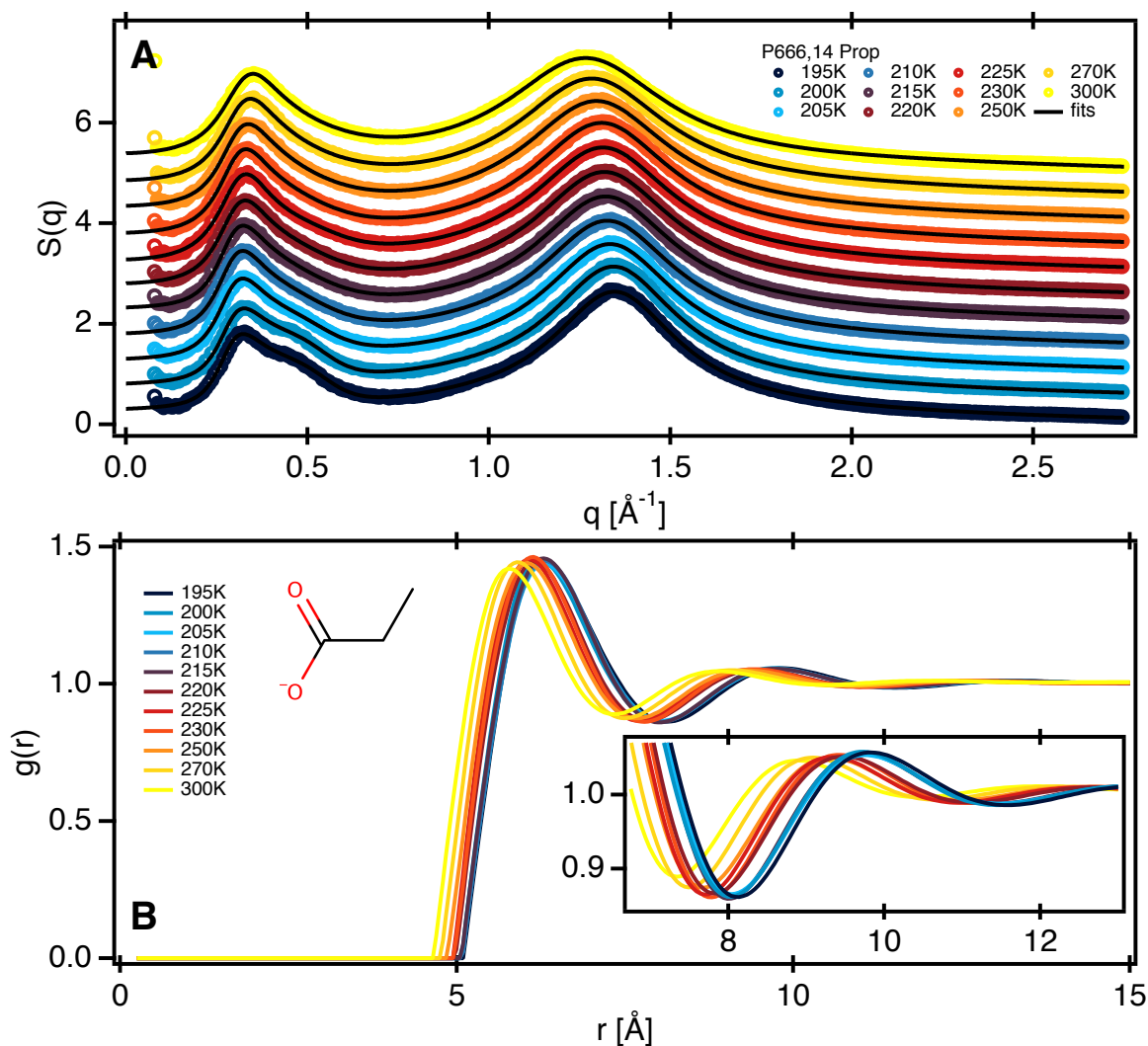


Figure 4.3: Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[\text{P}_{666,14}]^+[\text{Prop}]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[\text{P}_{666,14}]^+[\text{Prop}]^-$ at various temperatures calculated from fits to $S(q)$ data.

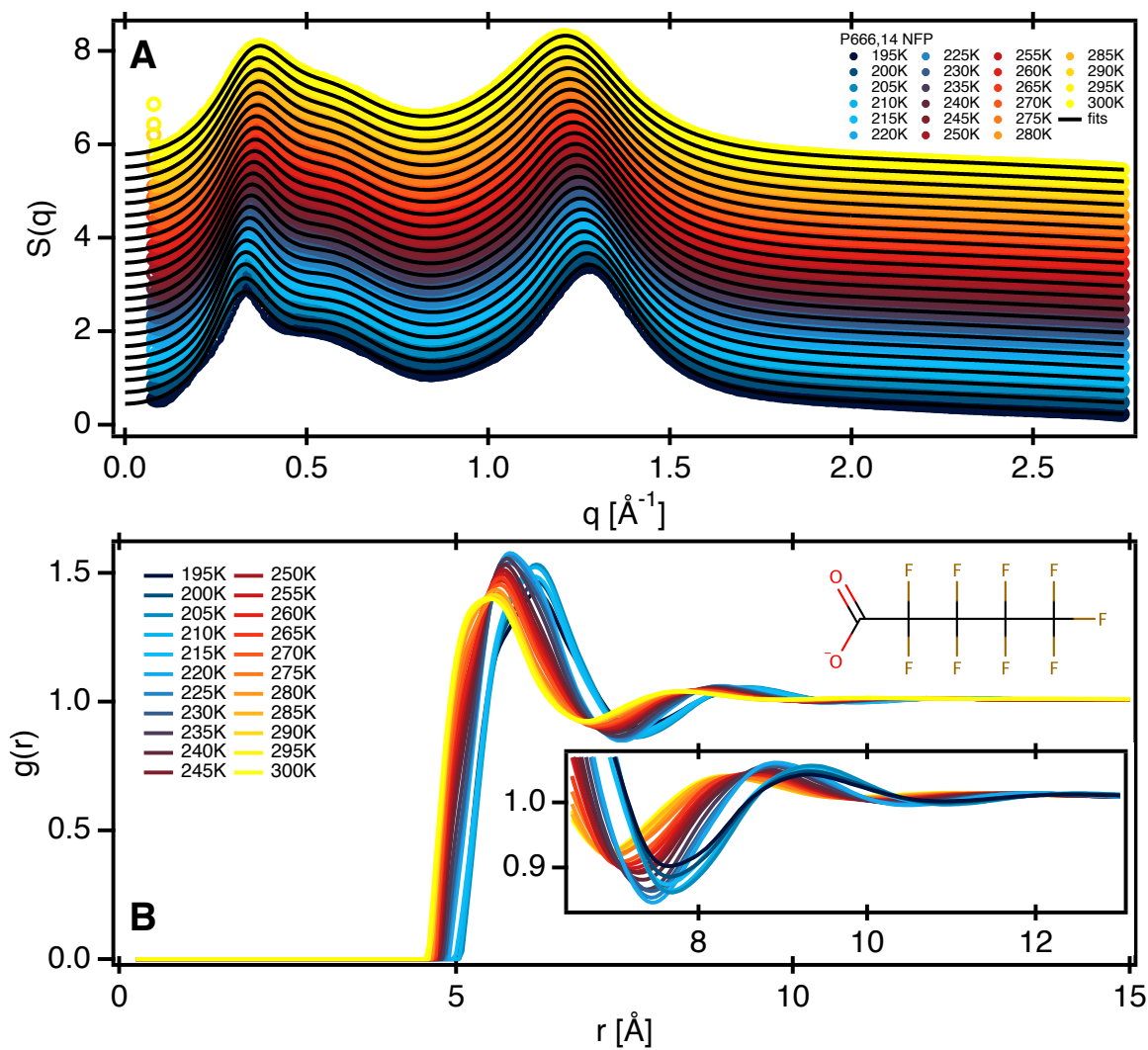


Figure 4.4: Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[\text{P}_{666,14}]^+[\text{NFP}]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[\text{P}_{666,14}]^+[\text{NFP}]^-$ at various temperatures calculated from fits to $S(q)$ data.

compared to BH_4 and Prop, corresponding to a shorter charge alternation distance. It appears that the complex nature of the structure of these ionic liquids leads to seemingly counterintuitive results. However, as the details of the structural analysis are further elaborated in this discussion, these observations will be met with satisfactory explanation in terms of the current understanding of ionic liquid structures.

Proceeding to the case of NFBS, the $S(q)$ data at various temperatures shown in Figure 4.5A show similarities to the previous NFP case. Again, a clear shoulder in the intermediate charge alternation region is manifest just above $0.5 \text{ \AA}^{-1}$. Yet again, as in the previous cases, the polarity alternation peak is observed around $0.3 \text{ \AA}^{-1}$ shifting to slightly lower q with decreasing temperature, while the ion adjacency peak around $1.3 \text{ \AA}^{-1}$ shifts to slightly higher q as the temperature is lowered.

The $S(q)$ data measured at various temperatures for the bis(trifluoromethane)sulfonimide (TFSI) sample are shown in Figure 4.6A. At the higher temperatures, this sample definitely fits the profile of an archetypal ionic liquid displaying the hierarchical structure from adjacency to charge alternation to polarity alternation. The polarity alternation is positioned around $0.4 \text{ \AA}^{-1}$, followed by a shoulder in the charge alternation region around $0.75 \text{ \AA}^{-1}$. Then there is the ion adjacency peak around $1.4 \text{ \AA}^{-1}$. As the TFSI sample is cooled below 200K, an additional shoulder emerges right around $0.5 \text{ \AA}^{-1}$ in between the polarity alternation and charge alternation features, in contradistinction to the behavior of the ionic liquid systems shown above. The emergence of this peak is a clear and dramatic indication of changes to the structural organization of this ionic liquid occurring at a particular temperature.

In contrast to the conspicuous structural reorganization manifesting in the TFSI case below 200K, Figure 4.7A shows that the measured $S(q)$ data for the camphor sulfonate (CS) sample does not change in any perceptible way as the temperature of the sample is lowered aside from the slight shifts in the positions of the polarity alternation and ion adjacency peaks to lower and higher q values, respectively. In addition, the absence of any discernible shoulder in the charge alternation region should be noted. As previously mentioned, the absence of a peak or shoulder in this region does not indicate an absence of a charge alternation component to the structure, but merely results from the cancellation of

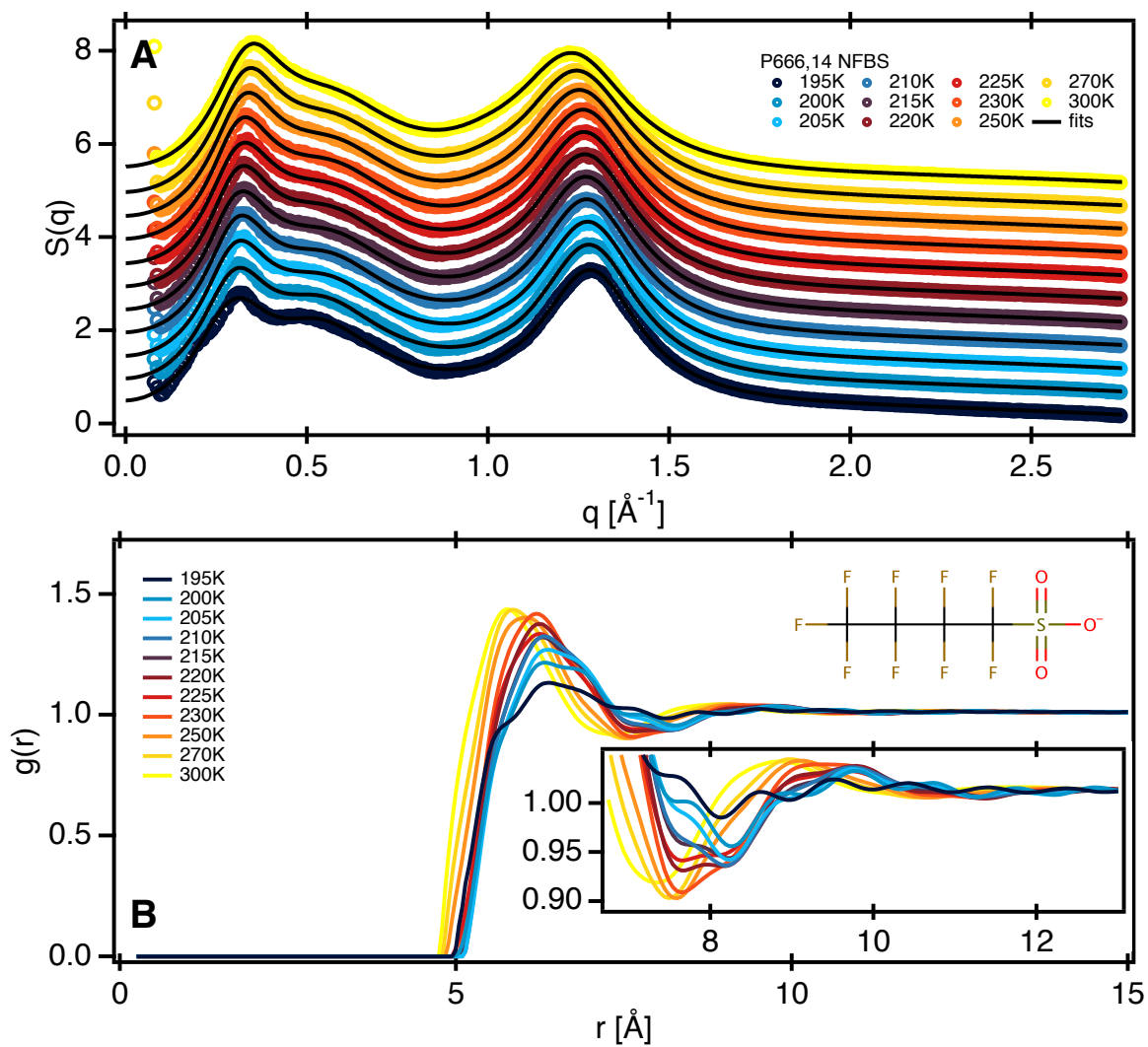


Figure 4.5: Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{666,14}]^+[NFBS]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{666,14}]^+[NFBS]^-$ at various temperatures calculated from fits to $S(q)$ data.

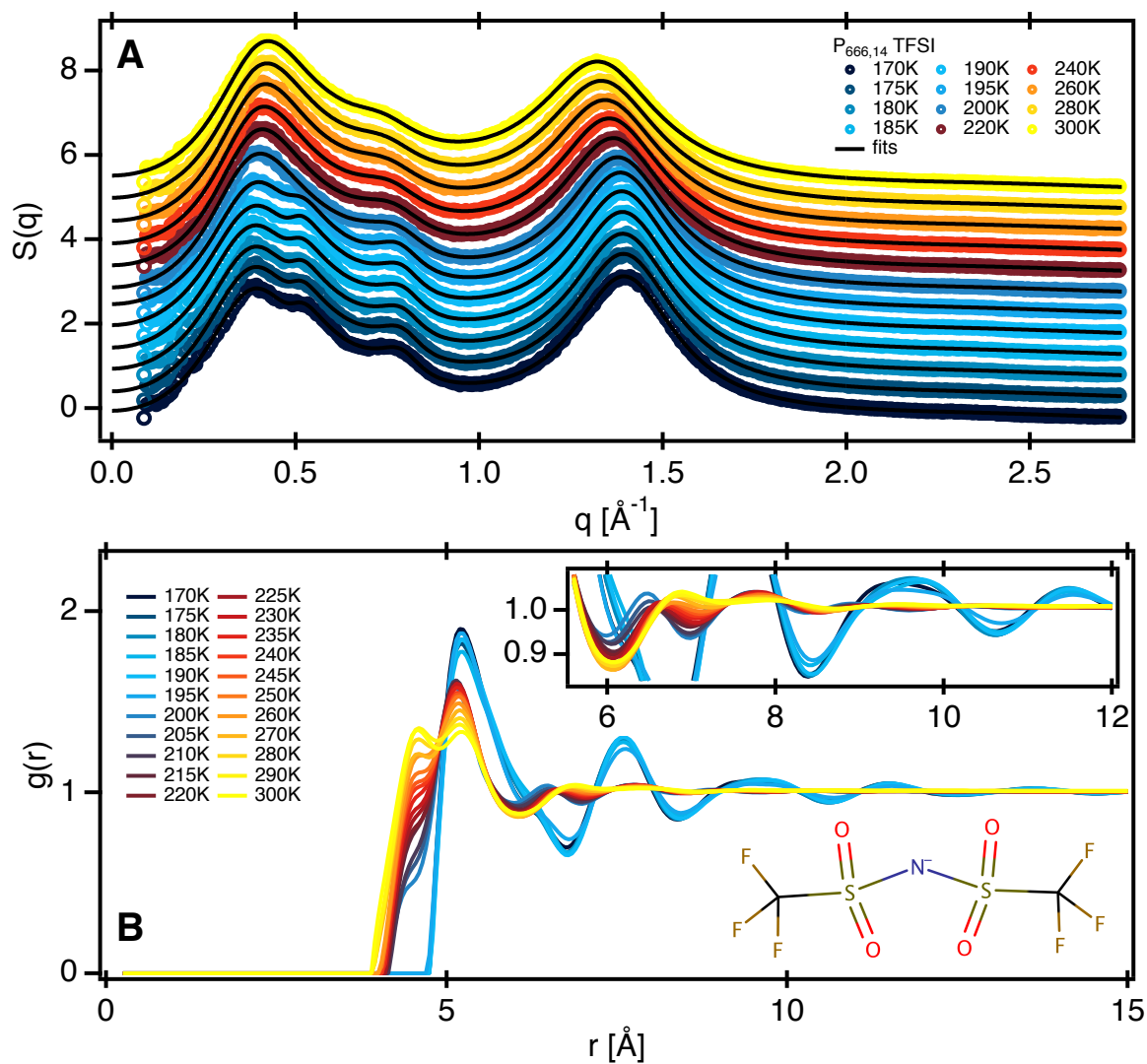


Figure 4.6: Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[P_{666,14}]^+[TFSI]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[P_{666,14}]^+[TFSI]^-$ at various temperatures calculated from fits to $S(q)$ data.

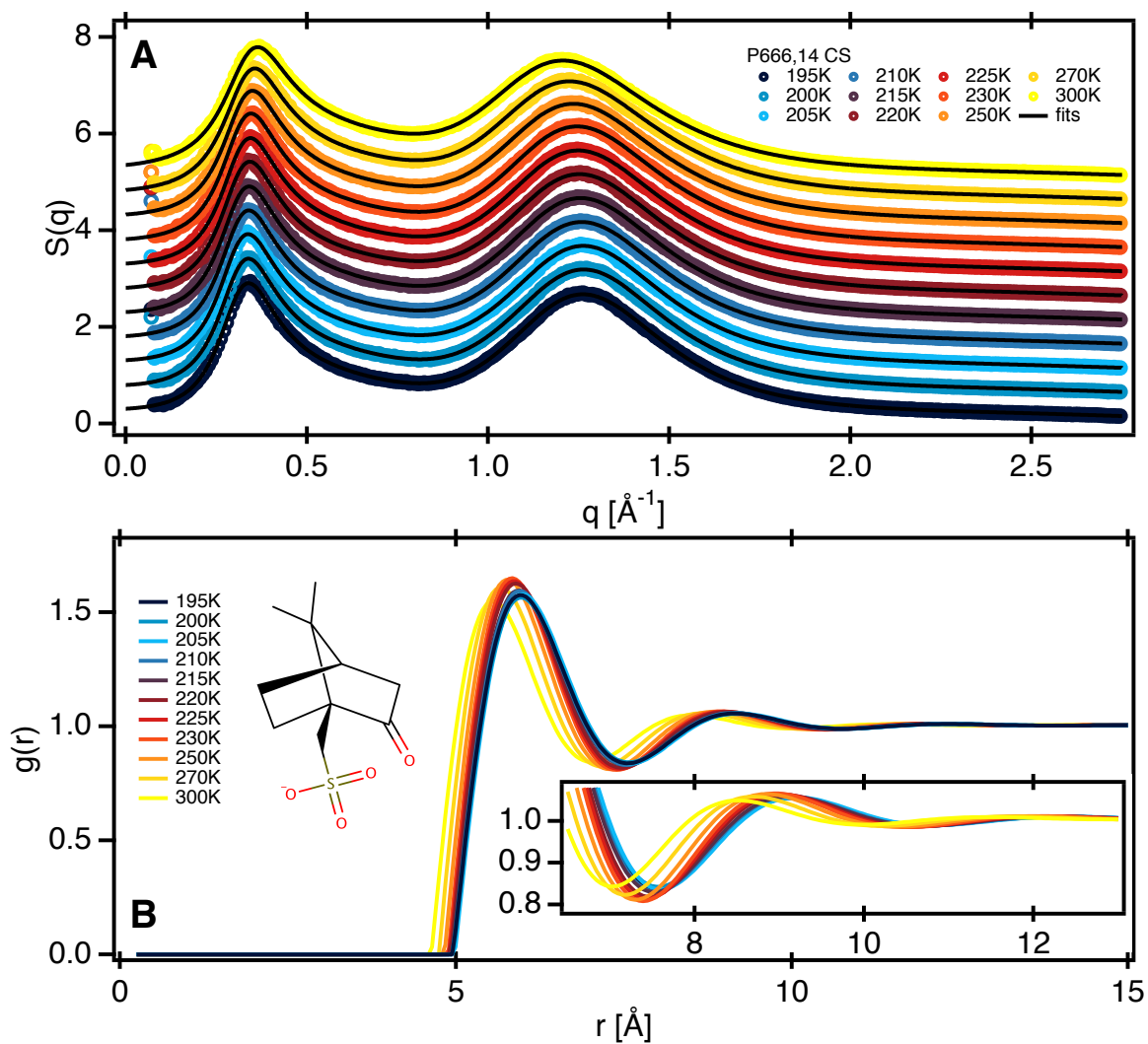


Figure 4.7: Temperature dependence of structural data. (A) Structure factor, $S(q)$, of $[\text{P}_{666,14}]^+[\text{CS}]^-$ at various temperatures. (B) Radial distribution function, $g(r)$, of $[\text{P}_{666,14}]^+[\text{CS}]^-$ at various temperatures calculated from fits to $S(q)$ data.

positive contributions to the structure factor from the correlation of ions of like charge with negative contributions from correlations between ions of opposite charge.

In order to understand the effect of temperature on the internal structure of the six P_{666,14}-based ionic liquids in this work, a detailed analysis of the measured $S(q)$ data is necessary. This is carried out by fitting the main features of the structural data with a set of model functions that account for the position, width, and amplitude of the peaks. A commonly utilized function to fit peaks such as those appearing in the $S(q)$ data of a wide variety of materials is the three-parameter Lorentzian function:

$$S_L(q) = I_0 \frac{\gamma^2}{\gamma^2 + (q - q_0)^2} \quad (4.1)$$

where q_0 is the position of the peak in reciprocal space, γ is the half-width at half-maximum related to the width of the peak, and I_0 is the intensity or amplitude of the peak. Modelling of peaks appearing in the measured $S(q)$ can be performed by fitting each individual feature with a Lorentzian function. This way of quantitatively fitting the data can only be done if the peaks are sufficiently separated from one another such that they do not overlap in reciprocal space. This is certainly possible for non-associating molecular liquids that have only one peak in $S(q)$ corresponding to the adjacency of nearest neighbor molecules. The average distance, d between the correlated components of the sample, also referred to as the periodicity of the structure, can be determined from the fitting parameters of the Lorentzian model from the expression:

$$d = \frac{2\pi}{q_0} \quad (4.2)$$

In general, for any liquid that exhibits structural order on multiple length scales in the wide-angle X-ray scattering range covering about 0.1 to 4 Å⁻¹ including the ionic liquids in this work, the peaks in $S(q)$ corresponding to the ordered domains will have some overlap in the measured data. To fit this data, it is necessary to simultaneously fit the full range of the data with a linear combination of model functions.

Other models besides the Lorentzian have been proposed to describe structural data from X-ray scattering. The model proposed by Teubner and Strey was developed expressly to account for two known features of the structure of microemulsions, i.e. the alternation of

aqueous and organic domains and the decay of the periodic order over longer distances.[346] In the generalized Teubner-Strey (TS) model, the liquid structure associated with the alternation of spatial regions occupied by different types of molecules or molecular parts can be described using a damped, oscillatory correlation function, $G_{TS}(r)$, given by:

$$G_{TS}(r) = \frac{1}{r} \exp\left(-\frac{r}{\xi}\right) \sin\left(\frac{2\pi r}{d} - \varphi\right) \quad (4.3)$$

where d is the periodicity of the alternating structure, ξ is the correlation length corresponding to the exponential decay of the periodic ordering. An additional parameter, φ , accounts for the phase of the oscillations corresponding to asymmetry of the peak.[347] $G_{TS}(r)$ can be used to describe the alternation between polar and apolar regions in ionic liquids. Similarly, the charge alternation structure in ionic liquids can also be described as a periodic ordering of alternating positively and negatively charged moieties and thus, can be modelled using $G_{TS}(r)$. The structure factor, $S_{TS}(q)$, in reciprocal space can be obtained from $G_{TS}(r)$ by the Fourier transform, yielding:

$$S_{TS}(q) = I_0 4\pi \frac{\Delta^2 \cos\varphi - (q^2 - q_0^2) \sin\varphi}{\Delta^4 + (q^2 - q_0^2)^2} \quad (4.4)$$

where q_0^2 is the peak position in q^2 , Δ^2 is the width (half-width at half-maximum) of the peak in q^2 , φ is the phase of the oscillation, and I_0 is the height of the peak.

The real space distances of the TS model, the periodicity, d , and the decay length, ξ , are related to the parameters in the structure factor representation by the following two equations.

$$\Delta^2 = \frac{4\pi}{\xi d} \quad (4.5)$$

$$q_0^2 = \left(\frac{2\pi}{d}\right)^2 - \frac{1}{\xi^2} \quad (4.6)$$

Inverting these equation to get d and ξ yields:

$$d = \frac{\sqrt{8\pi}}{\beta_+} \quad (4.7)$$

$$\xi = \frac{\sqrt{2}\beta_+}{\Delta^2} \quad (4.8)$$

where:

$$\alpha^2 = \sqrt{\Delta^4 + q_0^4} \quad (4.9)$$

$$\beta_{\pm} = \sqrt{\alpha^2 \pm q_0^2} \quad (4.10)$$

In addition, the integrated area under the TS peak can be calculated from the fitting parameters by the equation:

$$I_0 A_{TS} = I_0 \sqrt{2} \pi^2 \frac{\Delta^2 \cos \varphi - \beta_-^2 \sin \varphi}{\alpha^2 \beta_-} \quad (4.11)$$

The method utilized to fit the structural data given in Figures 4.2A-4.7A is as follows. The raw $I(q)$ data as measured by wide-angle X-ray scattering was first corrected by subtraction of a blank measurement. The subtracted $I(q)$ data were fit using a linear combination of two $S_{TS}(q)$ functions to account for the polarity and charge alternation features and one $S_L(q)$ function to describe the ion adjacency peak. For the Prop and CS samples, one additional Lorentzian function was included to account for broad baseline features. In the cases of BH₄, NFP, and NFBS, two additional Lorentzians were needed to fully describe the data. In addition, for the TFSI sample, the emergence of an additional peak intermediary between the polarity and charge alternation peaks required the addition of a third $S_{TS}(q)$ function to fit the data at temperature below 200K. Once suitable fits were obtained describing the full range of the wide-angle X-ray scattering data, the fitting data was used to calculate the radial distribution function using Equation 3.51. The atomic number density factors, ρ_0 , appearing in this equation were estimated based on correlations relating ionic volumes to molar volumes in ionic liquids.[3] Ionic volumes for the ions in this study were obtained from group contributions given in the same reference except for the BH₄ and CS anion volumes, which were calculated using the Marvin software package from ChemAxon. The ionic volumes and resulting densities are given in Table 4.1. In an iterative fashion, the $I(q)$ data was normalized such that the calculated $g(r)$ functions decayed asymptotically to unity,

Table 4.1: Ionic volumes, ν^+ and ν^- [nm³], of the P_{666,14} cation and the six anions along with molecular weights, MW [g/mol], estimated molar volumes, V^{est} [cm³/mol], and atomic number density, ρ_0 [Å⁻³], at a reference temperature of 298.15 K. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

IL	MW	ν^+	ν^-	V^{est}	ρ_0
P _{666,14} BH ₄	498.707	0.805	0.037	580.5	0.110
P _{666,14} Prop	556.927	0.805	0.105	627.4	0.107
P _{666,14} NFP	746.899	0.805	0.259	733.6	0.096
P _{666,14} NFBS	782.949	0.805	0.288	753.5	0.094
P _{666,14} TFSI	763.997	0.805	0.230	713.6	0.098
P _{666,14} CS	715.147	0.805	0.204	695.4	0.113

i.e. $g(r) \rightarrow 1$ as $r \rightarrow \infty$. The structural data normalized in this way is therefore renamed $S(q)$. In addition to the parameters describing the three primary regions of the structure factor of these ionic liquids, the average coordination number in the first solvation shell, n_1 , was calculated by integrating $g(r)$ according to Equation 3.52. The results of this analytical procedure, yielding the temperature dependence of the structural parameters, are given in the following sections along with a discussion of their relationship to the possible liquid-liquid transition that is proposed to occur in this family of ionic liquids.

4.1.1 Polarity alternation

We begin by examining the temperature dependence of the polarity alternation structure corresponding to the first sharp diffraction peak in the $S(q)$ data. This feature arises due to the alternation of polar, ion-rich regions and apolar, alkyl-rich regions present in the ionic liquid structure. These regions form due to strong Coulombic interactions tending to pack the ions into a network of alternating charges excluding the weakly interacting alkyl chains via solvophobic effects. In the P_{666,14}-based ionic liquids this results in a percolated, bicontinuous network of alternating polar and apolar domains in the normal liquid state. This type of structure can be well-described using the TS model, with the periodicity of polarity alternation, d_{pol} , corresponding to the average distance separating two polar domains across the apolar domain and the correlation length, ξ_{pol} , describing the decay distance of the periodic structure.

Figure 4.8 shows the temperature dependence of d_{pol} for the six P_{666,14}-based ionic liquids in this study. As observed in the $S(q)$ data (Figures 4.2A-4.7A), the size of the polarity alternation structure tends to increase with decreasing temperature. Furthermore, a discontinuous change in d_{pol} is observed for the BH₄, Prop, NFP, NFBS, and TFSI samples at some characteristic temperature. The changes seen in the BH₄, Prop, and NFP samples show a discontinuous increase in d_{pol} on the order of about 0.5 Å as the samples are cooled below the transition temperature. Close inspection of the NFBS sample (bottom row, center in Figure 4.8) reveals that d_{pol} increases by roughly 0.5 Å at a temperature of 220 K as the sample is cooled. Compare these results to the plot for the CS sample (bottom row, right in Figure 4.8), which appears to show only a continuous increase in d_{pol} with no sudden changes

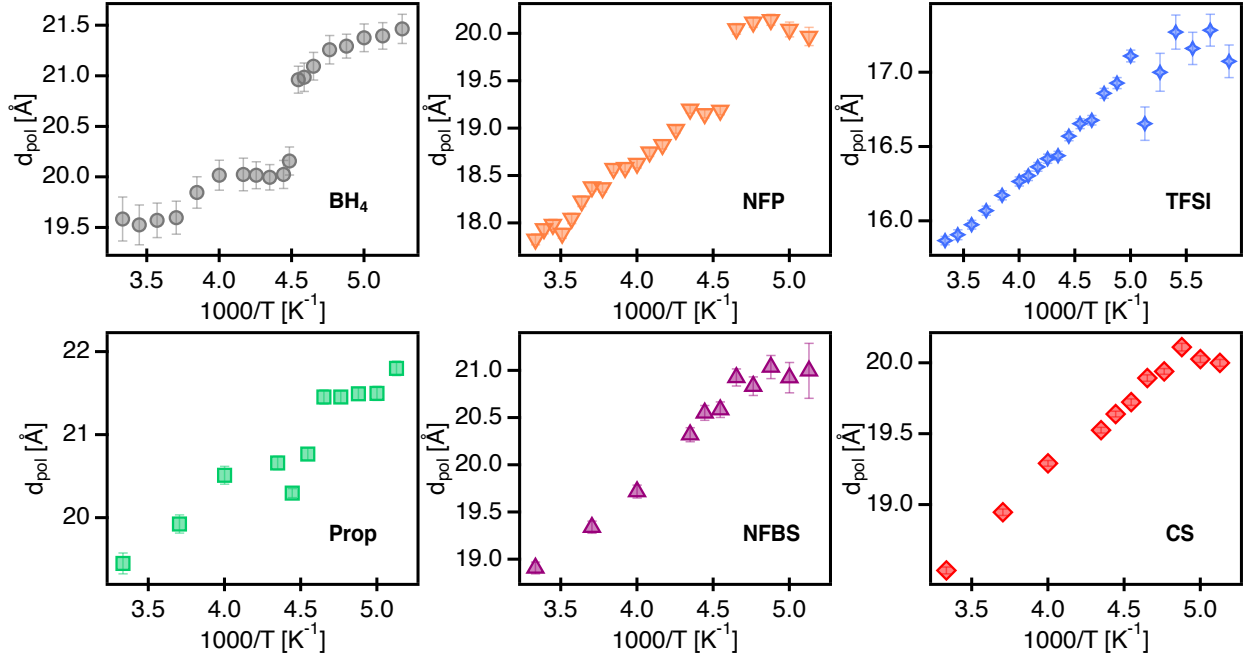


Figure 4.8: Temperature dependence of the polarity alternation periodicity. Periodicity of polarity alternation, d_{pol} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

on the order of 0.5 Å as the temperature is decreased down to 205 K, where the data plateaus corresponding to the formation of the glassy state. Note that in the TFSI case (top row, right in Figure 4.8), the discontinuity appearing in the temperature dependence in d_{pol} shows a sharp decrease on the order of 0.5 Å as the sample is cooled below 200 K in contradistinction to the BH₄, Prop, NFP, and NFBS samples. This first set of results tells us that a structural reorganization occurs for certain anions paired with the P_{666,14} cation at some characteristic transition temperature. Whether these structural changes correspond to a first order liquid-liquid transition will be addressed as the details of the behavior of the systems are borne out in later sections. For now, we can define a characteristic temperature corresponding to discontinuities in the temperature dependence of the structural quantities describing these ionic liquids and attempt to understand how the overall structure is changing at the characteristic temperature, T_x .

From the data presented in Figure 4.8, we observe the general tendency of the length of the polarity alternation periodic structure to increase as the samples are cooled from 300 K down to below 200 K with the five samples, BH₄, Prop, NFP, NFBS, and TFSI showing a large discontinuity in this length scale. Let us now examine the temperature dependence of the correlation lengths, ξ_{pol} , associated with the decay distance of the periodic polarity alternation structure given in Figure 4.9. Generally, the correlation length, ξ is related to the long range order of the periodic structure. Larger ξ values correspond to more ordered structures over a longer range. When ξ is smaller than the periodic length, d , this indicates the presence of large fluctuations in the structure on local scales. The data in Figure 4.9 shows an interesting trend between the correlation length associated with the polarity alternation and the anion sizes. In terms of the anion volumes given in Table 4.1, we have BH₄ < Prop < CS < TFSI < NFP < NFBS. Comparing this to the range of ξ_{pol} for each anion, ξ_{pol} tends to larger values with decreasing anion size, indicating that the long-range order of the periodic polarity alternation structure is inversely related to the size of the anion. The TFSI case presents an exception to this trend, showing significantly lower values for ξ_{pol} than the other samples. This is likely due to a trade-off with charge ordering in these systems, as will be discussed in the next section.

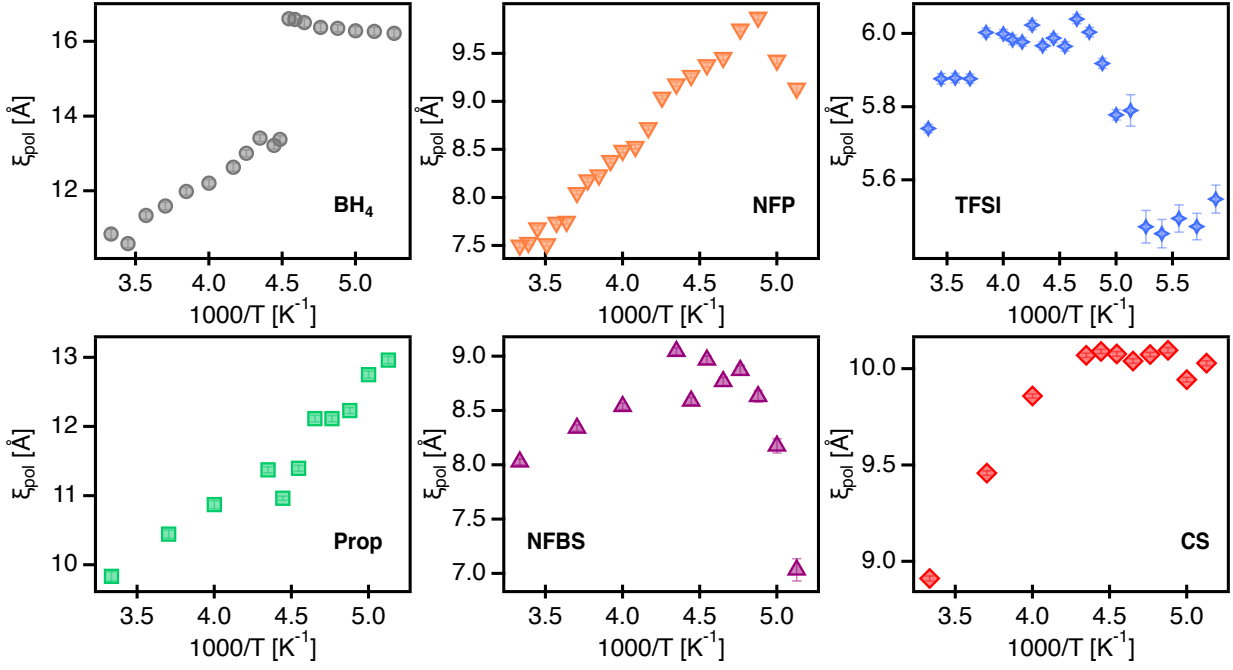


Figure 4.9: Temperature dependence of the polarity alternation correlation length. Correlation length of polarity alternation, ξ_{pol} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

Considering the trends in the temperature dependence of ξ_{pol} for each anion in Figure 4.9, at higher temperatures far above the characteristic temperature defining the reorganization of the ionic liquid structure, ξ_{pol} increases as the sample is cooled indicating an increase in order of the polarity alternation structure. As the temperature approaches the structural transition temperature, T_x , ξ_{pol} diverges drastically for the BH_4 sample (top row, left in Figure 4.9) increasing by over 2 Å at $T_x \approx 220$ K. A similar trend is also seen in the Prop case (bottom row, left in Figure 4.9), only the increase in ξ_{pol} is less than 1 Å occurring at $T_x \approx 215$ K. The increase in ξ_{pol} at T_x is not seen in the other samples. Instead, ξ_{pol} for the NFP and NFBS samples (top and bottom respectively, center in Figure 4.9) increases before dramatically dropping off as the samples vitrify. In the TFSI case (top row, right in Figure 4.9), ξ_{pol} dramatically decreases at $T_x \approx 200$ K. For the CS sample (bottom row, right in Figure 4.9), ξ_{pol} is essentially constant in the supercooled liquid above T_g .

Figure 4.10 shows the temperature dependence of the normalized correlation length, ξ_{pol}/d_{pol} , for the six anions studied. This ratio reports the relative order of the periodic structure independently from the size of the structure.[347] For the case of $\xi_{pol}/d_{pol} < 1$, large local fluctuations in the distance separating the polar regions are present. As ξ_{pol}/d_{pol} approaches unity, the size of the local fluctuations are diminished. When $\xi_{pol}/d_{pol} > 1$, mesoscopic order beyond the local scale is present. The same trend in overall order of the polarity alternation structure with anion size is evident from Figure 4.10, again with the exception of the TFSI sample (top row, right in Figure 4.10).

Figure 4.11 shows the integrated peak area of the polarity alternation structure, $(I_0 A_{TS})_{polar}$, with respect to inverse temperature for the six ionic liquids studied. These plots show essentially the inverse of the trends observed in ξ_{pol} (Figure 4.9). This is because the correlation length is inversely related to the peak width.[347] Hence, the quantity $(I_0 A_{TS})_{polar}$ is also a reporter of the overall order of the periodic structure, with smaller $(I_0 A_{TS})_{polar}$ corresponding to a more ordered state.

4.1.2 Charge alternation

Here we discuss the temperature dependence of the charge alternation structure corresponding to the intermediate range in the $S(q)$ data. This structure corresponds to the ordering

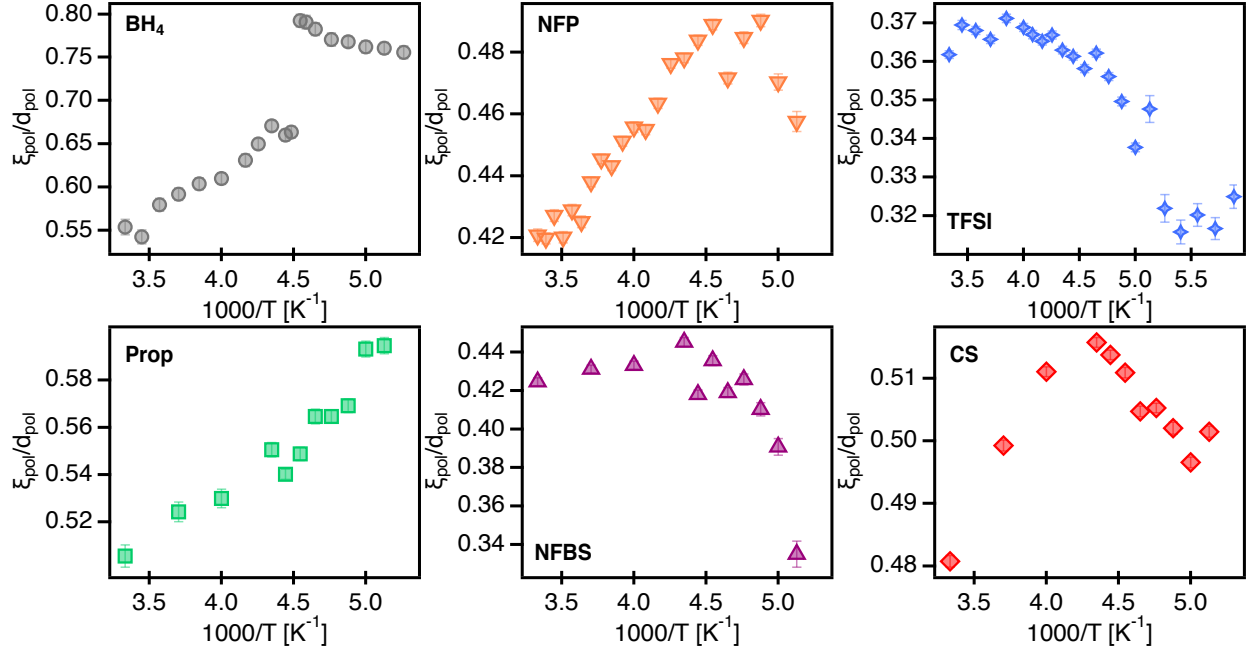


Figure 4.10: Temperature dependence of the normalized polarity alternation correlation length. Normalized correlation length of polarity alternation, ξ_{pol}/d_{pol} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH_4 , NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

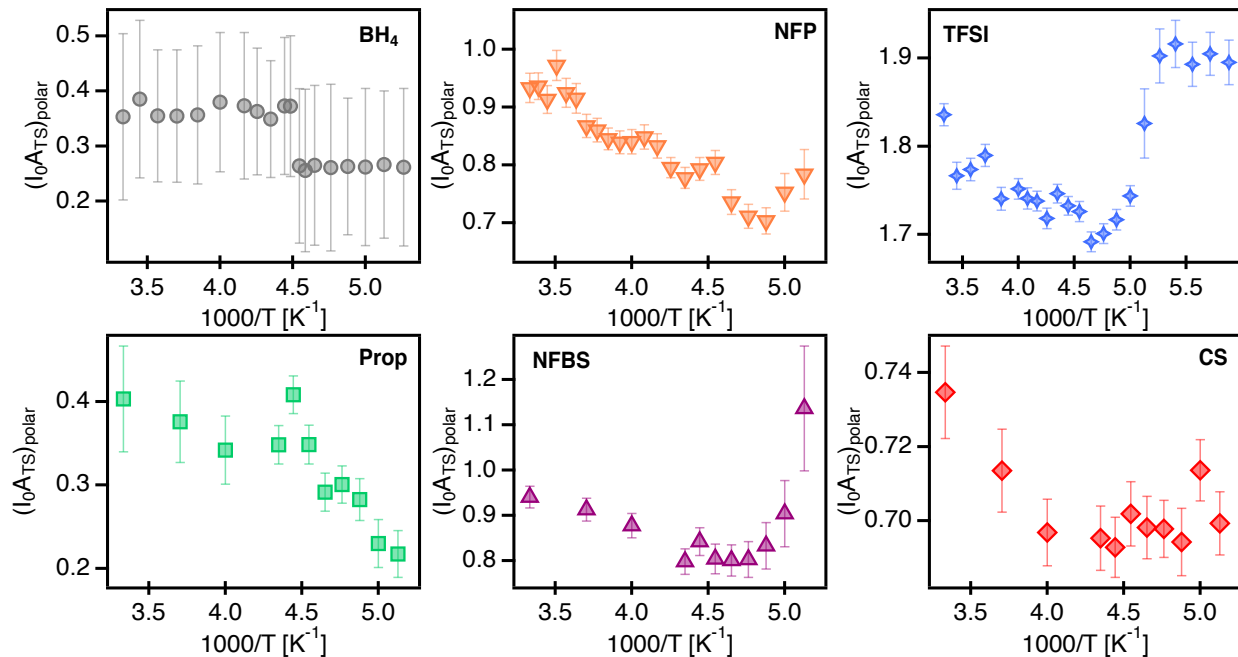


Figure 4.11: Temperature dependence of the polarity alternation integrated peak intensity. Integrated peak intensity of polarity alternation, $(I_0 A_{TS})_{pol}$, versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

of alternating positive and negative charges that comprise the 3-dimensional, percolated charge network in the normal liquid state of $P_{666,14}$ -based ionic liquids. Figure 4.12 shows the temperature dependence of the periodicity of charge alternation, d_{ch} , for the six ionic liquids in this study. Since anions are the main reporters of structure in ionic liquids due to their higher electron density, d_{ch} can be thought of as the distance between two anions separated by a cation head group, although contributions from cation-cation and cation-anion correlations are also present in the total scattering function. It is due to the negative contributions from cation-anion correlations resulting in antipeaks that the charge alternation peak is often observed as a weak shoulder or not at all in the measured $S(q)$ data.[4] Despite this fact, the charge alternation structure is still present in all ionic liquids, but fits to this region carry larger error in the parameters when the charge alternation peak is extremely weak. For the BH_4 sample (top row, left in Figure 4.12), d_{ch} decreases discontinuously by about 0.5 Å at T_x . In the Prop sample (bottom row, left in Figure 4.12), d_{ch} shows a non-monotonic change in its temperature dependence around T_x and is lower in the low temperature liquid state compared with the high temperature, normal liquid state. In both the NFP and NFBS samples (top and bottom respectively, center in Figure 4.12), d_{ch} is roughly constant at just below 11 Å in the high temperature liquid state. However, at $T_c \approx 215$ K for both of these samples, their behavior diverges. NFP shows a dramatic decrease in d_{ch} of about 1 Å at T_x before increasing again as the sample approaches the glass transition. The NFBS case does not show a sudden change in d_{ch} at T_x , but it begins to rise sharply below T_x increasing by over 1.5 Å as the sample is cooled to the glassy state. TFSI (top row, right in Figure 4.12) shows yet another behavior where d_{ch} decreases monotonically with decreasing temperature before plateauing and remaining essentially constant below T_x . For the CS sample (bottom row, right in Figure 4.12), d_{ch} increases slightly with decreasing temperature reaching a constant value in the glassy state.

Figure 4.13 shows the temperature dependence of the correlation length of the charge alternation structure, ξ_{ch} for the six ionic liquids. It appears that, for all of the ions except for CS, ξ_{ch} tends to increase in the low temperature state. To clarify, the BH_4 sample shows a statistically significant jump in ξ_{ch} at T_x . The same behavior is observed in the TFSI case, but to a larger extent.

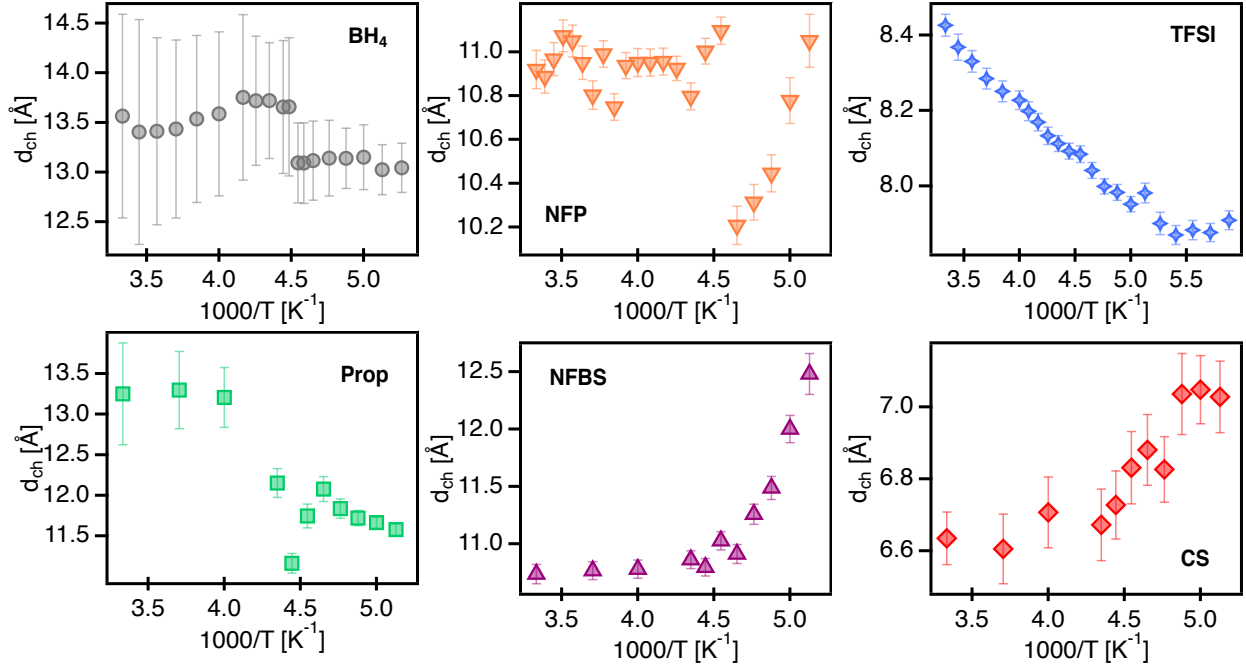


Figure 4.12: Temperature dependence of the charge alternation periodicity. Periodicity of charge alternation, d_{ch} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

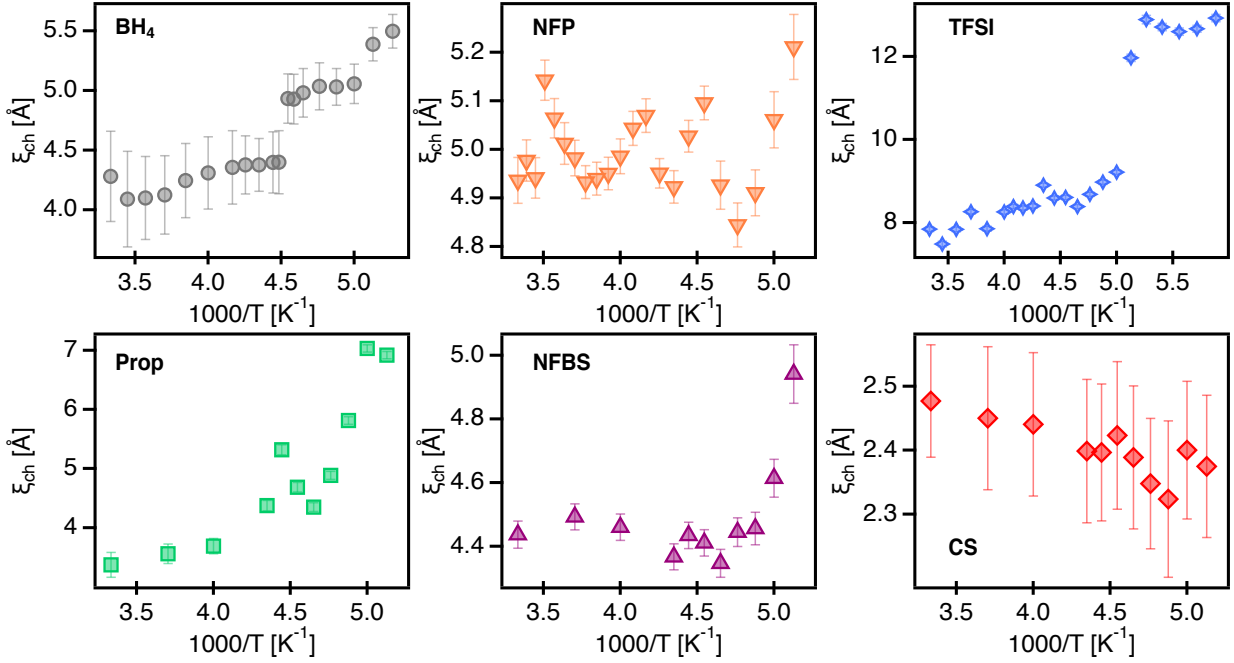


Figure 4.13: Temperature dependence of the charge alternation correlation length. Correlation length of charge alternation, ξ_{ch} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

To better understand the changes in charge ordering, we can look at the normalized correlation length of charge alternation, ξ_{ch}/d_{ch} , shown with respect to inverse temperature in Figure 4.14. A discontinuous increase in ξ_{ch}/d_{ch} occurs in the BH₄, NFP, and TFSI samples (top row, left, center, and right, respectively, in Figure 4.14) indicative of an increase in charge ordering. The Prop sample (bottom row, left in Figure 4.14) shows a non-monotonic increase in ξ_{ch}/d_{ch} with decreasing temperature, also reflective of increased charge ordering. In contrast, both the NFBS and CS samples (bottom row, center and right, respectively, in Figure 4.14) show a decrease in charge ordering as the temperature is lowered. Note that for all of the ionic liquids except the TFSI case, ξ_{ch}/d_{ch} is less than unity. The TFSI case is unique, showing ξ_{ch}/d_{ch} greater than one, indicating charge ordering on the scale of multiple ion pairs.

Figure 4.15 shows the integrated area of the charge alternation feature, $(I_0 A_{TS})_{charge}$, with respect to inverse temperature for the six ionic liquids studied. As in the case of polarity alternation, these plots largely show the inverse of the trends observed for the correlation lengths, ξ_{ch} , in Figure 4.13. Non-monotonic changes in the temperature dependence of $(I_0 A_{TS})_{charge}$ are observed in the BH₄, Prop, NFP, NFBS, and TFSI samples occurring around T_x in each system.

4.1.3 Ion adjacency

Next, we move to the ion adjacency region. The peak in this region, around $1.3 \text{ \AA}^{-1}$ for the ionic liquids studied here, manifests from numerable different contributions from correlations between adjacent atoms, reflecting both intra- and intermolecular interactions. The ion adjacency peak in ionic liquids can be thought of as nearest neighbor ion correlations. Figure 4.16 shows the temperature dependence of the ion adjacency distances, d_{adj} , for the six ionic liquids studied. In general, d_{adj} decreases linearly as the sample is cooled reflecting an increase in local density as thermal motions of the molecules slow down and fluctuations due to the thermal kinetic energy of the molecules diminish. The data in Figure 4.16 shows a slight shift towards larger d_{adj} near the characteristic transition temperature, T_x , in the BH₄, Prop, NFP, NFBS, and TFSI samples. This suggests a slight decrease in local density near T_x . For the TFSI case, there is a drop in d_{adj} below T_x , indicative of a sudden increase in lo-

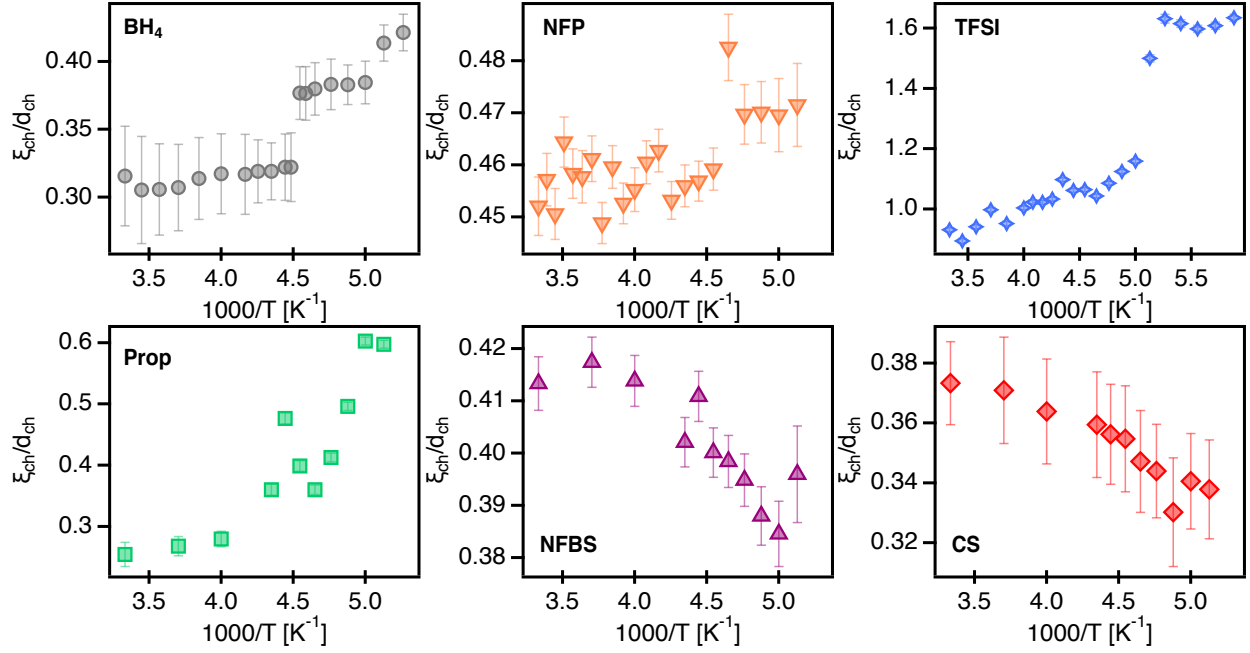


Figure 4.14: Temperature dependence of the normalized charge alternation correlation length. Normalized correlation length of charge alternation, ξ_{ch}/d_{ch} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

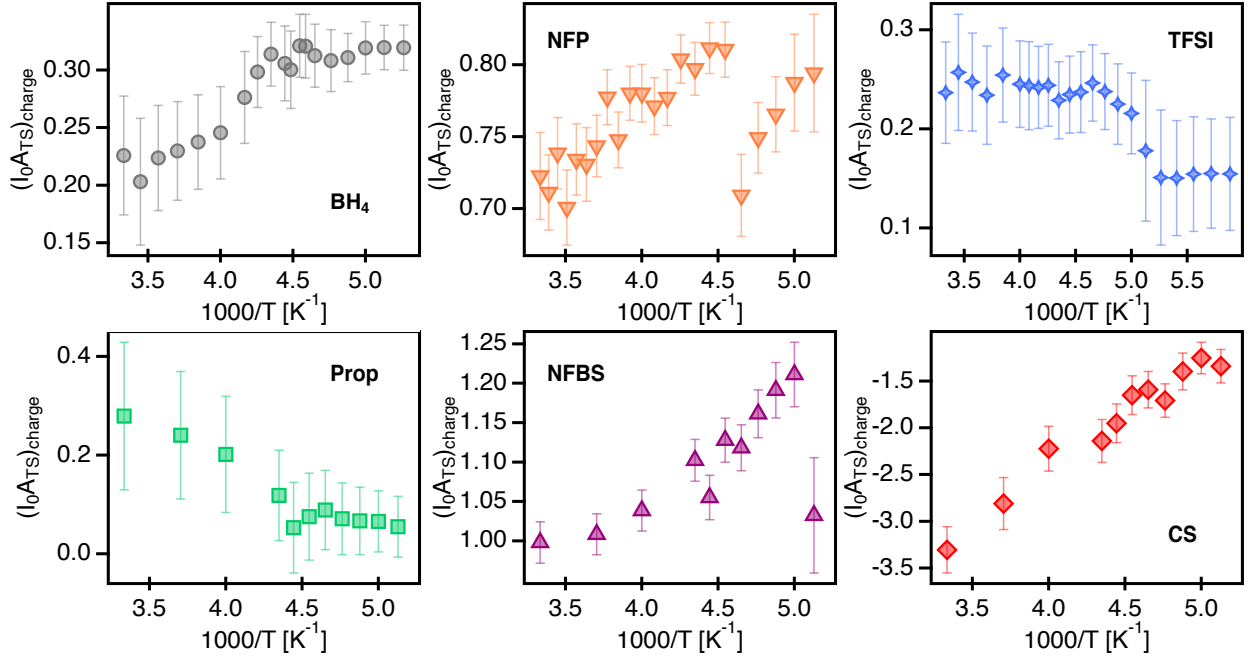


Figure 4.15: Temperature dependence of the charge alternation integrated peak intensity. Integrated peak intensity of charge alternation, $(I_0 A_{TS})_{\text{ch}}$, versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

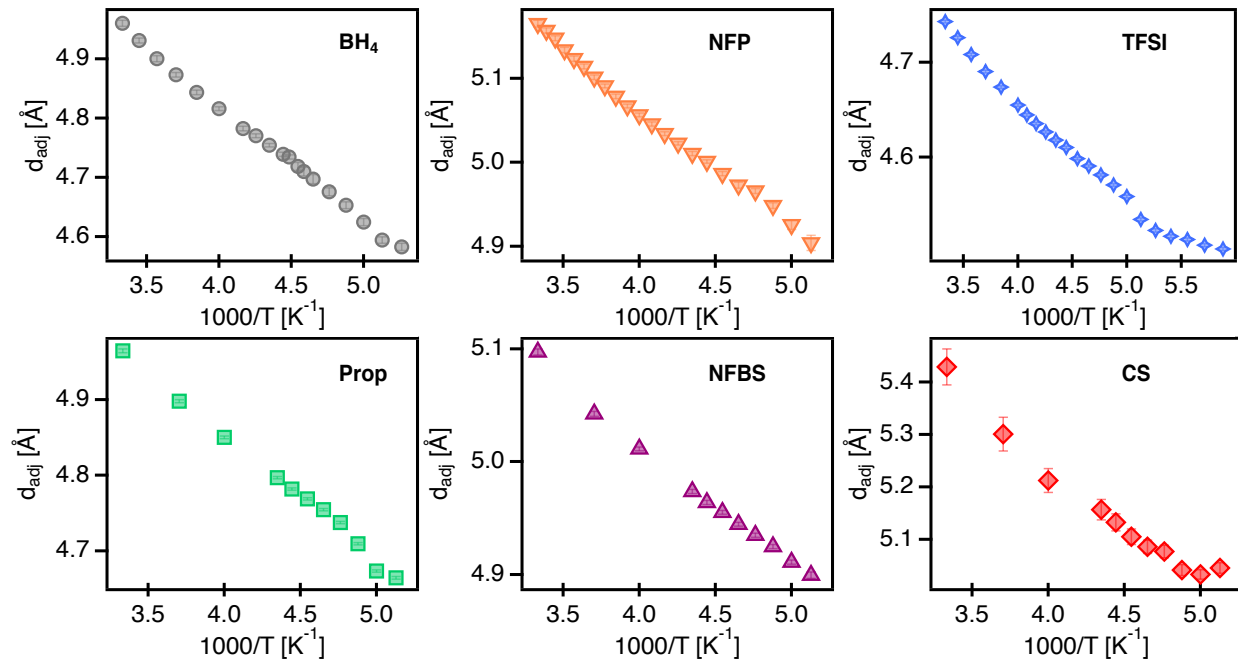


Figure 4.16: Temperature dependence of the ion adjacency correlation length. Correlation length of ion adjacency, d_{adj} , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

cal density across the transition in this sample. A change in the temperature dependence of d_{adj} is also observed in the CS sample, occurring at the glass transition.

Figure 4.17 shows the temperature dependence of the intensity of the ion adjacency peak, $(I_0)_{adj}$, for the six ionic liquids in this work. The intensity of this peak increases with decreasing temperature in the high temperature liquid state for the BH₄, Prop, NFP, NFBS, and TFSI samples. The opposite trend is observed in the CS case. Changes in the peak intensity are reflective of changes in the local electron density of the correlated structures. Therefore, it makes sense that a decrease in the average distance between adjacent ions would be correlated to an increase in local electron density. The anticorrelation for the CS case suggests additional interactions affecting the local charge density. A slight shift in the temperature dependence of $(I_0)_{adj}$ is observed in the Prop, NFP, and NFBS samples near T_x . In stark contrast, the BH₄ and TFSI samples show large changes in $(I_0)_{adj}$ at T_x . For the BH₄ case, a large decrease in $(I_0)_{adj}$ occurs at T_x . However, $(I_0)_{adj}$ shows a discontinuous jump below T_x .

In a sense, the changes in the ion adjacency peak are the most difficult to understand owing to the large number of intra- and intermolecular contributions to this feature in the scattering data. Nevertheless, the adjacency peak is the reporter of extremely localized structure so even small deviations from continuous, monotonic temperature dependence of the position or intensity of this peak reflect reorganization of the liquid structure on the local scale.

4.1.4 Average ion coordination number

Finally, we discuss the temperature dependence of the average ion coordination number, n_1 , which represents, for instance, the average number of anions coordinated to a central cationic center in the first coordination shell or nearest neighbor radius. The size of the first coordination shell corresponds to the first minimum in $g(r)$ or between 6 and 8 Å in this set of ionic liquids (see Figures 4.2B-4.7B). The number of ions of one type that can coordinate to a central, oppositely charged ion depends on the strength of the electrostatic interactions between the ions as well as steric effects related to the geometry of the ions. Coulombic attraction can tightly bind oppositely charged ions together, forming an ionic bond. How-

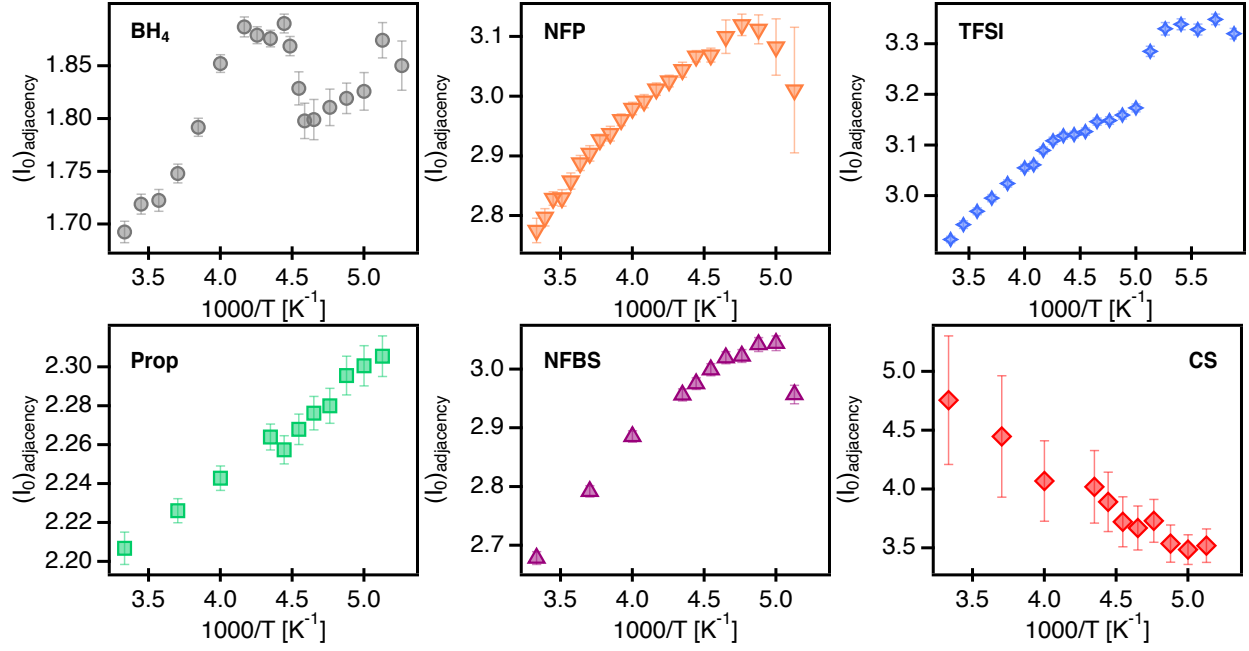


Figure 4.17: Temperature dependence of the ion adjacency peak intensity. Peak intensity of ion adjacency, $(I_0)_{adj}$, versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

ever, geometric constraints limit the distance of approach and impose volumetric constraints on the number of ions that can access the minimum approach distance. In ionic liquids, the strength of the electrostatic attraction is sufficient to hold the ions in a dense state, but geometric factors such as size, asymmetry, and charge distribution maintain the ion separation distance resulting in weakly coordinated states or ionic associations that are not true ionic bonds. This scenario of geometric frustration offers a simple explanation for the tendency of certain pairings of cations and anions to form ionic liquids with low melting temperatures as opposed to crystalline ionic solids, e.g. salt, with extremely high binding energies and melting temperatures. This also suggests an explanation for the excellent glass-forming ability of many ionic liquids. Ionic liquids are liquids precisely because the individual ions possess sufficient thermal kinetic energy to randomly overcome the attractive electrostatic potential acting to bind them together. Thus, the ions are mobile and can respond to an external field gradient giving rise to fluid flow in response to a shear stress or momentum gradient and ionic conduction in response to an electric field or potential gradient.

Due to the constraints of geometric frustration as well as net charge neutrality, the cations and anions in ionic liquids form local structures that are arranged in bulk morphologies depending on the relative sizes of the ions and especially on the presence and length of apolar alkyl chains attached to the ion species, which do not experience strong electrostatic interactions. In ionic liquids with short alkyl chains ($n_c < \sim 6$), typically on the cation, the ions are arranged in a dense charge network dotted with isolated apolar islands in a continuous polar sea.^[101] As the length of the alkyl chain is increased beyond the percolation limit, ionic liquids experience a morphology change from isolated islands to a bicontinuous structure exhibiting a continuous polar network segregated from a continuous apolar domain. Further increasing the alkyl chain length can lead to the formation of ionic liquid crystal phases.^[283] Depending on the number of alkyl chains attached to the central cation, which affects the number of allowed nearest neighbor interactions, the branching of the polar network defines its morphology as either globular or filamentous, the latter of which defines the polar network of the normal liquid state in P_{666,14}-based ionic liquids.^[101]

The morphology of the polar network depends directly on the average coordination of the ions. In the filamentous structure exhibited by quaternary cation systems with all long alkyl chains including P_{666,14}-based ionic liquids, the ions are arranged in strands of alternating charge corresponding to a typical coordination number of 2 with each cation, say, sandwiched by two anions. Based on this simplified approach, assuming the ions in the filamentous polar network are typically coordinated to two other ions forming the local strand, one can hypothesize primitive ion coordination states defined by integer values of the ion coordination number. In this scheme, $n_1=1$ corresponds to an ion pair, $n_1=2$ corresponds to a triplet, $n_1=3$ corresponds to a quartet, and so on. Geometric and electronic constraints impose a certain maximum coordination number for a given combination of ion species, however this exact value is not important for describing the majority of ionic liquid morphologies. In the filamentous case, the structural components that make up the polar network can be assigned to the primitive coordination states, with $n_1=1$ defining a terminating strand, $n_1=2$ related to the continuation of the strand, $n_1=3$ corresponding to branches, and $n_1=4$ assigned to the crossing of two strands. In describing the ion coordination numbers in a real ionic liquid, n_1 can take on fractional (non-interger) values depending on the relative distances of the ions occupying the first coordination shell because the boundary of the shell is diffuse due to thermal fluctuations. The situation is further complicated by partial and transient occupation of the coordination sphere. The complex nature of ion coordination in ionic liquid systems can be simplified by regarding the coordination state of an ion as a linear combination of the primitive integer states weighted by the probability associated with the ion occupying a given state. Summing over all ions in the system and taking the average yields the average ion coordination number defined in Equation 3.52. In this way we can define a link between the local structure and the global behavior of the ionic liquid system.

Defining the local ion coordination number as a probability-weighted linear combination of primitive coordination states allows us to define the normal liquid structure and the locally favorable structures of Tanaka’s phenomenological two order parameter model of the liquid state as distinct subsets of the total set of possible allowed linear combinations of the primitive states. Each combination in the subsets defining the normal liquid structure

and the locally favored structures relates to a particular arrangement of the ions defining a degenerate state, with the total number of allowed combinations in each subset determining its degeneracy. Then, the normal liquid structure is described by a linear combination of degenerate states. The locally favored structures are defined in a similar way. An average coordination number can be defined for both the normal and locally favored structures. We can then express the average ion coordination of the system under specific thermodynamic conditions as a function of the fraction of locally favored structures, ψ :

$$n_1(\psi) = \psi n_\psi + (1 - \psi) n_\rho \quad (4.12)$$

where n_ψ is the average coordination number of locally favored structures, n_ρ is the average coordination number of the normal liquid structure. A first order liquid-liquid transition is defined by a discontinuity in ψ at the transition temperature, T_t , which would correspond to a discontinuity in n_1 at a liquid-liquid transition in an ionic liquid system described in this way. Figure 4.18 shows the temperature dependence of the average ion coordination number for each of the ionic liquids in this work as calculated from the X-ray scattering data. There are clearly discontinuities in n_1 at the characteristic temperature, T_x associated with the structural changes observed in the previous sections in the BH₄, NFBS, and TFSI samples. Thus, we can immediately make the claim that these systems undergo a true, first order liquid-liquid transition at $T_t = T_x$. The situation is less clear in the other systems. In the Prop sample, n_1 increases at T_x , but the jump is on the order of the experimental error, so concluding that there is a discontinuity here is a tenuous assertion. Similarly, in the NFP sample, n_1 appears to continuously increase from a high temperature value to a low temperature value. There is a slight increase in n_1 at T_x , but again the change is smaller than the experimental error. If we compared the situations of the Prop and NFP samples to the plots of $g(r)$ for these two samples (Figures 4.3B and 4.4B, respectively), it is clear that the first minimum in $g(r)$ shifts to higher r at T_x . This, along with discontinuities observed in other structural parameters for these two systems, suggests that they also undergo a first order liquid-liquid transition at $T_t = T_x$. As to why n_1 for the Prop and NFP systems appear to change continuously, there are a number of possible scenarios that could lead to this result

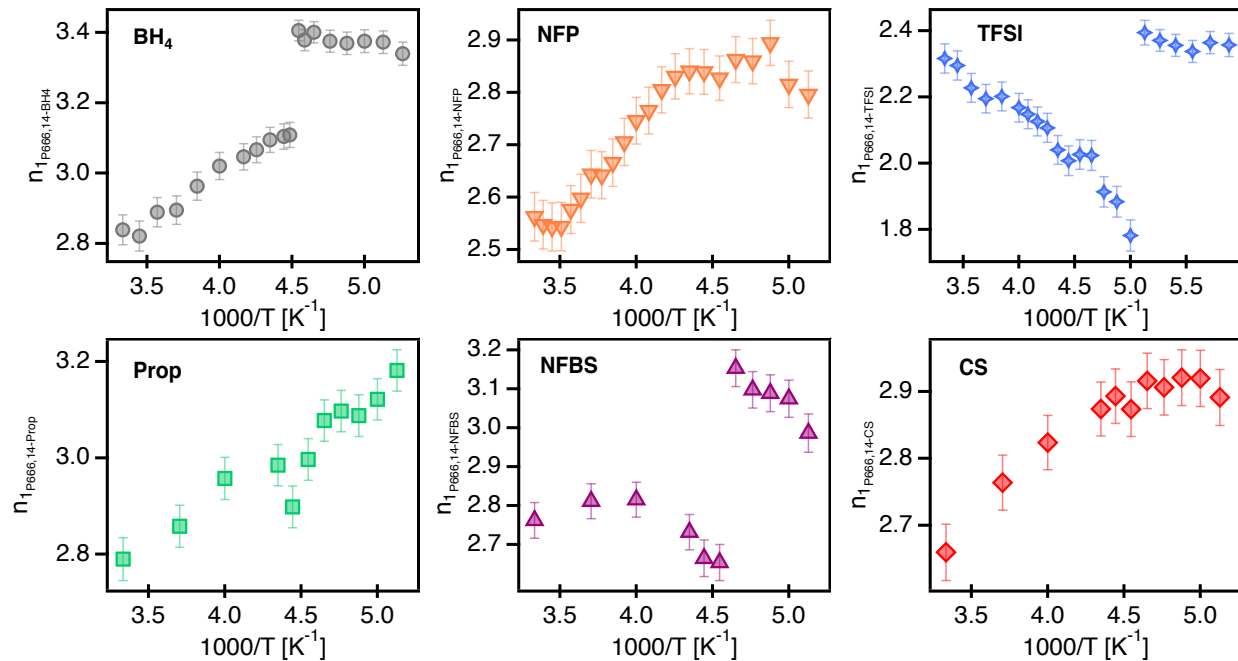


Figure 4.18: Temperature dependence of the ion coordination number. Ion coordination number, n_1 , versus $1000/T$ for the six ILs studied. Top row, from left to right: BH₄, NFP, TFSI. Bottom row, from left to right: Prop, NFBS, CS.

while still having a discontinuous change in ψ . The most probable explanation is that, since n_ρ and n_ψ are averages over degenerate states each of which is composed of probability-weighted combinations of primitive states, n_ρ and n_ψ could be similar quantities, leading to smaller changes in n_1 at T_t , so the changes appear continuous within experimental error. This situation will be resolved in the following chapter on the dielectric behavior of these ionic liquids (see Chapter 5, Section 5.2). In contrast, the CS sample, which also shows a continuous increase in n_1 up to a limiting value around $n_1=2.9$, showed no clear discontinuities in the other structural parameters that were discussed previously that would allow us to define a characteristic temperature associated with some kind of structural reorganization. Since there is also no clear shift in the first minimum in $g(r)$ (Figure 4.7B), we conclude that the CS sample does not undergo a liquid-liquid transition at ambient pressure at a temperature above the glass transition temperature of this system.

4.1.5 The second diffraction peak in low temperature P_{666,14} TFSI

Referring to the $S(q)$ data for the P_{666,14} TFSI sample shown in Figure 4.6, the emergence of an additional peak slightly above $0.5 \text{ \AA}^{-1}$ is evident at temperatures below 200 K. The second diffraction peak in the TFSI sample appears at an intermediate q -value between the features of the polarity alternation structure on the low q side and the charge alternation structure on the high q side. In the absence of computational simulations to reveal the specific sub-components of the ionic liquid structure contributing to the emergence of the second diffraction peak, we can only speculate as to its origin. Due to similarities in apparent intensity and relative proximity of the two features, it appears as though the first diffraction peak associated with the polarity alternation structure splits into two distinct levels of ordering, suggesting the second peak would originate from a new type of order in the alternation of polar and non-polar domains not present in the high temperature liquid state. The apparent splitting of the first diffraction peak at the characteristic temperature of the LLT in this IL suggests a direct signature of two-state behavior in the local ordering of the liquid structure, unequivocally pointing to a true first-order LLT. Despite this strong evidence for the LLT, without knowledge of the molecular level associations responsible for

its origins, we cannot definitively assign the two-state feature corresponding to the LLT as an explanation for the emergence of the second peak.

The temperature dependence of the structural parameters obtained from fits to the $S(q)$ data are shown in Figure 4.19. The periodicity, d_x , of this feature, given in panel A in the upper, left quadrant, is smaller than the periodicity of the polarity alternation structure of the TFSI sample, but it is on the order of the charge alternation periodicity seen in the BH_4 , Prop, NFP, and NFBS systems. Most telling is the fact that the normalized correlation length, ξ_x/d_x , of the second diffraction peak, seen in panel D in the lower, right quadrant, is greater than unity. Comparing this fact with the normalized correlation lengths of the polarity alternation structure ($\xi_{pol}/d_{pol} < 1$) and the charge alternation structure ($\xi_{ch}/d_{ch} > 1$) for this sample, it more closely matches the organization of the charge alternation structure. Is this second diffraction peak, perhaps, a reflection of charge ordering extending across an additional link in a chain of sequential ion pairs? Could it represent a second level of charge ordering with a distinct ion spacing? Again, without clear molecular level information concerning the contributions of the sub-components of the IL, no definitive assignment can be made. Determination of the origins of the second diffraction peak in $\text{P}_{666,14}$ TFSI should be regarded as a matter of urgency for future investigations of LLT in this system. For now, it can be taken to represent a clear indication of two-state behavior and a first-order LLT manifesting in this particular sample.

4.2 Using Raman spectroscopy to probe conformational order of alkyl chains in $\text{P}_{666,14} \text{BH}_4$

Raman spectroscopy can be used to study the conformational states of alkyl chains by examining the Raman modes associated with C-C and C-H motions. As a way of determining the conformations of the alkyl chains in a $\text{P}_{666,14}$ -based ionic liquid that exhibits a liquid-liquid transition to see how the conformations change between the high- and low-temperature liquid states, temperature dependent Raman measurements were performed on $\text{P}_{666,14} \text{BH}_4$. This system was specifically chosen for this study because the only carbon atoms in this sys-

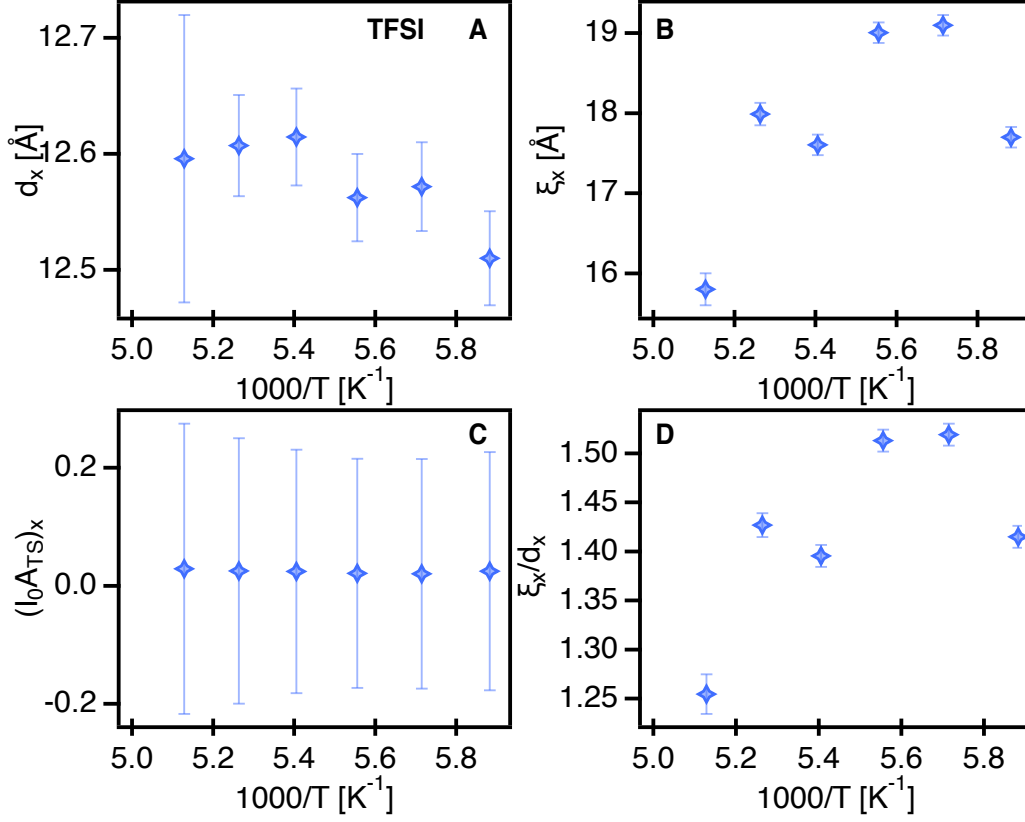


Figure 4.19: Temperature dependence of the structural parameters corresponding to the second diffraction peak in low-temperature $P_{666,14}$ TFSL. (A) Periodicity, d_x , of the second diffraction peak in low-temperature $P_{666,14}$ TFSL. (B) Correlation length, ξ_x , of the second diffraction peak in low-temperature $P_{666,14}$ TFSL. (C) Integrated peak intensity, $(I_0 A_{TS})_x$, of the second diffraction peak in low-temperature $P_{666,14}$ TFSL. (D) Normalized correlation length, ξ_x/d_x , of the second diffraction peak in low-temperature $P_{666,14}$ TFSL.

tem are in the alkyl chains attached to the $P_{666,14}$ cation. Furthermore, the $P_{666,14} BH_4$ shows clear evidence of a liquid-liquid transition occurring around $T_t=220$ K based on analysis of the wide-angle X-ray scattering data presented in the previous section.

The Raman measurements were performed using the Horiba LabRAM HR Evolution confocal Raman microscope with a 532nm excitation laser at 50% power, a 50x LWD objective, over three 15s accumulations, and 1800 gratings per mm filter to achieve 0.5cm^{-1} resolution. The $P_{666,14} BH_4$ sample was first dried under vacuum ($< 10^{-6}$ bar) at 340 K for 24 hours. A drop of the sample was then loaded into a Linkam THMS600 temperature stage with silica windows to control the temperature to within $\pm 0.1\text{K}$ using liquid nitrogen as the coolant, and the sample thickness was maintained at approximately $150\mu\text{m}$ using Teflon spacers. The sample was measured in the temperature range from 183K to 253K on cooling at 5K/min and heating at 10K/min pausing at each temperature for the duration of the measurement. Variations between the cooling and heating data were minimal.[6]

Particular regimes of the Raman spectra identified as reflective of the configuration of alkyl chains[348] were fit using a series of Gaussian peaks in order to quantify peak positions, intensities, and widths. Regions of interest included the $\nu(C - C)$ region between 1065 and 1130cm^{-1} , the $\tau(CH_2)$ region around 1300cm^{-1} , the $\delta(CH_2)$ and $\delta_a(CH_3)$ region between 1440 and 1458cm^{-1} , and the $\nu(CH_{2/3})$ region between 2800 and 3000cm^{-1} . The $\nu(C - C)$ region was normalized to the height of the peak at 1050cm^{-1} prior to peak fitting. Peak fitting of the $\delta(CH_{2/3})$ region was performed without prior normalization.

Regarding the extension and ordering of the polarity alternation structure which is dependent on the configuration of the alkyl chains on the $[P_{666,14}]^+$ cation, the Raman spectra (Figure 4.20) exhibit features associated with the structural transition stemming from changes in the aliphatic groups attached to the phosphonium cations[348, 349, 350]. Three distinct regions associated with vibrational modes of the alkyl chains are present in the Raman spectra between 1050 cm^{-1} and 1500 cm^{-1} (Figure 4.20A). The C-C stretching modes denoted $\nu(C - C)$ appear as three peaks around 1065 cm^{-1} , 1079 cm^{-1} , and 1130 cm^{-1} [348]. These modes provide information about the conformational order of the alkyl chains where the peaks at 1065 cm^{-1} and 1130 cm^{-1} indicate *trans* conformers ($\nu(C - C)_T$) and the peak at 1079 cm^{-1} corresponds to the *gauche* conformation. In Figure 4.20C, the

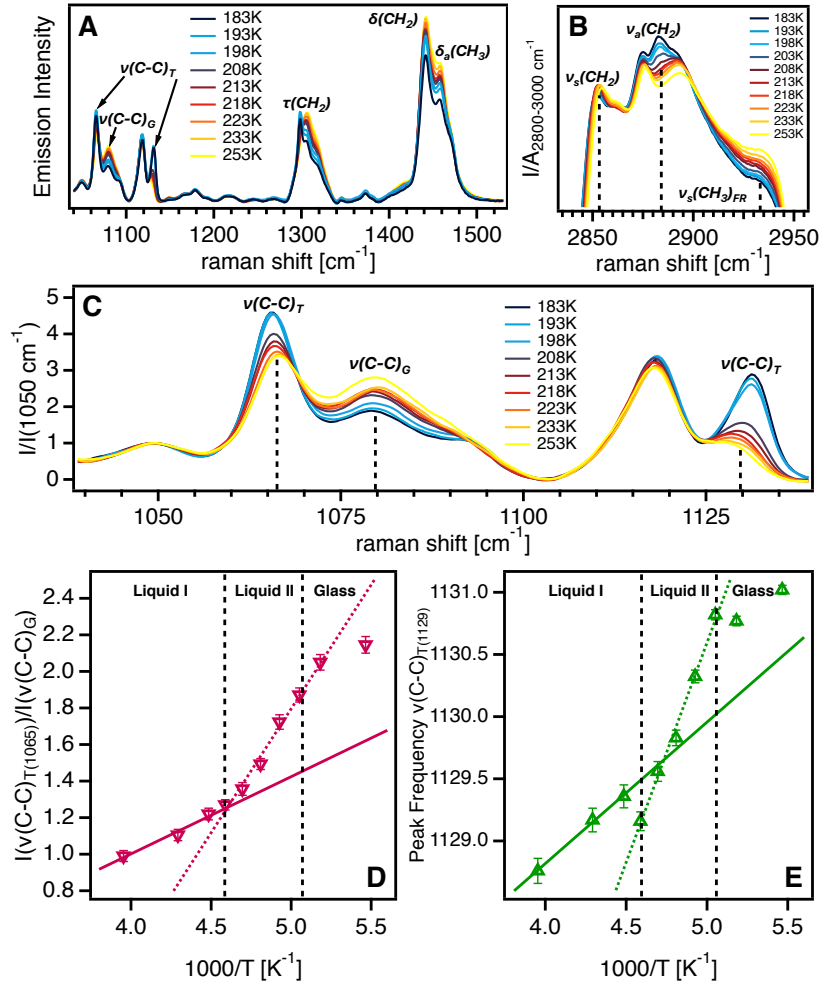


Figure 4.20: Ordering of alkyl chains across the LLT. (A) Raman spectra of $P_{666,14}BH_4$ at various temperatures from 1040 cm^{-1} to 1530 cm^{-1} . (B) Raman spectra of $P_{666,14}BH_4$ at various temperatures from 2835 cm^{-1} to 2955 cm^{-1} . (C) Normalized Raman spectra between 1040 cm^{-1} and 1140 cm^{-1} . (D) Ratio of the intensity of the $\nu(C-C)_T$ peak at 1065 cm^{-1} to the $\nu(C-C)_G$ peak at 1079 cm^{-1} . (E) Peak frequency of the $\nu(C-C)_T$ mode around 1130 cm^{-1} . Solid and dotted lines represent linear fits to the data to serve as guides for the eye. Vertical dashed black lines indicate the transition from liquid I to liquid II to the glassy state. Reproduced from [6].

region between 1040 cm^{-1} and 1140 cm^{-1} is zoomed in to show the changes in intensity and peak frequency of the $\nu(C - C)$ modes with temperature more clearly. The intensity ratio of the $\nu(C - C)_T$ peak at 1065 cm^{-1} to the $\nu(C - C)_G$ peak at 1079 cm^{-1} yields the relative number of *trans* to *gauche* conformers (Figure 4.20D). The trend of this ratio with respect to temperature shows a change in slope at the liquid-liquid transition corresponding to an increase in the number of *trans* conformers in the low temperature liquid II state. Likewise, the intensity and the peak frequency of the $\nu(C - C)_T$ peak around 1130 cm^{-1} is sensitive to the number of *trans* conformers in the liquid. The intensity of this peak increases as the liquid is cooled (Figure 4.20C) and the peak shifts to higher frequency (Figure 4.20E). The increase in the peak frequency of this mode (Fig 4.20E) exhibits a non-monotonic trend similar to the intensity ratio in Figure 4.20D with a change in slope observed at the liquid-liquid transition temperature, T_{L-L} , corresponding to an increase in the number of *trans* conformers and increased ordering of the alkyl chains. Spectral bands around 1300 cm^{-1} (Figure 4.20A) correspond to CH_2 twisting modes, denoted as $\tau(\text{CH}_2)$, are superimposed on other modes corresponding to methylene deformation[348]. The relative intensities and positions of these modes correspond to the degree of coupling between alkyl chains and the relative number of *trans* to *gauche* conformers. The shift in the dominance from the mode at 1305 cm^{-1} to the $\tau(\text{CH}_2)$ mode at 1300 cm^{-1} as the liquid is cooled reflects an increase in both chain coupling and the relative number of *trans* conformers. The peaks at 1440 cm^{-1} and 1457 cm^{-1} (Figure 4.20A) correlate to CH_2 bending denoted $\delta(\text{CH}_2)$ and antisymmetric CH_3 bending denoted $\delta_a(\text{CH}_3)$, respectively[348]. A decrease in the ratio of the integrated areas of these peaks $A[\delta_a(\text{CH}_3)]/A[\delta(\text{CH}_2)]$ (Figure 4.21C) is linked to reduced intramolecular motion of methylene and methyl groups and increased chain coupling. This quantity decreases monotonically with temperature down to T_g indicating the slowing down of local motions in the alkyl chains accompanying the dynamic glass transition. Due to the localized origins of these spectral bands, they are not sensitive to the structural reorganization associated with the LLT. The spectral region between 2800 cm^{-1} and 3000 cm^{-1} (Figure 4.20B) includes numerous overlapping peaks dominated by C-H stretching modes around 2852 cm^{-1} ($\nu_s(\text{CH}_2)$), 2883 cm^{-1} ($\nu_a(\text{CH}_2)$), and 2935 cm^{-1} ($\nu_s(\text{CH}_3)_{FR}$)[348]. The temperature evolution of these modes indicates increased chain coup-

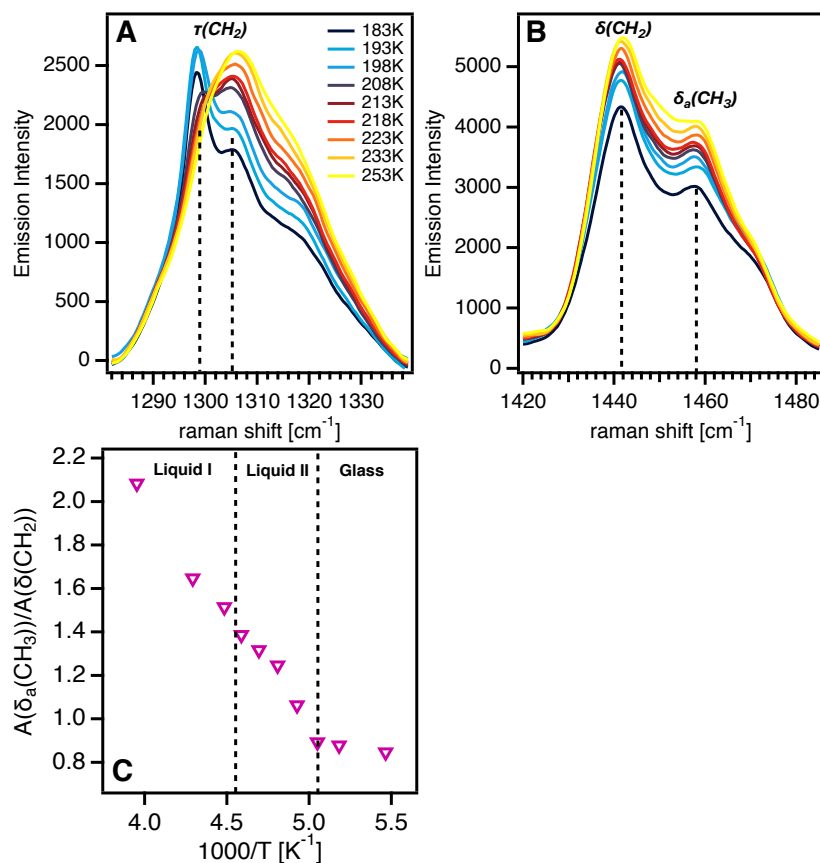


Figure 4.21: Detail of Raman spectra of $P_{666,14}BH_4$. (A) Raman spectra of $P_{666,14}BH_4$ between 1280 and 1340 cm^{-1} showing the $\tau(CH_2)$ (twisting) modes. (B) Raman spectra of $P_{666,14}BH_4$ between 1420 and 1485 cm^{-1} showing the $\delta(CH_2)$ (bending) modes. (C) Ratio of the integrated areas of the $\delta_a(CH_3)$ and $\delta(CH_2)$ modes. Reproduced from [6].

ling and conformational order. It is evident from Figure 4.20B that while the $\nu_a(CH_2)$ and $\nu_s(CH_3)_{FR}$ envelopes increase in intensity as the liquid is cooled, the $\nu_s(CH_2)$ mode diminishes which suggests the development of a more ordered arrangement of the alkyl chains.[6]

The regions of the Raman spectra around 1300cm^{-1} and $1440\text{-}1458\text{cm}^{-1}$ along with the ratio of the integrated areas of the $\delta_a(CH_3)$ to $\delta(CH_2)$ peaks are given in Figure 4.21. Note in Figure 4.21C, the ratio $A(\delta_a(CH_3))/A\delta(CH_2)$ decreases monotonically with temperature down to the glass transition reflecting the slowing of local motions in the alkyl chains. The $\nu(CH_{2/3})$ region was normalized based on the integrated area between 2800 and 3000cm^{-1} . [6]

4.3 Conclusions

The family of ionic liquids bearing the $P_{666,14}$ cation have been relatively well studied in terms of their structures in the high temperature liquid state. The bulk of these structural studies have been carried out using computational methods, specifically atomistic molecular dynamics simulations. These studies have revealed a wealth of information concerning the contributions from the cationic, anionic, polar, and apolar components of these liquids to the total structure factor. As a result, a comprehensive picture of the overall structures of these ionic liquids can be understood in terms of the contributions from individual parts of the molecular structures generating competing types of order due to the influence of competing local interactions. In the normal high temperature liquid state, $P_{666,14}$ -based ionic liquids are arranged in a continuously percolating, 3-dimensional, alternating charge network. The polar part of the network is comprised of strands or filaments of alternating charged groups, the cation head group and the anion. The filaments are dispersed throughout the liquid, separated and surrounded by apolar regions composed of the 14 carbon long alkyl tails on the quaternary phosphonium center and decorated by the shorter, 6 carbon long, alkyl tails.

The results of temperature dependent X-ray scattering measurements described in this chapter reveal discontinuities in the structural parameters characterizing the IL structure for the samples bearing the BH_4 , Prop, NFP, NFBS, and TFSI samples. These discontinuities appear in multiple structural quantities of each of the ILs where they are present, always

at the same characteristic temperature for a given IL system. These results suggest a temperature driven structural reorganization in each of the ILs that could be linked to the existence of a first-order liquid-liquid transition in these ILs. In contrast, discontinuities do not appear in the structural data for the CS sample, indicating LLT is not present. The general trend for the average ion coordination numbers across the LLT in these IL systems shows a dramatic increase in the number of ion associations. In addition, Raman spectroscopy was used to probe conformational order in the alkyl chains on the cation in the BH_4 system, revealing an increase in the number of *trans* conformers, an indication of enhanced order in the apolar domain of this IL system.

Chapter 5

Dielectric aspects of the liquid-liquid transition in ionic liquids

In this chapter, the temperature dependence of the dynamic and dielectric properties of the six ionic liquids in this study as reported by broadband dielectric spectroscopy (BDS) are presented covering a temperature range from 370 K to the glass transition temperature of these materials near 200 K. In order to understand the results presented here within the context of our current understanding of the application of dielectric spectroscopy to the study of ionic liquid systems, refer to Section 2.2. For details pertaining to the principles of dielectric spectroscopy and the measurement of ionic liquids and other glass-forming systems using BDS, see Chapter 3. The frequency dependent dielectric spectra measured under isothermal conditions during cooling and reheating of the samples will be presented in Section 5.1. Here, we will identify the different dynamic processes reported by dielectric spectroscopy in a series of P_{666,14}-containing ionic liquid systems corresponding to the six anions shown in Figure 4.1, i.e. borohydride (BH₄), propionate (Prop), nonafluoropentanoate (NFP), nonafluorobutanesulfonate (NFBS), bis(trifluoromethane)sulfonimide (TFSI), and camphor sulfonate (CS). In the subsequent section (Section 5.2), the static dielectric permittivity of the ionic liquids in this work will be discussed. The fourth section (Section 5.3) will be devoted to dynamic properties as reported by dielectric spectroscopy. Finally, we will conclude (Section 5.4) with a summary of the key findings from these dielectric studies as they relate to the liquid-liquid transition and the glass transition in these systems.

5.1 Temperature dependence of the dielectric spectra

Dielectric spectroscopy provides detailed information related to the dynamics of materials across a range of timescales. In addition, it can be used to measure macroscopic dielectric properties of the system, namely dc ionic conductivity and the static dielectric permittivity, also known as the dielectric constant of the material. This information is encapsulated in the frequency dependent complex dielectric function, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. As mentioned in Section 3.1, $\varepsilon^*(\omega)$ is related to the complex conductivity function, $\sigma^*(\omega) = i\varepsilon_0\omega\varepsilon^*(\omega)$. Based on this relation, a complete representation of the dielectric spectra is contained in the real part of the complex dielectric function, $\varepsilon'(\omega)$, and the real part of the complex conductivity function, $\sigma'(\omega)$. To further clarify the relaxation processes occurring in the sample, the derivative representation of the imaginary part of the complex dielectric function, defined as $\varepsilon''_{der} = (-\pi/2) [\partial\varepsilon'/\partial \ln(\omega)]$, proves useful. In this representation the individual relaxation phenomena appear as peaks near the characteristic frequency of the relaxation process. Since the contributions from dc ionic conductivity are relatively weak in $\varepsilon'(\omega)$, the derivative representation allows access to the relaxation peaks that are overshadowed by the dc ionic conductivity response that dominates in the imaginary part of the complex dielectric function in ion-containing systems.

Figure 5.1 shows the frequency dependent dielectric spectra for the P_{666,14} BH₄ sample at various temperatures above and below the liquid-liquid transition temperature, T_t , identified in the X-ray scattering data (see Chapter 4). The dielectric spectra is shown in as $\varepsilon'(\omega)$ (Figure 5.1A), $\sigma'(\omega)$ (Figure 5.1B), and $\varepsilon''_{der}(\omega)$ (Figure 5.1C). The main feature appearing in the $\varepsilon'(\omega)$ representation at high temperatures in the BH₄ sample is a step-like increase corresponding to the primary α -relaxation of the liquid. The high frequency portion of ε' contains contributions from localized molecular fluctuations as a secondary β -relaxation as well as electronic and atomic polarization contained in the high frequency limiting value, ε_∞ . The low frequency side of the α -relaxation shows a plateau value corresponding to the static dielectric permittivity of the material. At lower frequencies, the parasitic effects of electrode polarization contribute an immense frequency dispersion resulting from the accumulation of charges at the liquid-electrode interface. In addition, since these materials are composed of

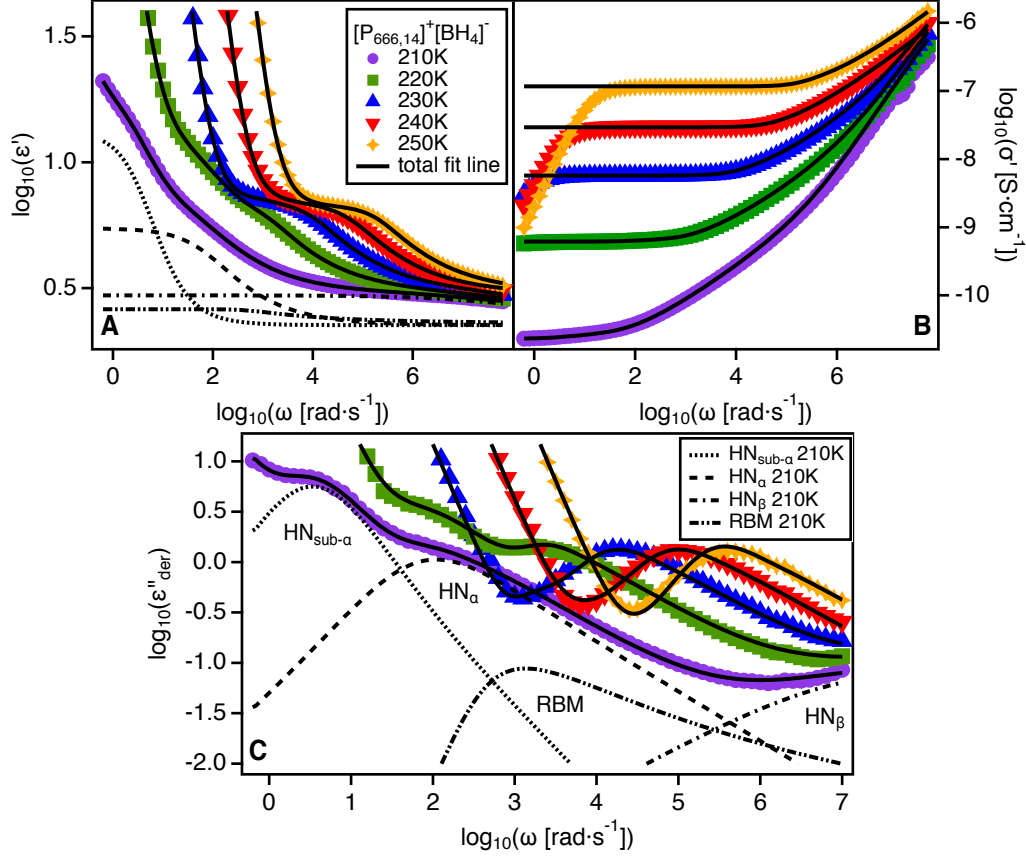


Figure 5.1: Dielectric spectra of $P_{666,14} BH_4$. (A) Real part of the complex dielectric function, ϵ' versus radial frequency, ω at various temperatures. (B) Real part of the complex conductivity, σ' versus radial frequency, ω at various temperatures. (C) Derivative representation of the imaginary part of the complex dielectric function, $\epsilon''_{\text{der}} = (-\pi/2) [\partial\epsilon'/\partial \ln(\omega)]$ versus radial frequency, ω at various temperatures. Solid black lines show fits to the data using a combination of Havriliak-Negami (HN) functions and the Random Barrier Model (RBM) with a power law function to account for electrode polarization (see Eqn. 5.1). Dashed lines show the individual HN functions (see Equation 3.41) and RBM function (see Equation 3.43) used to fit the 210K data. Note that the sub- α relaxation only appears in the spectra at or below 220K. Reproduced from [6].

mobile ions, they exhibit relatively high dc ionic conductivity, σ_0 . Contributions from σ_0 are relatively weak in the ε' representation, but appear prominently in the σ' representation, where σ_0 shows up as a frequency independent plateau. The change from the frequency dependent ac conductivity response at higher frequencies above the plateau in σ' to the dc conductivity response occurs at a characteristic frequency defined as the ion diffusion rate, ω_e . As will be demonstrated later in this chapter, the α -relaxation is coupled to the ion diffusion in these ionic liquids.

These contributions are sufficient to describe the high temperature dielectric response of the ionic liquids studied here. However, below the transition temperature ($T_x \approx 220K$ for the BH_4 case), an additional sub- α relaxation process emerges, clearly observed in the derivative representation in Figure 5.1C as an additional peak at a lower frequency than the α -relaxation. Slow relaxations, with respect to the α -relaxation, are observed in liquids where supermolecular structures collectively reorient in the response to the applied alternating electric field[351] or in the presence of internal polarizable interfaces where charges can accumulate at the boundary between regions of dissimilar dielectric properties.[287, 299, 303] The origin of the sub- α -relaxation below the transition temperature will be discussed in the next section.

Having identified the relaxation and polarization phenomena that appear in the dielectric spectra of $\text{P}_{666,14} \text{BH}_4$, we can employ a set of model functions to fit the complex dielectric function. The following equation contains the functions used to obtain the fits (solid black line in Figure 5.1).

$$\varepsilon^*(\omega) = \sum_{i=1}^n \left[\frac{\Delta\varepsilon_i}{[1 + (i\omega\tau_i)^{\beta_i}]^{\gamma_i}} \right] + \frac{\sigma_0}{\varepsilon_0} \left[\frac{\tau_e}{\ln(1 + i\omega\tau_e)} \right] + A\omega^{-\lambda} + \varepsilon_\infty \quad (5.1)$$

Here, we use a set of Havriliak-Negami (HN) functions to describe the α -, β -, and sub- α -relaxations. These contributions are described by the following parameters: $\Delta\varepsilon_i$ is the dielectric strength, τ_i is the HN relaxation time, β_i is the symmetric stretching parameter, and γ_i is the asymmetric stretching parameter. The second term in Equation 5.1 is the random barrier model used to account for the long-range ion diffusion, where σ_0 is the dc ionic conductivity and τ_e is the characteristic ion diffusion time. The next term is a

frequency dependent power law accounting for the effects of electrode polarization where A is a prefactor and λ is the exponent describing the fractal nature of the phenomena. Finally, the ε_∞ term accounts for the limiting high frequency contributions from electronic and atomic polarization. Modelling the individual contributions to the complex dielectric function in the way produces fits in good agreement with the data, as seen in Figure 5.1.

Application of this analytical procedure to the other ionic liquid systems studied allows us to ascertain the dynamic behavior and dielectric properties of these materials across a wide temperature range. Shown in Figure 5.2 are the dielectric data in the derivative representation, ε''_{der} , for the six ionic liquids in this work at various temperatures. In the BH_4 , Prop, NFP, and NFBS samples, an emergent sub- α -relaxation is observed at temperatures below the transition temperatures, T_x , identified in the structural data suggesting that the slow process is related to the low temperature liquid state described by the dominance of locally favorable structures. The TFSI sample however, does not appear to show a slow relaxation below T_x , but rather the breadth and strength of the α -relaxation apparently increase and the position of the maximum in ε''_{der} shifts to lower frequencies below T_x . In contrast, the CS sample, which showed no discontinuities in the structural parameters, shows only a progressive shift of the α -relaxation to lower frequencies as the sample is cooled.

5.2 Static dielectric permittivity and the dipole correlation environment

The static dielectric permittivity, ε_s , is a property of a material related to its ability to store energy from an imposed electric field. It is defined as the dielectric response of the material in the static limit ($\omega \rightarrow 0$) and as such, contains contributions from the dielectric relaxation and polarization phenomena observed in the frequency dependent complex dielectric function. Values of ε_s can be determined from the parameters obtained from fits to the dielectric data contained in the expression:

$$\varepsilon_s = \Delta\varepsilon_{sub-\alpha} + \Delta\varepsilon_\alpha + \Delta\varepsilon_\beta + \frac{\sigma_0\tau_e}{\varepsilon_0} + \varepsilon_\infty \quad (5.2)$$

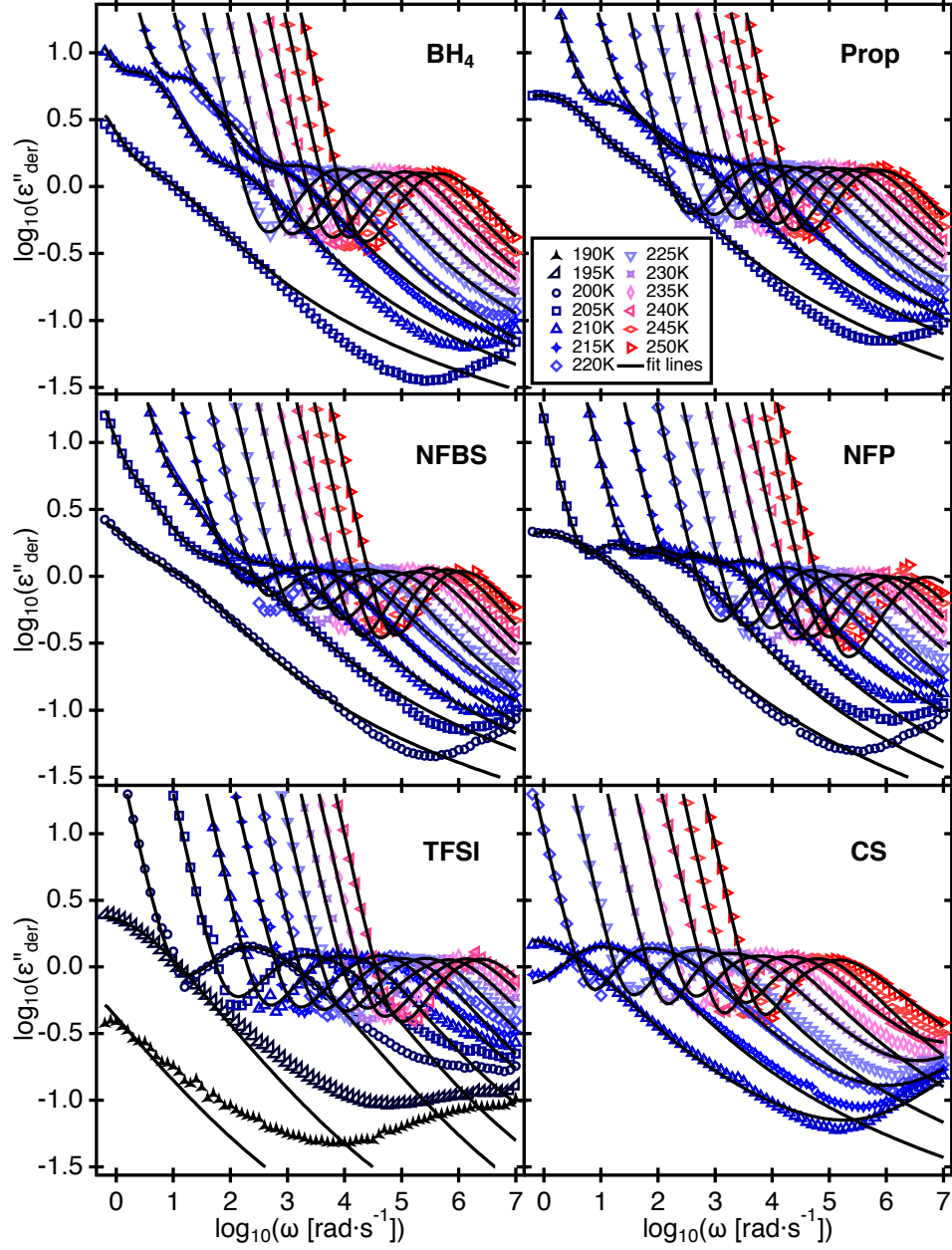


Figure 5.2: Derivative representation of the imaginary part of the complex dielectric function of $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid black lines represent fits to Equation 5.1 without including the β -relaxation term.

where $\Delta\varepsilon_{sub-\alpha}$, $\Delta\varepsilon_\alpha$, and $\Delta\varepsilon_\beta$ are the dielectric strengths of the slow relaxation, the α -relaxation, and the β -relaxation respectively, σ_0 is the dc ionic conductivity, τ_e is the timescale of ion diffusion, and ε_0 is the vacuum permittivity. The final term, ε_∞ , contains the contributions from electronic and atomic polarization.

Figure 5.3 shows the static dielectric permittivity, ε_s , for the six ionic liquids in this study as a function of $1000/T$. A step-like increase in ε_s is observed for the BH₄, Prop, NFP, NFBS, and TFSI samples occurring at the transition temperature, T_t . Note that in the case of the CS sample, ε_s remains roughly constant across the range of temperatures for which it could be determined, showing only a slight increase with decreasing temperature.

We can use the Onsager equation (Equation 3.29) to relate the temperature dependence of ε_s to the effective dipole moment of the constituent liquid particles, i.e. a cation-anion pair. The Onsager equation is valid if the dipole moments of neighboring particles are randomly oriented and cross-correlations in the dipole moment correlation function are negligible, meaning there is no preferential alignment of the dipole moments. This case corresponds to $g_k=1$ in the Kirkwood-Fröhlich equation (Equation 3.30). In this version of the equation, the Kirkwood-Fröhlich correlation factor, g_k , accounts for preferential alignment of neighboring dipoles, with $g_k > 1$ describing the tendency of the dipoles to align in parallel resulting in an increase in the observed ε_s and $g_k < 1$ corresponding to anti-parallel alignment of neighboring dipoles resulting in a decrease in ε_s . Since g_k is related to the average number of nearest neighbor dipoles, z , and the average of the cosine of the angle between the neighboring dipole moments, $\langle \cos \gamma \rangle$, by the relation $g_k = (1 + z\langle \cos \gamma \rangle)$, the degree of correlation between neighboring dipoles will be related to the local coordination environment of the ions in the liquid. Thus, in a manner similar to the description of the average ion coordination number (see Section 4.1.4), we can assert that the normal liquid structures and the locally favored structures of the phenomenological two order parameter model of the liquid state would correspond to unique dipole correlation states defined by g_ρ and g_ψ , where g_ρ is the Kirkwood-Fröhlich correlation factor associated with the normal liquid structures and g_ψ is the Kirkwood-Fröhlich correlation factor describing the locally favorable structures. Furthermore, since the normal liquid structures are defined by two-body pair correlations

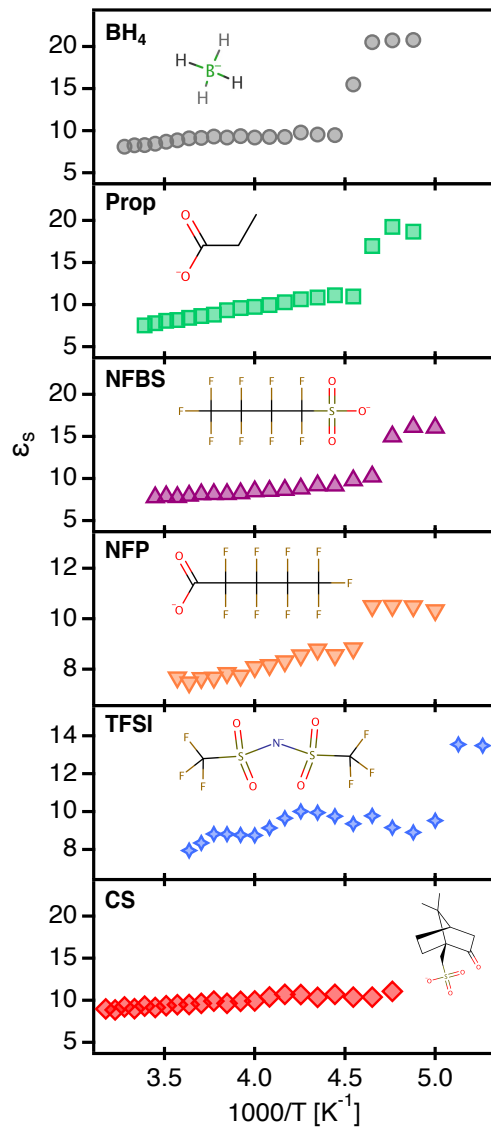


Figure 5.3: Static dielectric permittivity versus $1000/T$ for $P_{666,14}$ -based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS.

with the density, ρ , as the governing order parameter, we expect the value of g_ρ to be close to unity in ionic liquids. However, the value of g_ψ would likely differ from unity since the locally favored structures are defined by many-body interactions. Based on this interpretation, a discontinuous jump in the fraction of locally favored states corresponding to the first order liquid-liquid transition at T_x would result in a discontinuity in ε_s .

$$g_k(\psi) = \psi g_\psi + (1 - \psi) g_\rho \quad (5.3)$$

If we assume that the high temperature liquid state is defined by $g_k \approx g_\rho=1$, then we can use the Onsager equation to calculate the effective dipole moment of the system, μ^{eff} , which is a constant for a given cation-anion pair. In this way, we can lump changes to the “real” dipole moment into g_k describing the dipole correlation environment. The values of μ^{eff} calculated from the Onsager equation, given in Table 5.1, can then be used to determine the temperature dependence of g_k .

Figure 5.4 shows the temperature dependence of g_k for the six ionic liquids in this study. The dashed black lines on the plots indicate $g_k=1$ corresponding to random orientation of neighboring dipoles. A clear discontinuity is observed in g_k at the transition temperature, T_t , in the BH₄, Prop, NFP, NFBS, and TFSI samples, while g_k remains relatively constant close to unity in the CS case. This finding represents independent and complimentary corroboration for the identification of a first order liquid-liquid transition in these five P_{666,14}-based ionic liquids based on structural changes observed via wide-angle X-ray scattering.

Analysis of the static dielectric permittivity can be extended further by employing a recently developed model that attempts to refine the predictive capability of the Onsager approach using a statistical field theoretic treatment of polar fluid systems in the construction of the dipolar renormalized gaussian fluctuation (DRGF) theory.[1, 2] The approach of the DRGF theory arrives at the following equation linking the static dielectric permittivity, ε_s , to the average dipole moments of the species in the system, $\bar{\mu}_i$, with the index i corresponding to each molecular species present:

$$\frac{(\varepsilon_s - 1)(2\varepsilon_s + 1)}{\varepsilon_s} = 3y \left(\frac{2y^2 + 3y + 9}{(y + 3)^2} \right) \quad (5.4)$$

Table 5.1: Effective dipole moments calculated from the Onsager equation (Equation 3.29), $\mu_{\text{Onsager}}^{\text{eff}}$ [D], and using the equation given in references [1, 2], $\mu_{\text{DRGF}}^{\text{eff}}$ [D], for the $\text{P}_{666,14}$ cation paired with the six anions along with estimated ion pair number densities, N^{est} [nm^{-3}], at a reference temperature of 298.15 K[3]. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Cation-Anion	$\mu_{\text{Onsager}}^{\text{eff}}$	$\mu_{\text{DRGF}}^{\text{eff}}$	N^{est}
$\text{P}_{666,14}$ BH_4	5.43	6.53	1.04
$\text{P}_{666,14}$ Prop	5.21	6.57	0.96
$\text{P}_{666,14}$ NFP	5.21	6.55	0.82
$\text{P}_{666,14}$ NFBS	5.06	6.94	0.80
$\text{P}_{666,14}$ TFSI	4.53	6.81	0.84
$\text{P}_{666,14}$ CS	4.73	7.32	0.87

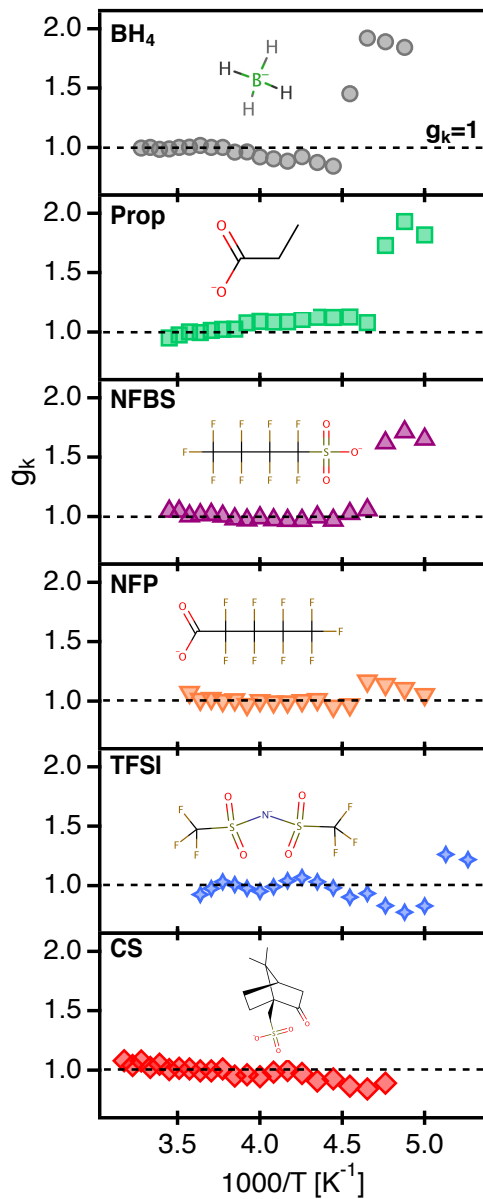


Figure 5.4: Kirkwood-Fröhlich dipole correlation factors versus $1000/T$ for $P_{666,14}$ -based ionic liquids. Top to bottom: BH₄, Prop, NFBS, NFP, TFSI, CS.

where the expression of the right-hand side of Equation 5.4 is given in terms of the dimensionless dipole interaction strength, y , which is determined as the sum over individual molecular species i in the system by the expression:

$$y = \sum_i \frac{\beta \bar{\mu}_i^2 N_i}{3\varepsilon_0} \quad (5.5)$$

where N_i is the number density of species i , $\beta = 1/k_B T$ is the inverse of the temperature scaled by the Boltzmann constant, and ε_0 is the vacuum permittivity. Using Equation 5.4, we can compute the temperature dependence of the dimensionless parameter y from the measured values of ε_s . Figure 5.5 shows the dimensionless dipole interaction strength, y , plotted as a function of $N/3\varepsilon_0 k_B T$ normalized by the value at the transition for the six P_{666,14}-based ILs studied. Note that, for the CS case, the first-order LLT is not present, but a marked change in the temperature dependence of the dimensionless dipole interaction strength is observed here, indicated by a crossover from a characteristic high-temperature dependence, showing y increasing with decreasing T , to distinct low-temperature behavior, with y remaining roughly constant with decreasing T , signaling the identification a characteristic temperature where the properties of this system shift. Quantitative determination of the crossover temperature, T_x , for the case of P_{666,14} CS by analyzing the dynamic data is detailed in Section 5.3. The other IL systems show a sharp increase in the dimensionless dipole interaction strength at T_x indicative of LLT. Note the use of T_x to refer to the characteristic crossover temperature for both the cases of first-order LLT and the continuous changes seen in the CS sample. This is done deliberately to highlight the fact that the underlying physical origin of the phenomena is the same in both instances. The primary difference is that, in the BH₄, Prop, NFP, NFBS, and TFSI cases where a first-order LLT is present, $T_x = T_t$ corresponding to the first-order transition line emanating from the liquid-liquid critical point. For each IL system, with a single dipolar species comprised of the P_{666,14} cation paired with each of the six anions, we can compute an effective dipole moment for the system based on the high-temperature data using Equation 5.5. The effective dipole moments based on the DRGF theory computed for each cation-anion pair are tabulated in Table 5.1, along side the values based on the Onsager equation. Comparing the values from the two approaches, it is

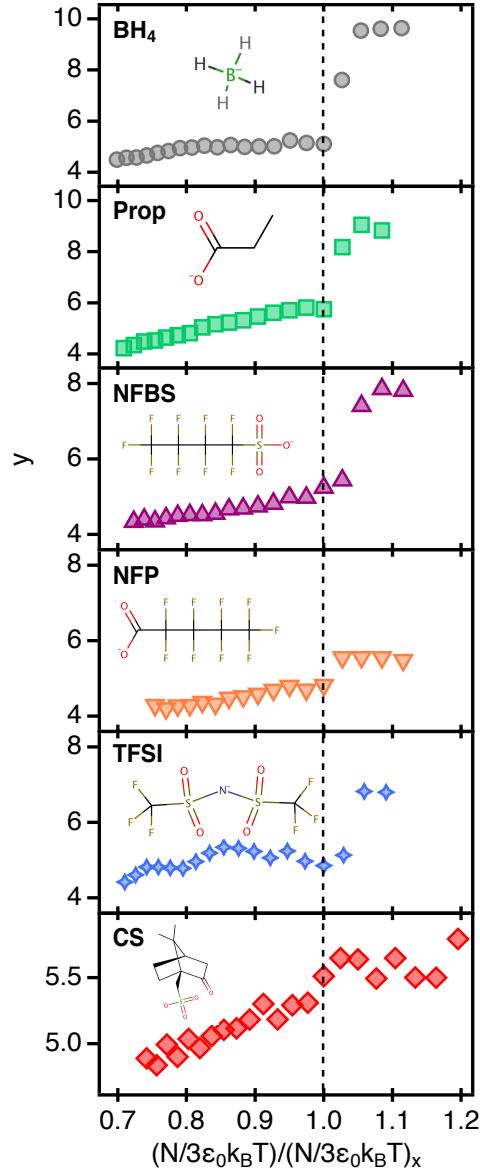


Figure 5.5: Dimensionless dipole interaction strength, y , given by the DRGF theory[1, 2] versus $N/3\epsilon_0 k_B T$ normalized by the value at the transition for $\text{P}_{666,14}$ -based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS.

apparent that the effective dipole moments obtained from the DRGF theory are larger than those based on the Onsager equation. Note that the Onsager equation employed in these calculations takes into account the high frequency limiting permittivity value, ε_∞ , in addition to ε_s to estimate the effective dipole moment. The DRGF theory does not depend on ε_∞ , which explains the large discrepancy in the tabulated values.

The DRGF theory has been developed specifically to take multiple types of dipoles into account to describe the static dielectric permittivity of mixtures.[2] By assuming that we can describe the IL systems under consideration as mixtures of ρ -states (NLS) and ψ -states (LFS), we can write Equation 5.5 in terms of the order parameter ψ corresponding to the fraction of LFS:

$$y = \frac{\beta N_0}{3\varepsilon_0} [\psi \bar{\mu}_\psi^2 + (1 - \psi) \bar{\mu}_\rho^2] \quad (5.6)$$

where $\bar{\mu}_\psi$ and $\bar{\mu}_\rho$ are the average dipole moments of the LFS and NLS, respectively, and N_0 is the number density of dipoles, assuming the difference in the density between the two states is negligible. We can rewrite Equation 5.6 to get an expression for ψ , given by:

$$\psi = \frac{y \frac{3\varepsilon_0}{\beta N_0} - \bar{\mu}_\rho^2}{\Delta \bar{\mu}^2} \quad (5.7)$$

where $\Delta \bar{\mu}^2 = \bar{\mu}_\psi^2 - \bar{\mu}_\rho^2$. In order to compute values for ψ , we make the assumptions that i) above the characteristic transition temperature, ψ varies between a lower limit of 0 and an upper limit of 0.5 and ii) below the characteristic transition temperature, ψ varies between a lower limit of 0.5 and an upper limit of 1. The assumptions allow us to determine suitable values for $\bar{\mu}_\psi^2$ and $\bar{\mu}_\rho^2$ to restrict ψ to fit the constraints given by the TOP model. The values of ψ calculated using Equation 5.7 for each IL system are plotted in Figure 5.6 as a function of transition temperature normalized inverse temperature, T_x/T . Solid curves in each panel represent the logistic ansatz for $\psi(T)$ given by Equation 5.16, discussed in Section 5.3 below. While this approximation relies on the above assumptions to define the limits imposed on the values of ψ , the DRGF theory for mixtures effectively yields the temperature dependence of ψ from measured values of ε_s by imposing only the constraints defined by the TOP model and the definition of the order parameter ψ . Based on this model, it is obvious that the Prop sample shows the closest to a logistic dependence for ψ . For the other ILs that show a

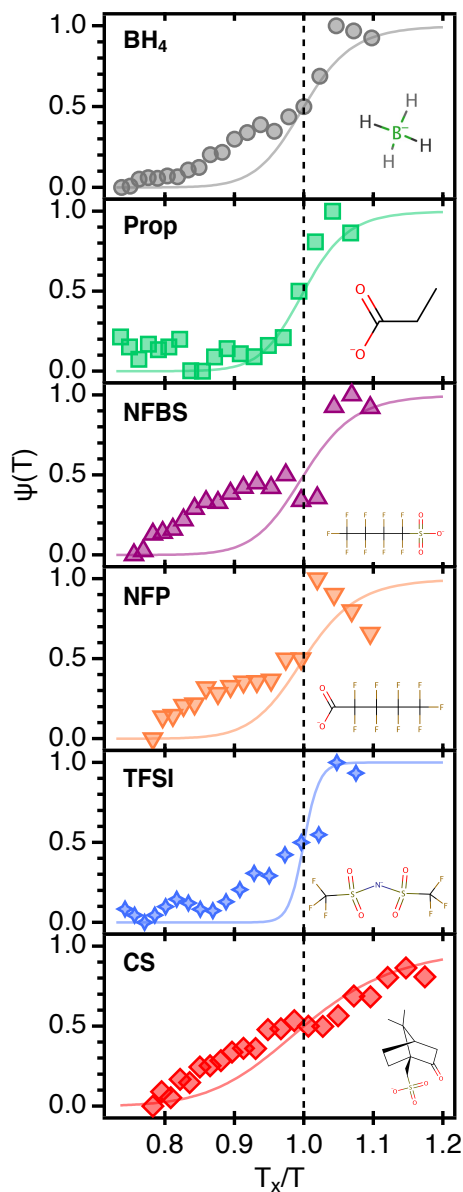


Figure 5.6: Fraction of LFS, $\psi(T)$, determined by the method in [2] versus T_x/T for $P_{666,14}$ -based ionic liquids. Top to bottom: BH_4 , Prop, NFBS, NFP, TFSI, CS. Lines show the logistic ansatz for $\psi(T)$ given by Equation 5.16, discussed in Section 5.3.

first-order LLT, ψ shows a strong increase with decreasing temperature approaching the transition. All cases showing LLT, i.e. BH₄, Prop, NFBS, NFP, and TFSI, show a stark increase in ψ following the transition. In contrast, the P_{666,14} CS sample shows a steady, continuous increase in ψ with decreasing T crossing through $\psi = 0.5$ at the crossover temperature corresponding to a shift in temperature dependent behavior for this system. The data in Figure 5.6 represents reasonable behavior for systems showing a first-order LLT, or a continuous crossover between high-temperature and low-temperature liquid behavior corresponding to an increase in LFS in the CS case, in agreement with the predictions of the TOP model. It should be noted that this reasonable agreement with the model was not a given based on the DRGF theory for mixtures and the constraints from the TOP model, but was also manifested by the measured values of ε_s obtained from the analysis of the BDS data for these six P_{666,14}-based IL systems, suggesting the two-state description of these fragile ILs is congruent with the physical nature of the liquids themselves.

5.3 Dynamics and dc ionic conductivity

Fitting the experimental dielectric data using Equation 5.1 provides information related to the dynamics of the underlying dipole reorientation and ion transport processes that contribute to the complex dielectric function. We can calculate the frequency of maximum loss of the reorientation processes from the HN parameters by Equation 3.42. This gives the relaxation rate for the structural (α) and secondary (β) processes, as well as the slow (sub- α) process if it is present, for each temperature measured with the shape parameters, β and γ , accounting for the distribution of relaxation times of the underlying reorientation process. Simultaneously, the quantities related to ion transport, dc ionic conductivity (σ_0) and the characteristic ion diffusion rate ($\omega_e = 1/\tau_e$), are obtained from the RBM term (Equation 3.43) in Equation 5.1 for each temperature. Figure 5.7 shows the Arrhenius plot of the dielectric rates, ω_α (black circles), ω_e (blue squares), $\omega_{sub-\alpha}$ (brown stars), and ω_β (green triangles), as a function of $1000/T$ [K^{-1}] for the P_{666,14} BH₄ sample. The β -relaxation rate shows typical Arrhenius-like temperature dependence corresponding to a single activation energy. This process manifests in the dielectric data at higher frequency than the ion transport and struc-

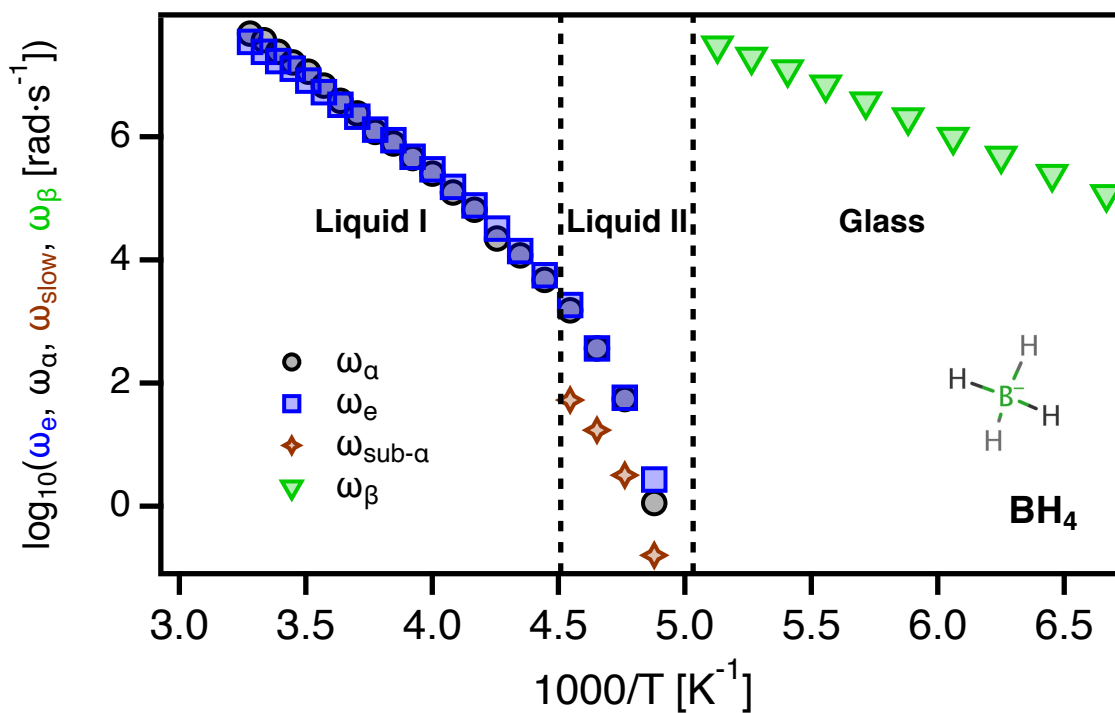


Figure 5.7: Arrhenius plot of the relaxation rates for $\text{P}_{666,14} \text{BH}_4$. The black circles represent $\omega_\alpha = 1/\tau_\alpha$, the structural relaxation rate. The blue squares correspond to ω_e , the characteristic charge transport rate from the RBM. The brown stars show $\omega_{\text{sub-}\alpha}$, the rate of the emergent slow relaxation appearing at the LLT. The green inverted triangles indicate ω_β , the secondary β -relaxation rate associated with the librating alkyl chains on the $\text{P}_{666,14}$ cation.

tural relaxation processes and is attributed to local fluctuations of the cationic alkyl chains.[298, 300] Since the β -relaxation is only observed prominently within the frequency window of the dielectric measurements at low temperatures close to and below the glass transition temperature, we will not consider it further in the discussion of dynamics across the transition from the high-temperature liquid state (HTLS) to the low-temperature liquid state (LTLS).

It is evident from the ω_α and ω_e data shown in Figure 5.7 for the BH_4 sample and in Figure 5.8 for all six ionic liquids in this work that the dynamics of the structural relaxation and ion transport cannot be described by a single activation energy. Rather, we see critical slowing of the structural and ion transport rates as the liquids are cooled from room temperature down to the glass transition temperature of the material. This behavior is common in many glass-formers and is often well-described by the empirical Vogel-Fulcher-Tammann (VFT) equation:

$$X(T) = X_\infty \exp \left[\frac{\epsilon D T_0}{T - T_0} \right] \quad (5.8)$$

$$\log_{10} X(T) = \log_{10} X_\infty + \frac{\epsilon D T_0 \log_{10} e}{T - T_0} \quad (5.9)$$

where X is a dynamic observable, e.g. viscosity (η), diffusivity ($\mathcal{D}$), structural relaxation time ($\tau_\alpha=1/\omega_\alpha$), and dc ionic conductivity (σ_0), X_∞ is the high temperature limiting value of X , D is a parameter related to the fragility of the material, and T_0 is the so-called Vogel temperature, sometimes referred to as the ideal glass transition temperature based on its association with the Kauzmann temperature, T_K , where the configurational entropy of the supercooled liquid is thought to vanish.[95, 125, 127, 138, 293, 333, 352] The coefficient, ϵ , is equal to 1 for $X = \eta$ or τ_α and -1 for $X = \mathcal{D}$, ω_α , or σ_0 . The data in Figure 5.8 show that the temperature dependence of the rate of ion transport and the structural relaxation rate are similar. In addition, the dynamics of the slow sub- α -relaxation, when present, follows the same VFT-like behavior as the structural and ion diffusion processes at a rate approximately 1 order of magnitude slower than that of the α -relaxation.

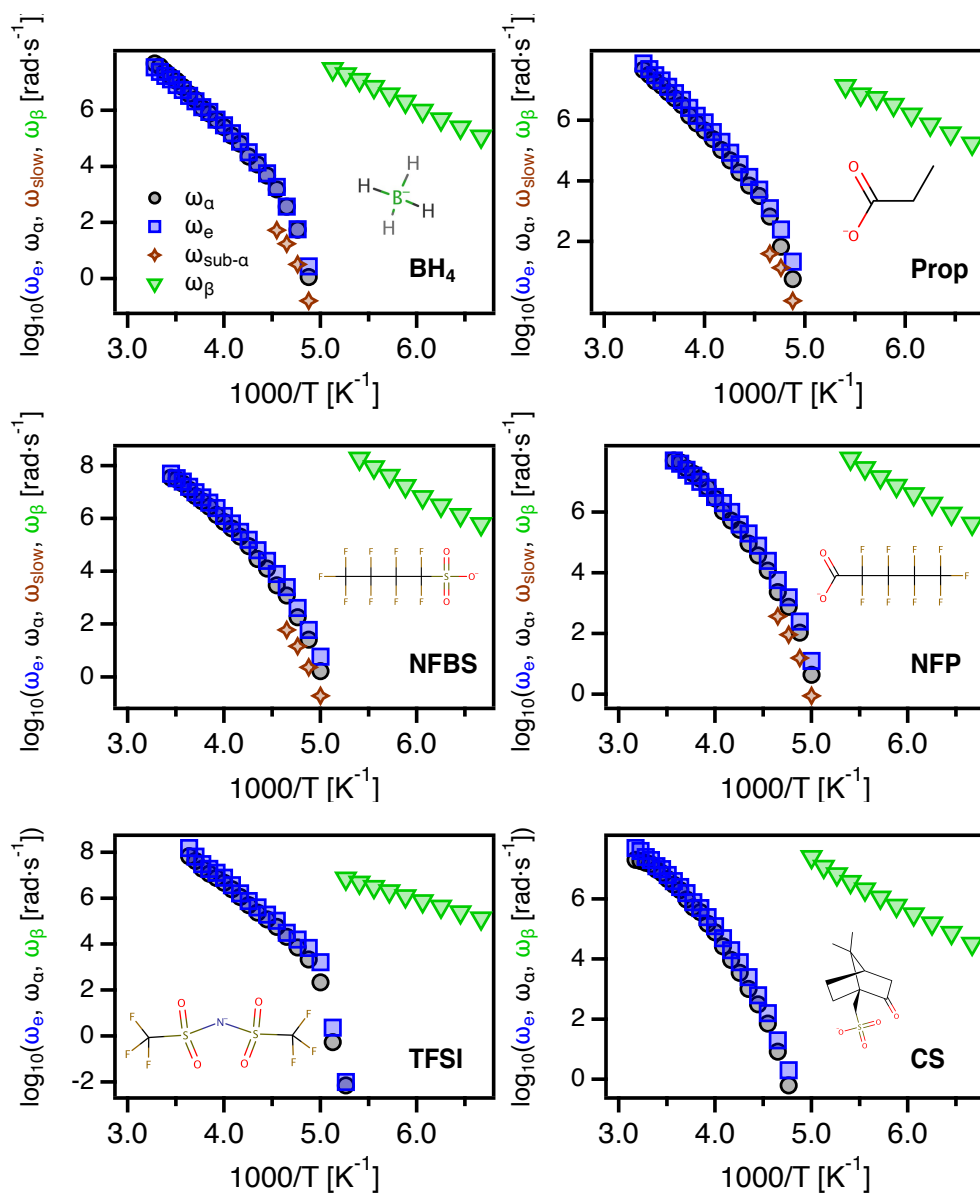


Figure 5.8: Arrhenius plots of the relaxation rates for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.

Regarding the similar temperature dependence of ω_e and ω_α , an empirical relation between long-range ion transport and the reorientation of ionic dipoles has been observed for many ion-containing systems including ionic liquids. Named for Barton, Nakajima, and Namikawa, who first introduced it, the BNN relation can be stated as:

$$\sigma_0 = p\varepsilon_0\Delta\varepsilon\omega_e \quad (5.10)$$

where σ_0 is the dc ionic conductivity, $\Delta\varepsilon$ is the dielectric strength of the dipole reorientation process, ω_e is the rate corresponding to the onset of dc ionic conductivity, ε_0 is the vacuum permittivity, and p is a parameter typically close to unity which depends on the coupling between ac and dc conductivity.[337, 353, 354] The BNN relation has been found to hold for numerous ion-containing systems, notably the aprotic ionic liquids[289, 294, 296, 300, 304], where it indicates a coupling between long-range ion motion and local ion reorientation associated with structural dynamics. For the ionic liquids in this work, the coupling between dc ionic conductivity and the structural relaxation can be checked by invoking the BNN relation demonstrating the proportionality between σ_0 and ω_α . Figure 5.9 showing σ_0 versus ω_α on a log – log scale indicates that the BNN relation holds for these ionic liquids and validates the assumption that σ_0 is coupled to the structural relaxation in these systems across the entire temperature range of the measurements.

The validity of the BNN relation for the six ionic liquids in this study suggests that the temperature dependence of charge transport and structural dynamics can both be described by the VFT equation and should have common values for the fragility index, D , and the Vogel temperature, T_0 . We can evaluate what those parameters are using a method proposed by Stickel *et al.*[125] based on the derivative of the logarithm of the dynamic quantity with respect to inverse temperature. Application of this differential analysis to the VFT equation yields:

$$\frac{d(\log_{10} X)}{d(1/T)} = (\epsilon DT_0) \left(1 - \frac{T_0}{T}\right)^{-2} \log_{10} e \quad (5.11)$$

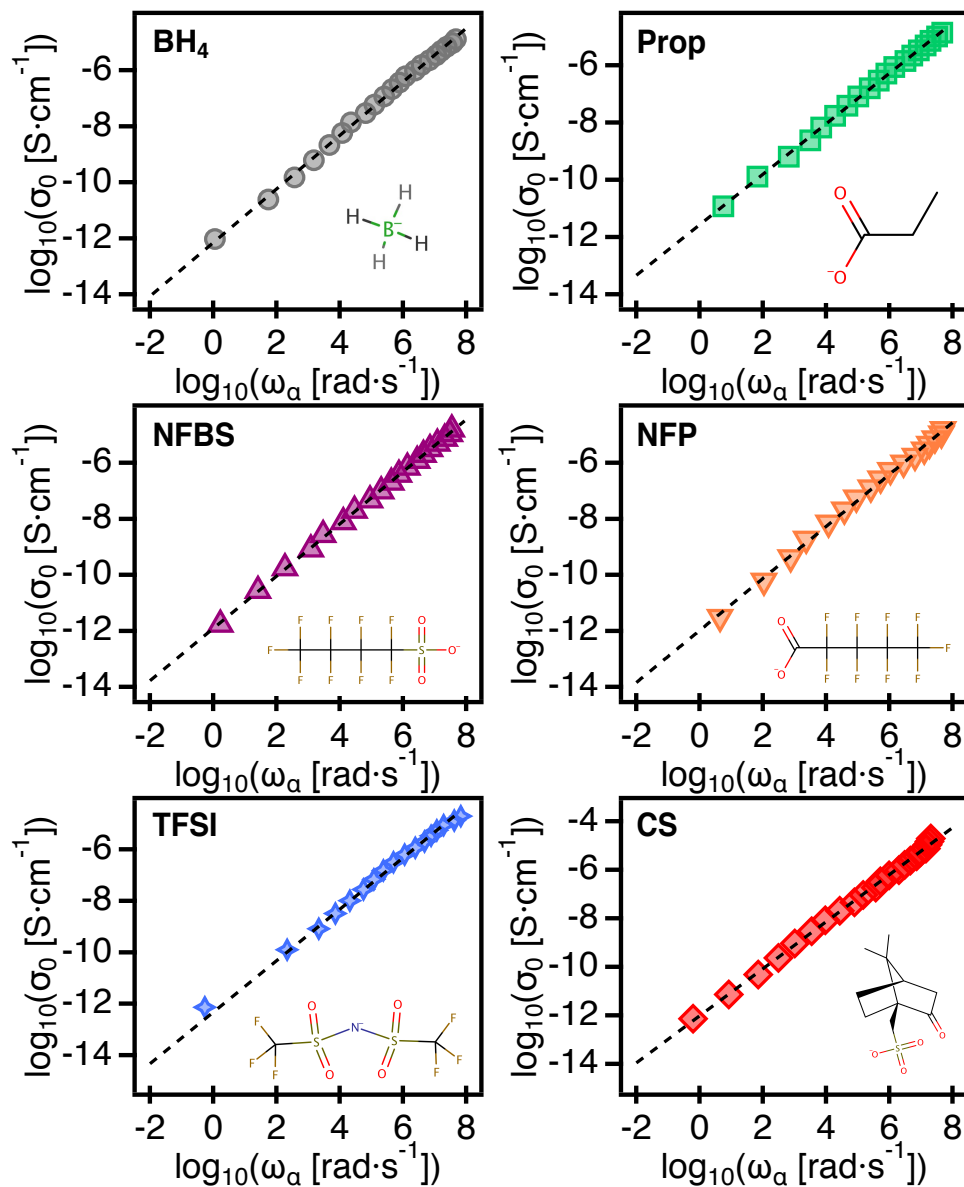


Figure 5.9: BNN plots for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.

The Stickel function is then defined by:

$$\Phi(T) = \left[\epsilon \frac{d(\log_{10} X)}{d(1/T)} \right]^{-1/2} = (DT_0 \log_{10} e)^{-1/2} \left(1 - \frac{T_0}{T} \right) \quad (5.12)$$

giving a linear dependence in inverse temperature with negative slope for dynamics following VFT-like behavior. This differential analysis is commonly used as a model-free method of determining changes in dynamic behavior with regard to temperature. It also proves to be a useful method to accurately determine the VFT parameters, D and T_0 , in cases where the dynamics can be described by the VFT equation. Figure 5.10 shows $\Phi(T)$ as a function of inverse temperature, computed from σ_0 for the six ionic liquids studied. It is immediately clear from the plots that the temperature dependence of σ_0 is well-described by the VFT equation based on the inverse linear dependence of the differential quantity with respect to inverse temperature. Furthermore, a dynamic shift in these ionic liquids is evident from a kink in the differential quantity corresponding to a change in slope. We conclude that the full temperature range of the conductivity data requires two sets of VFT parameters to accurately describe the dynamic behavior in these systems. Similar dynamic crossover behavior has been observed in a variety of glass-forming liquids, including other ionic liquid systems.[160, 188, 192, 196, 355, 356, 357]

Based on the Stickel method, the crossover temperature, T_B , can be determined by the intersection of the two VFT fit lines. For measurements carried out at ambient pressure (~ 0.1 MPa), the crossover temperature, T_B , corresponds to a specific value of σ_0 , which, in turn, is related to a particular structural relaxation time based on the BNN relation. The universality of crossover behavior in the dynamics of glass-forming systems has been debated for decades. Goldstein proposed a crossover from liquid-like to viscous flow where the height of barriers in the potential energy landscape of the liquid exceeds the thermal energy of the constituent particles and predicted the crossover at a structural relaxation time of $\tau_\alpha \sim 10^{-9} s$. [358] The ensuing decades led to more refined experimental data suggesting the universality of the dynamic crossover in glass-forming systems. The mode-coupling theory of the dynamic glass transition, introduced in the 1980s, identified a critical-like temperature,

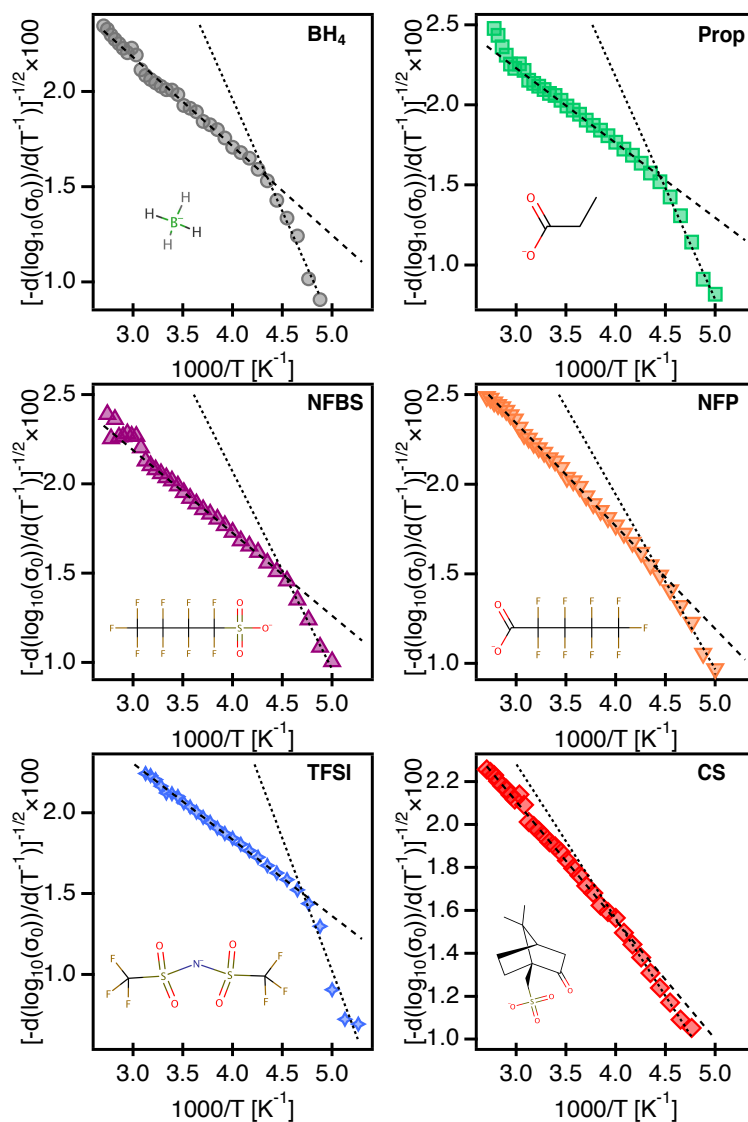


Figure 5.10: Stickel plots of dc ionic conductivity for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid and dashed lines represent VFT fits to the high temperature and low temperature regions of the data, respectively.

$T_c > T_g$, apparently related to the dynamic crossover. This approach held the crossover temperature as more fundamental to the glass transition than T_g . [183, 184] Detailed analysis of experimental data for a wide variety of glass-forming systems, including covalently-bonded glasses, hydrogen-bonded liquids, polymeric systems, ionic glasses, and molecular liquids, led to the conclusion that the structural relaxation time corresponding to dynamic crossover adopted a universal value of $\tau_\alpha(T_c) \sim 10^{-7} s$. [355] In fact, the data revealed a range of times for the crossover, while still indicating the significance of the timescale at which the dynamic crossover occurs. The crossover phenomena in supercooled liquids has been described as a transition from liquid-like dynamics at high temperature to solid-like dynamics at low temperatures. In studies of the pressure dependence of the dynamic crossover behavior, the characteristic timescale was found to be invariant to changes in the thermodynamic conditions. [356] This further reveals the importance of the characteristic timescale associated with the dynamic crossover, while also suggesting that rather than a universal value of the characteristic time for all glass-forming systems, the value of $\tau_\alpha(T_c)$ is a unique descriptor of the dynamic glass transition for a particular system that varies depending on intermolecular interactions between the constituent particles of the liquid. Thus, the dynamic crossover represents the transition from weakly coupled motion of neighboring liquid particles to highly cooperative motion governed by the interaction of many liquid particles spanning regions larger than the size of the constituent particles.

The dynamic crossover is closely related to the concept of liquid fragility. The fragility, m , of a glass-former is defined as:

$$m = \left. \frac{\partial(\epsilon \log_{10} X)}{\partial(T_g/T)} \right|_{P, T=T_g} = D \frac{T_0}{T_g} \left(1 - \frac{T_0}{T_g} \right)^{-2} \log_{10} e \quad (5.13)$$

which can be calculated from the VFT parameters describing the temperature dependence of the liquid dynamics. Since the parameters of the VFT description of the temperature dependence of liquid dynamics change in the vicinity of the characteristic timescale of dynamic crossover, the fragility of the liquid also changes. Defining the fragility for the high temperature liquid behavior requires extrapolation to a hypothetical glass transition temperature at $\tau_\alpha(T_g) = 100s$. This allows us to draw a qualitative distinction between

glass-formers depending on whether the low temperature fragility is higher or lower than the high temperature fragility.[192] The slopes corresponding to the high and low temperature VFT behavior observed in the Stickel plots (Figure 5.10) crossing at T_B indicate that these $P_{666,14}$ -based ionic liquids exhibit a dynamic shift from lower fragility in the high temperature regime to higher fragility in the low temperature regime. This can also be verified from the calculated fragility values based on the VFT fitting parameters, given in Table 5.2.

Having identified a crossover in the dynamics for these $P_{666,14}$ -based ionic liquids, the question becomes, “How is the change in dynamic behavior related to the structural (static) changes observed in a subset of $P_{666,14}$ -based ionic liquids corresponding to a first-order liquid-liquid transition?” In an effort to attempt a satisfactory answer to this question, we shall again invoke the two order parameter model of the liquid state to explain the observed dynamic crossover in these ionic liquids based on the order parameter of the liquid-liquid transition, i.e. the fraction of locally favored states, ψ .

The Stickel analysis shown in Figure 5.10 gives the VFT parameters, D and T_0 , for both the high and low temperature dynamics for each of the six ionic liquids in this work (see Table 5.2). Those parameters can then be transferred to fit the actual $\sigma_0(T)$ data, shown for the six ionic liquids in Figure 5.11. Based on the validity of the BNN relation for these ionic liquids, we can transfer the VFT parameters from the Stickel analysis to fit the actual $\tau_\alpha(T)$ data (shown in Figure 5.12), as well.

It is evident from these plots that using two separate VFT functions provides a reasonable description of the full temperature range of the dynamic data and that the method of transferring the VFT parameters from the Stickel analysis is a valid procedure to obtain the VFT fitting parameters for both the σ_0 and τ_α data. What follows, then, is a discussion of the dynamic crossover behavior as a reflection of the two state description of local structure in the $P_{666,14}$ -based ionic liquids.

We begin by reviewing the two state model as applied to the liquid state. In the two state description of the liquid state, there exist two competing types of local ordering on the molecular level corresponding to two coupled order parameters, the density order parameter, ρ , and the bond orientation order parameter, ψ , defined by the fraction of locally favored structures. Energetically (or entropically) favorable interactions correlated across multiple

Table 5.2: Parameters from VFT fits to $\tau_\alpha(T)$ and $\sigma_0(T)$ including glass transition temperatures, T_g , and fragilities, m . The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	$\log \tau_\infty$	$\log \sigma_\infty$	D	$T_0(K)$	$T_g^{VFT}(K)$	m	$T_B(K)$	T_B/T_g
<i>High Temperature Liquid State</i>								
BH ₄	-12.1	-0.34	14.5	128.1	185.2	46	229.7	1.24
Prop	-12.8	-0.40	12.8	130.9	180.2	54	224.9	1.25
NFP	-12.0	-0.41	10.0	140.6	184.2	59	225.5	1.22
NFBS	-12.2	-0.08	13.0	132.0	184.5	50	220.4	1.19
TFSI	-12.4	0.12	12.8	127.7	176.7	52	212.9	1.20
CS	-11.7	-0.52	11.0	146.9	198.3	53	247.0	1.25
<i>Low Temperature Liquid State</i>								
BH ₄	-8.3	-4.0	2.9	176.8	198.4	95	229.7	1.16
Prop	-8.1	-4.4	2.1	179.8	196.2	121	224.9	1.15
NFP	-9.6	-2.6	4.0	166.9	192.2	88	225.5	1.17
NFBS	-8.3	-3.8	3.2	170.1	193.3	85	220.4	1.14
TFSI	-7.9	-4.3	1.7	177.6	190.7	145	212.9	1.12
CS	-10.5	-1.6	7.2	162.1	202.5	63	247.0	1.22

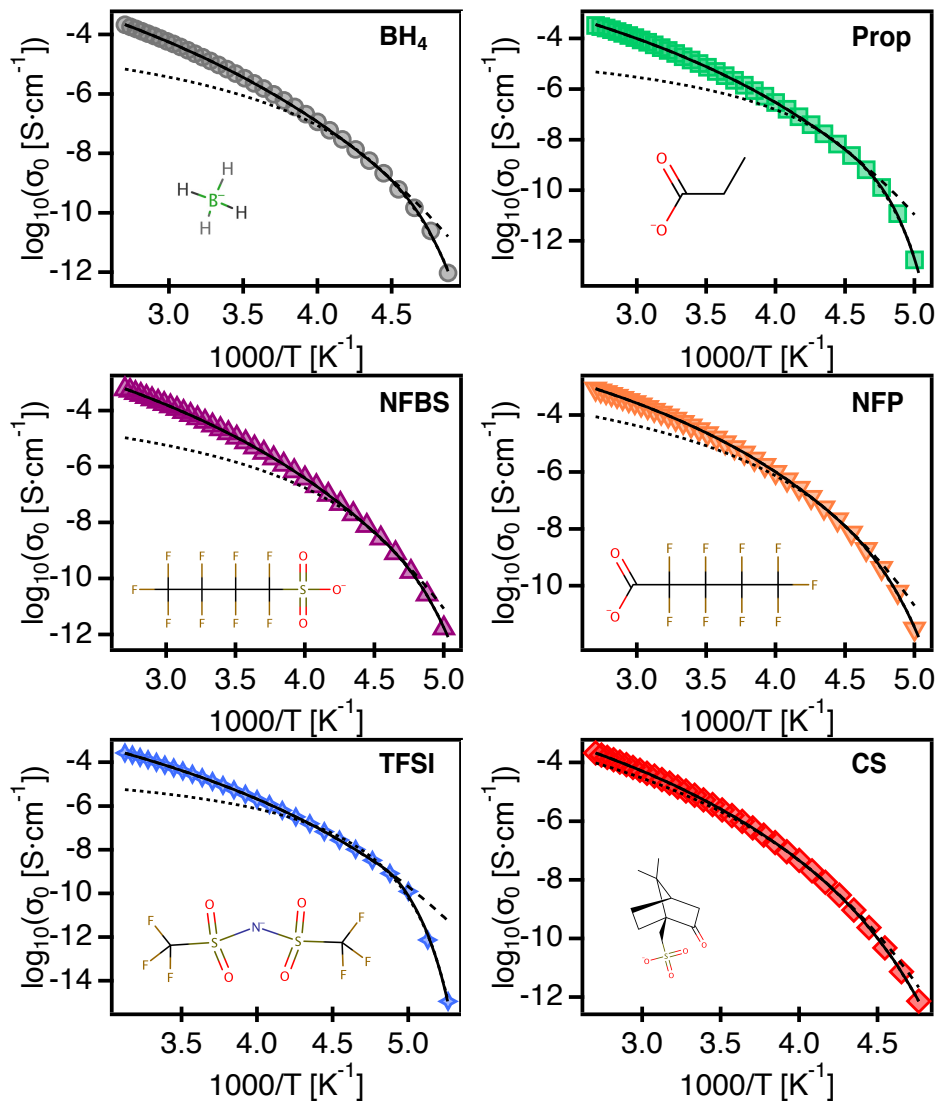


Figure 5.11: Arrhenius plots of dc ionic conductivity for $P_{66,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid and dashed lines matching the color of the symbols represent individual high and low temperature VFT fits, respectively. The solid black lines are fits to Equation 5.17 based on the two order parameter model.

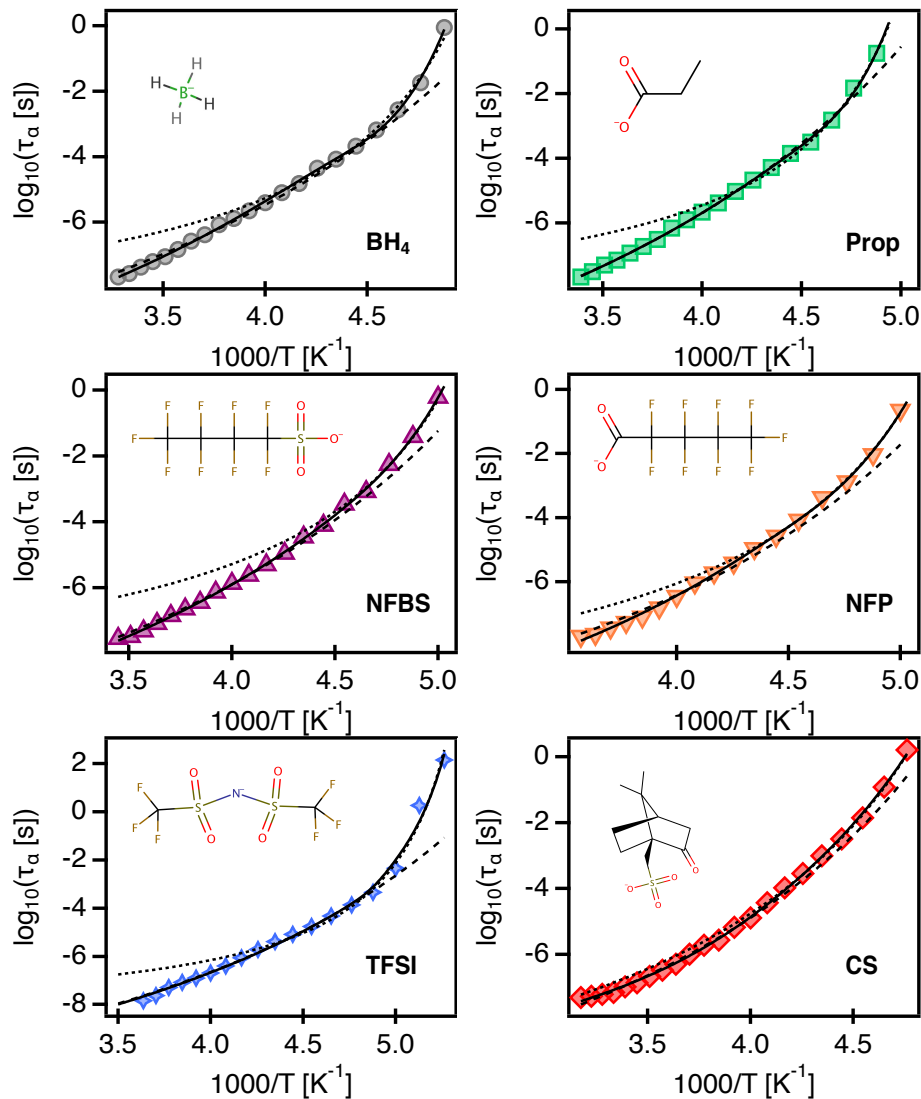


Figure 5.12: Arrhenius plots of the structural relaxation times for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS. Solid and dashed lines matching the color of the symbols represent individual high and low temperature VFT fits, respectively. The solid black lines are fits to Equation 5.17 based on the two order parameter model.

molecules leads to short-range ordering resulting in the emergence of locally favored structures (LFS) in the ground state forming and annihilating in a disordered sea of normal liquid structures (NLS) in the excited state. The conventional view of the liquid state as an isotropic, disordered collection of molecules (particles) is described by just one order parameter, namely the density order parameter (ρ), which successfully describes the gas-liquid phase transition. Density ordering is driven by maximizing local density, but in the condensed liquid state the matter is not so simple because of the complexity of many-body interactions which become increasingly important as density increases. Molecules or liquid particles will tend to favor certain local packing symmetries differing from the packing preferred by density ordering. For the simplest case of spherical particles, competition between hard-sphere repulsion and attractive interactions leads to the distinction between different types of local ordering: density which acts to minimize the distance between nearest-neighbors and locally favored icosahedral structures, thought to be the preferred ordering in atomic and metallic liquids, with five-fold axes, acting to generate a high degree of local symmetry while simultaneously frustrating crystal nucleation.[5, 14, 150, 153, 179, 181, 195, 219, 313, 315, 359, 360, 361, 362, 363, 364, 365] In the case of water and other tetrahedral liquids that prefer tetrahedral coordination, molecules conforming to local tetrahedral symmetry, which minimizes intermolecular (hydrogen bonding) interaction energy, are spaced further apart than in the normal liquid structure controlled by density ordering. In these cases, as in any physical description of a liquid based on this type of two-state feature, we propose a minimal structural element corresponding to the local packing symmetry stabilized by short-range bond ordering that maximizes the quality of intermolecular bond-like interactions. This unique minimal structural element defines the locally favored structures assigned to the ground state of the two-state model. The excited state is then defined by the higher energy packing structures of the normal liquid state controlled by density ordering. In this scenario, owing to the uniqueness of the local favored structures, the liquid state is described by a disordered, normal liquid structure in which the molecules adopt the higher energy, excited state configurations with unique locally favored structures having a finite lifetime being randomly created and annihilated, due to their energetic favorability and disordering effects of thermal fluctuations, respectively.

Thus, as the liquid is cooled and thermal energy removed, the fraction of locally favored structures increases. It is the fraction of these locally favored structures that defines the order parameter, ψ , associated with short-range bond ordering.

In the case of ionic liquids, we propose the existence of uniquely-defined local packing symmetries corresponding to the arrangement of charges and correlation of dipoles that specify the ground state of the LFS in contradistinction to the disordered normal liquid structures of the excited state. The validity of such a two-state description of ionic liquid structure is not fully tested, but it is supported by the current state of knowledge regarding intermolecular interactions and resulting liquid structures in neat ionic liquids in which charge ordering and steric effects compete for dominance. In fact, it appears very reasonable to expect that local constraints of charge ordering should compete with density ordering leading to the existence of unique LFS with well-defined local packing symmetry. What is lacking is a uniquely-defined structural descriptor of the LFS in ionic liquids that can be probed experimentally and computationally. We have no doubt that such a descriptor can be defined for a variety of ionic liquids, but *a priori* knowledge of the structural descriptor defining the LFS is not essential to test the overall predictions of the two-state model, including dynamic and thermodynamic anomalies and the existence of the first-order liquid-liquid transition.

If we assume *a priori* the existence of such uniquely-defined LFS for ionic liquids, then the state of the liquid can be described by the two order parameters, density (ρ) and the fraction of LFS (ψ). As described above, ψ is inversely related to the temperature of the system. We can therefore imagine a situation in which, at sufficiently high temperature, ψ is practically zero and the liquid is dominated by the NLS controlled by density ordering. Even when ψ is non-zero but very small, LFS will be randomly distributed throughout the liquid and isolated so their contributions to the dynamics of the system will be minimal. So the dynamics of the high temperature liquid state (HTSL) will be exclusively based on the behavior of the NLS, which may exhibit some degree of cooperative motion resulting in non-Arrhenius behavior. As the fraction of LFS increases as the liquid is cooled, some threshold may be reached at which point regions or clusters of LFS begin behaving cooperatively resulting in dynamic heterogeneity and dynamic crossover where the dynamics of the system becomes dominated

by the behavior of the LFS. At sufficiently low temperatures, ψ approaches unity, at which point the dynamics of the system are fully described by the behavior of the LFS typifying the low temperature liquid state (LTLS). As discussed in Chapter 2, the threshold value for ψ corresponds to the critical value of $\psi_c = 1/2$. Thus, in the two-state model of the liquid state, the dynamic crossover arises in the vicinity of maximal change in $\psi(T)$ centered at T_x where $\psi(T_x) = 1/2$. Tanaka proposed the generalized two-state Arrhenius equation to account for non-Arrhenius behavior and the fragile-strong dynamic crossover in water, given by:

$$X(T) = X_\infty \exp \left[\frac{E_a^{0,X} + \Delta E_a^X \cdot \psi}{k_B T} \right] \quad (5.14)$$

where X is a dynamic quantity, e.g. τ_α , X_∞ is a prefactor, $E_a^{0,X}$ is the background activation energy without LFS, $\Delta E_a^X = E_a^{X,\psi} - E_a^{X,\rho}$ is the difference in activation energy of the LFS and the NLS, respectively, and k_B is the Boltzmann constant. The apparent activation energy depends on the order parameter, ψ , which is temperature dependent.[5, 14, 16, 213, 366] This simple model is based on the assumption that, at high temperature, the dynamics of the system obey the Arrhenius law and behave as though the LFS have no impact. The apparent non-Arrhenius behavior is observed when ψ is changing rapidly close to the critical value. Upon crossing the line where $\psi = 1/2$, the influence of ψ on the apparent activation diminishes as ψ approaches a constant value, presumably close to unity. Thus, the non-Arrhenius behavior, embodied by the liquid fragility, diminishes, giving rise to the fragile-strong crossover. This simple model may be appropriate for some systems under specific conditions. However, in the case of P_{666,14}-based ILs, which exhibit fragile (non-Arrhenius) behavior in their dynamics across a wide range of temperatures where accurate measurements can be made, a more suitable model for the mixture of the two states is desired. Various methods of generalizing dynamic behavior in terms of the two-order parameter model have been proposed.[167, 214, 367] An appropriate function to model the dynamic behavior of fragile ionic liquids would need to account for non-Arrhenius behavior across the entire accessible temperature range of the data. Furthermore, we require a suitable ansatz to approximate the temperature dependence of ψ in lieu of a proper structural descriptor that could tell us what $\psi(T)$ looks like for each IL. The ansatz should behave similarly to the

approximate behavior predicted by the two-state model, which gives the following expression for the equilibrium value of $\psi(T)$:

$$\psi(T) = \frac{1}{1 + \exp\left(\frac{\Delta E - T\Delta\sigma + P\Delta v}{k_B T}\right)} \quad (5.15)$$

Here, $\Delta E = E_\rho - E_\psi$ is the energy difference between the NLS and the LFS, $\Delta v = v_\rho - v_\psi$ is the difference in volume between the two states, $\Delta\sigma = k_B \ln\left(\frac{g_\rho}{g_\psi}\right)$ is the entropy difference between the ρ -states and the ψ -states given by the degeneracy, g_i , of each state, and k_B is the Boltzmann constant.[5, 213] Note that this equation specifically neglects the cooperativity term in the mean free energy, J in Equation 2.9, which is necessary for the first-order liquid-liquid transition, so this approximation is only valid for systems far from the critical point of the LLT or in cases where the critical point and likewise the first-order LLT are absent. Nevertheless, we will assume the general form of the temperature dependence of ψ will resemble the logistic function centered at $\psi = 1/2$ with a maximum value of unity and a minimum of zero. We are certainly lacking the specificity of the behavior of $\psi(T)$ at the first-order transition and in the critical region, but we can approach the singularity at the LLT by varying the steepness of the logistic function with a free parameter, δT , which gives the width in temperature over which $\psi(T)$ changes from 0.1 to 0.9. The logistic ψ -ansatz is given by:

$$\psi(T) = \left(1 + \exp\left[\frac{(4.394(T - T_x))}{\delta T}\right]\right)^{-1} \quad (5.16)$$

where T_x is the temperature corresponding to $\psi = 1/2$. [214] The ψ -ansatz allows for switching from high temperature (“pure” ρ -state) to low temperature (“pure” ψ -state) behavior across an arbitrary temperature range, so we can approach a singularity in $\psi(T)$ for the case where $\delta T \rightarrow 0$. With this form for $\psi(T)$, we can describe the full temperature range of dynamics for the P_{666,14}-based ILs studied. We write the dynamic equation as:

$$\log_{10} X(T) = \psi(T) \log_{10} X_\psi(T) + (1 - \psi(T)) \log_{10} X_\rho(T) \quad (5.17)$$

where X can be either σ_0 or τ_α . Assuming a VFT dependence for the “pure” ρ - and ψ -states, corresponding to the high temperature liquid state (HTLS) and low temperature liquid state

(LTLS) behavior, respectively, $X_\rho(T)$ and $X_\psi(T)$ are given by:

$$X_i(T) = X_{\infty,i} \exp \left[\frac{D_i T_{0,i}}{T - T_{0,i}} \right], \quad i = \psi, \rho \quad (5.18)$$

where the dynamics of the two states are described by a unique set of VFT parameters. Whereas above we described the dynamics of the ILs by two separate VFT equations, with 6 free parameters total plus the crossover temperature, here we have introduced a single additional parameter, δT , that describes the temperature range in which the two dynamic behaviors are mixed, i.e. the width of the transition. Furthermore, we assume that the VFT parameters obtained from the Stickel analysis and subsequent fitting of separate VFT functions to the high and low temperature data above and below T_B (see Table 5.2) should be partly transferrable to the two-state VFT equation with the ψ -ansatz. We can use the parameters from Table 5.2 as initial estimates for the new set of parameters as a test of how well they describe the data with the mixing of states around the transition. The solid black lines in Figures 5.11 and 5.12 represent fits to the $\sigma_0(T)$ and $\tau_\alpha(T)$ data, respectively, with the fitting parameters given in Table 5.3.

The first thing to note is that values of T_x obtained from the application of the two-order parameter (TOP) model to the dynamics of this set of fragile ILs are generally lower than the T_B values obtained from the Stickel analysis and they agree reasonably well with the emergence of the structural and static anomalies for the BH₄, Prop, NFP, NFBS, and TFSI samples discussed in the previous sections (see Chapter 4 for the discussion of structural anomalies and Section 5.2 for the anomalies in the static dielectric permittivity). The values for δT are somewhat broad for the BH₄, Prop, NFP, and NFBS anions, around 30K, and they are slightly larger for the σ_0 fits compared to the τ_α fits. The width of the transition for the TFSI sample is significantly smaller, ~ 10 K for both σ_0 and τ_α , while the crossover in the CS sample spans 75K, about three-quarters of the range of the measured data. Note that the widths of the transition region obtained from these fits are on par with the width of the enthalpic peaks measured by DSC (see Chapter 6 below). Better fits using this model were obtained by fixing the T_0 values for the two states to the values obtained from the Stickel analysis and letting the other parameters fit freely. Fitting in this manner gave values for

Table 5.3: Parameters from TOP-VFT fits to $\sigma_0(T)$ and $\tau_\alpha(T)$. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	$T_x(K)$	$\delta T(K)$	$\log X_{\infty, \psi}$	D_ψ	$T_{0, \psi}(K)$	$\log X_{\infty, \rho}$	D_ρ	$T_{0, \rho}(K)$
$X = \sigma_0$								
BH ₄	218.4	34	-3.7	3.1	176.8	-0.32	14.5	128.1
Prop	213.5	30	-4.1	2.3	179.8	-0.38	12.9	130.9
NFP	219.1	37	-2.5	4.1	166.9	-0.41	10.0	140.6
NFBS	219.1	35	-3.6	3.3	170.0	-0.08	13.1	131.9
TFSI	204.2	10	-4.2	1.7	177.7	0.09	12.7	128.0
CS	246.5	75	-1.6	7.3	162.0	-0.54	11.0	146.9
$X = \tau_\alpha$								
BH ₄	218.4	31	-10.7	3.9	176.8	-12.9	16.5	128.1
Prop	213.5	30	-8.9	2.7	179.8	-12.8	15.0	130.9
NFP	219.1	26	-9.9	4.2	166.9	-13.0	11.7	140.6
NFBS	219.1	20	-8.5	3.3	170.0	-12.6	13.9	131.9
TFSI	204.2	9	-7.2	1.5	177.7	-12.5	12.8	128.0
CS	246.5	75	-9.8	6.9	162.0	-10.7	8.7	146.9

the prefactors, $\log X_{\infty, i}$, and the strength parameters, D_i , differing slightly from the previous analysis and gave slightly different values for the σ_0 and τ_α fits.

The values of T_x and δT obtained from the TOP-VFT model allow us to calculate the temperature dependence of ψ for the ILs in this study, in so far as the ψ -ansatz describes the switching from the HTLS behavior to the LTLS behavior. Figure 5.13 shows $\psi(T)$ calculated from Equation 5.16 for each IL in this study using the parameters from Table 5.3. The top panel in Figure 5.13 showing $\psi(T)$ with respect to $1000/T$ reveals a trend in the crossover temperatures across the ILs studied, showing that T_x is positively correlated with the width of the crossover. The CS sample, having the widest crossover with no detection of static structural anomalies indicative of a first-order LLT exhibits the highest $T_x \sim 245\text{K}$. The BH_4 , Prop, NFP and NFBS samples are clustered together at a lower $T_x \sim 220\text{K}$. These samples also exhibited similar values of $\delta T \sim 30\text{K}$, suggesting a weak first-order (almost second-order) transition. With the lowest $T_x \sim 205\text{K}$, the TFSI sample shows the sharpest transition, $\delta T \sim 10\text{K}$, indicating a sudden and dramatic transition from the dynamics of the HTLS to that of the LTLS. Coupled with the structural data (see Figure 4.6 in Chapter 4, Section 4.1) showing the emergence of a second diffraction peak at low q among other discontinuities in the structural parameters, notably the average coordination number (n_1 , see Figure 4.18) and the normalized charge ordering correlation length (ξ_{ch}/d_{ch} , see Figure 4.14), the sharp dynamic transition in TFSI supports the conclusion that $\text{P}_{666,14}$ TFSI undergoes a true, first-order liquid-liquid transition at $T_x \approx 200\text{K}$ at ambient pressure.

In the bottom panel of Figure 5.13, the calculated $\psi(T)$ data is plotted against T_x -normalized inverse temperature, with T_x corresponding to the condition $\psi(T_x) = 1/2$. In this representation, a comparison of the steepness of the crossover behavior is readily made. Of particular interest is the observation of the clustering of the BH_4 , Prop, NFP, and NFBS samples. This may be reflective of the superficial similarities between the anions in this set; the BH_4 and Prop samples are the smallest in this study, the Prop and NFP samples share the carboxylate moiety, the NFP and NFBS share the perfluorinated butyl tail. A satisfactory explanation for similar transition behavior that captures the disparities in the static structural anomalies based on the identification of a unique structural descriptor for each of these four $\text{P}_{666,14}$ -based ILs is critical to understanding the seemingly subtle nature

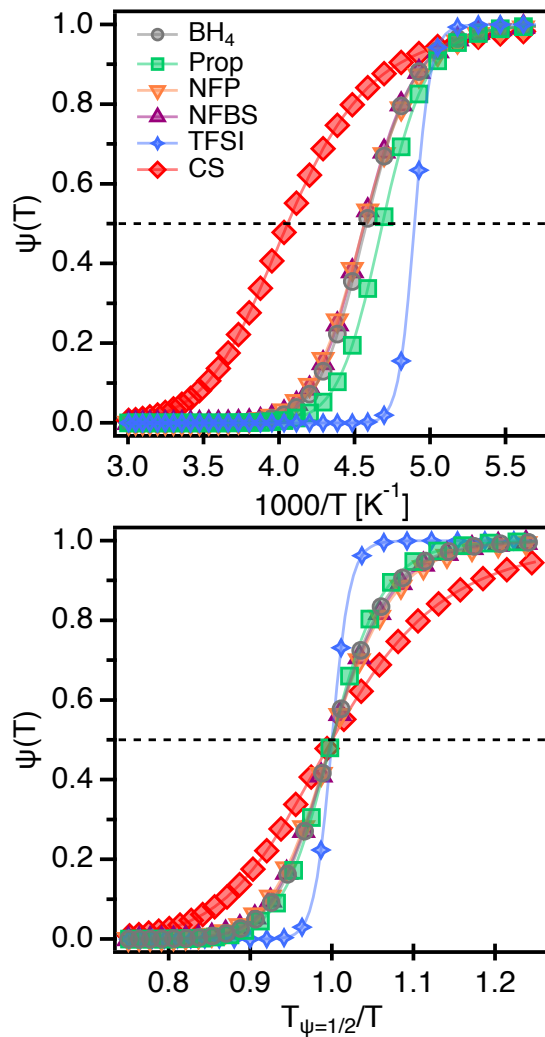


Figure 5.13: Fraction of locally favored states calculated from Equation 5.16. Top panel: $\psi(T)$ versus $1000/T[K^{-1}]$. Bottom panel: $\psi(T)$ versus $T_{\psi=1/2}$ -normalized inverse temperature.

of the LLT in these systems.

By way of wrapping up the discussion regarding the analysis of the dynamic crossover behavior observed in the six ILs in this work, we turn our attention to the values tabulated in Table 5.4, which collects the arguably most significant quantities describing the switching from the NLS dynamics to the LFS dynamics and the dynamic glass transition. In general, the cases of LLT show lower T_g values and higher fragilities. The quantity, T_x/T_g , is reflective of the fragility of the liquid, as well, and is correlated to the width of the crossover region. The value of the ψ -ansatz at T_g is also listed, more as a curiosity than anything. The significance of the variation in these values, from 0.9 to 0.99, is not fully understood. However, within the framework of the two state description of the liquid state, the transition (be it first-order, second-order, or a continuous crossover) from the ρ -state characterized by the NLS at high temperatures to the ψ -state of LFS at low temperatures, the dynamic arrest at the calorimetric glass transition is a consequence of frustration or competition between the NLS, the LFS, and the equilibrium crystal structures. In a sense, if the formation of LFS inhibits the growth of the crystal structure by erecting a higher energy barrier toward the formation of the prototypical crystalline states, which can only form by diffusion of liquid particles to the lattice boundary, then an increase in LFS as the liquid is cooled will favor vitrification. However, if the LFS share commonalities in density and symmetry with the equilibrium crystal structures, an increase in LFS with decreasing temperature will favor the fall into the low entropy crystal state.

Largely absent from the discussion thus far, although its significance was highlighted at the beginning, is any mention of the characteristic timescale of the dynamic crossover, i.e. $\tau_\alpha(T_x) = \tau_\alpha(\psi = 1/2)$, which we may refer to as τ_x . As mentioned previously, early attempts to lay a theoretical foundation for the dynamic glass transition predicted a crossover from “liquid-like” diffusive dynamics to a viscous flow regime characterized by “solid-like” behavior typified by cage-rattling motion where particles become spatially bound to neighboring molecules and the particles relax cooperatively.[116, 139, 142, 143, 164, 177, 183, 184, 185, 355, 368, 369, 370] The frameworks developed to describe the dynamic glass transition predicted this crossover should happen at a particular timescale of the relaxation

Table 5.4: Parameters related to the dynamic crossover and the glass transition from TOP-VFT fits to $\tau_\alpha(T)$. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	$\log \tau_x$	$T_g^{TOP}(K)$	m	T_x/T_g	$\psi(T_g)$
BH ₄	-3.1	199.8	107	1.09	0.92
Prop	-2.6	198.4	113	1.08	0.90
NFP	-4.0	192.3	89	1.14	0.96
NFBS	-3.5	193.4	86	1.13	0.96
TFSI	-3.0	190.5	137	1.07	0.99
CS	-4.6	202.3	59	1.22	0.93

dynamics. As the quantity and quality of experimental evidence for crossover behavior amassed, the threshold relaxation time at which the dynamic crossover should occur shifted to longer timescales.[191, 355] With the wealth of literature data related to this phenomena that abounds, we can be confident in stating that the dynamic crossover does not occur at some universal timescale for glass-forming systems as a whole, but the value of τ_x is a unique property of a particular system. Furthermore, pressure dependent measurements of the dynamic glass transition indicate that the value of τ_x is invariant to the thermodynamic conditions of its measurement, i.e. the temperature, T_x , varies with pressure, while the measured value of τ_x remains constant.[356] This behavior is exactly what is predicted by the two order parameter model, which gives the pressure dependence of T_x :

$$T_x(P) = \frac{(\Delta E + P\Delta v)}{\Delta\sigma} \quad (5.19)$$

in terms of the difference between the ρ -states and the ψ -states. This temperature corresponds to $\Delta G = \Delta E - T\Delta\sigma + \Delta vP = 0$ and an equilibrium value of $\psi = 1/2$. In liquids where a liquid-liquid critical point (LLCP) exists, this equation gives the coexistence line of the first-order LLT for $T < T_c$, where $T_c = J/2k_B$ with J accounting for the cooperative formation of LFS. For $T > T_c$, $T_x(P)$ is the so-called Widom line associated with the thermodynamic and dynamic anomalies observed in the vicinity of the critical point. Further still, far from the elusive LLCP, the equilibrium line accounts for static and dynamic Schottky-like anomalies. Indeed, cases where a liquid exhibits an underlying two state feature despite the absence of the LLCP or first-order LLT are possibly the norm, yet even in cases such as these, the two order parameter predicts crossover behavior at the equilibrium line. In the same way that the parameters describing the two state feature of a particular liquid are uniquely defined by the pair potential and many-body correlations describing intra- and intermolecular interactions that define the liquid structures, the parameter describing the crossover in dynamic behavior, i.e. τ_x , is uniquely defined for a particular liquid arising from time dependent correlations of the same underlying two state feature. If we step back and look at the values in Table 5.4 corresponding to $\log \tau_x$ for the six ILs in this study, we notice the obvious fact that the anions that show LLT when paired with the P_{666,14}

cation exhibit the longest timescales corresponding to the dynamic transition. The CS case, representing the only IL included in this study that does not exhibit anomalous structural changes that would suggest LLT, is characterized by the fastest crossover timescale, which falls into the slower range of τ_x reported in the literature for typically molecular glass-formers.[13, 186, 188, 191, 192, 196, 355, 356, 357, 371, 372, 373] A curious comparison can be made between the anomalies found in the family of ILs containing the $P_{666,14}$ cation, which show up in cases having $\tau_x > 100\mu s$, and a unique molecular liquid that has the distinction of being the most definitive example of LLT in a molecular liquid to date. We are speaking, of course, about triphenyl phosphite (TPP), which has received a copious amount of attention as a prototypical example of LLT.[27, 28, 29, 30, 84, 86, 199, 209, 232, 235, 236, 374] The curiosity arises from the values of τ_x observed in these ILs compared to that of TPP. In a paper from R. Richert and C.A. Angell[191], a table is presented which lists values of $(-\log \tau_x)$ for a variety of molecular glass-formers. The typical range of values for $(-\log \tau_x[s])$ is between 6.6 and 9 with the exception of BMPC, for which $(-\log \tau_x) = 4.4$, close to the value reported here for $P_{666,14}$ CS. But the true outlier is TPP, with a $-\log \tau_x = 3.6$, squarely in the range of the $P_{666,14}$ -based ILs showing a LLT. This observation is, as stated above, more of a curiosity than a revelation. Still, it begs the question, “Is there a connection between the magnitude of τ_x for a given system and the existence of anomalous properties indicative of the LLT?” Further, careful study of anomalous LLT-like behavior in these ILs and others of various cation-anion composition may lead the way toward answering this question. For now, we marvel at the peculiarity of this connection and shift focus to a more concrete connection between the static anomalies arising in the $P_{666,14}$ -family of ILs and the crossover in the dynamic behavior.

Figure 5.14 shows the correlation between the static dielectric permittivity (ε_s , discussed in Section 5.2) and the crossover in dynamic behavior occurring at τ_x . It is evident that a dramatic change in the dipole correlation environment manifests at the timescale of the dynamic shift in the ILs shown in the top five panels corresponding to the BH_4 , Prop, NFP, NFBS, and TFSI anions which is linked to the proposed LLT in this set of fragile ILs. Somewhat surprisingly, but at the same time a result that would otherwise be expected of a glass-forming liquid with evidence of a corresponding dynamic shift, the CS sample shows a



170

marked change in the behavior of the of ε_s at timescales longer than the value of τ_x for this system. This provides evidence of an underlying structural change corresponding to the change in dynamic behavior that manifests at the crossover timescale, suggesting that, even though no signatures of a first-order LLT are observed in the data for P_{666,14} CS, a change in local structural ordering corresponding to an increase in the fraction of LFS occurs in this sample as it is cooled from the HTLS down to the glass transition through a smooth transition from the HTLS dominated by NLS (ρ -states) to the LTLS in which local structural ordering is dominated by LFS (ψ -states). Thus, we understand the shift in dynamic behavior as an emergent property of the liquid with its origin in the two state feature characterizing local structural ordering.

5.4 Conclusions

We conclude this chapter by summarizing the key findings related to the evidence for liquid-liquid transition in a set of fragile ionic liquids bearing the trihexyltetradecylphosphonium cation as reported by broadband dielectric spectroscopy. First, an additional slow relaxation was observed in the ILs containing the BH₄, Prop, NFP, and NFBS anions. While the slow relaxation is not present in the dielectric spectra for the TFSI case, the primary structural relaxation shifts to much lower frequencies and the width and intensity of the structural relaxation both increase below the characteristic temperature corresponding to structural reorganization. In contrast, no significant changes are identifiable in the CS sample by visual inspection of the dielectric spectra. The static dielectric permittivity, ε_s , determined by fitting the frequency dependent dielectric spectra measured under isothermal conditions at different temperatures ranging from above room temperature to low temperatures approaching the glass transition, revealed a step-like increase at temperatures corresponding the characteristic temperatures of structural reorganization observed for the BH₄, Prop, NFP, NFBS, and TFSI anions. Analysis of ε_s was performed using the Onsager equation with the Kirkwood-Fröhlich dipole correlation factor, indicating a change in the local coordination environment is the underlying cause for the increase in ε_s . This analysis was also carried out using an equation derived using renormalized Gaussian fluctuation theory with specific

applicability in determining the contributions to ε_s from components of the liquid with different effective dipole moments. This equation was employed as a method of estimating the temperature dependence of the order parameter, ψ , corresponding to the fraction of LFS, revealing that the increase in ε_s can be attributed to a discontinuous change in ψ at the characteristic temperature. This analysis can also explain the temperature dependence of ε_s in the CS sample, indicating two state behavior in the absence of LLT. In the following section, the dynamic behavior of the P_{666,14}-based ILs included in this study was analyzed by fitting the temperature dependence of the dc ionic conductivity, σ_0 , and the structural relaxation times, τ_α , using the VFT equation. A dynamic crossover was observed in all of the samples studied, necessitating two sets of VFT parameters to describe the full temperature range of the measurements. An ansatz was introduced to approximate the temperature dependence of the order parameter, ψ . By incorporating this ansatz into a single equation which includes two sets of VFT parameters to account for the two state behavior of the liquids, fits of the full temperature range of the dynamic data were achieved. It was observed that the relaxation times corresponding to the transition or crossover temperatures suggest a distinction between types of liquids with fast crossover times being observed in systems where no LLT is observed and slow crossover times corresponding to liquids exhibiting LLT behavior with an idiosyncratic relaxation time distinguishing the two regimes on the order of $100\mu s$. Finally, the changes observed in ε_s are found to correspond to the crossover relaxation time, τ_x .

Chapter 6

Thermodynamics of the liquid-liquid transition in ionic liquids

In this chapter, thermodynamic data as reported by differential scanning calorimetry is presented for the ionic liquids (IL) in this study. In the first section (Section 6.1), the calorimetric data obtained from heating and cooling cycles is discussed for the six ILs, focusing on evidence of a thermodynamic phase transition in the supercooled liquid and analysis of the glass transition. The second section (Section 6.2) deals with the experimentally measured isobaric heat capacity, $C_p(T)$, and discussion of the anomalous peak associated with the liquid-liquid transition (LLT) is given. An attempt is made to link the heat capacity at the glass transition to the structural (Chapter 4) and dynamic (Chapter 5) anomalies outlined in the previous chapters. In the third section (Section 6.3, calculations of the configurational entropy, $S_c(T)$, from the $C_p(T)$ data are presented. A discussion of the relation between $S_c(T)$ and dynamics is given with a focus on the changes associated with the LLT. Section 6.4 outlines the connections between the results from this chapter with the results discussed in the earlier chapters (Chapters 4 & 5) with an emphasis on understanding the data in terms of the phenomenological two order parameter model of the liquid state. The key findings are then summarized in Section 6.5.

6.1 Calorimetric Investigations of the Phase Transition and the Glass Transition

We begin the discussion of the thermodynamics of the liquid-liquid transition in $P_{666,14}$ -based ionic liquids by examining the thermograms obtained via thermal cycling using differential scanning calorimetry (DSC) experiments. DSC is the most common technique used to study the phase behavior and the glass transition in liquids, including organic molecular liquids, inorganic glass-formers, metallic glass-formers, water, atomic liquids, and ionic liquids to name a few.[83, 95, 129, 131, 134, 282, 305, 310, 332, 334, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384] DSC is a simple and reliable technique that can accurately measure the heat flow into and out of a sample and the corresponding temperature change over time as the sample is either heated or cooled. Since physical or chemical processes occurring within a sample involve an associated generation or consumption of heat, these processes can be readily measured via DSC. Phase transitions, including crystallization, melting, and polymorphic transitions, involving the evolution or absorption of latent heat, manifest as exothermic or endothermic peaks depending on the temperature path of the measurements.

The glass transition, to the best of our current understanding, is not a first-order thermodynamic phase transition, but rather a change from an equilibrium, metastable supercooled liquid to a kinetically-arrested, configurationally-frozen, non-equilibrium state where the particles of the system have insufficient time to rearrange to the metastable equilibrium configuration of the supercooled liquid.[115, 134, 156, 185, 385, 386, 387] However, an underlying thermodynamic origin of the glass transition cannot be ruled out.[116, 151, 193, 377, 388, 389, 390] The glass transition is closely related to the concept of ergodicity, denoted by the equivalence between the time and ensemble averages of the system implying that the system has sufficient time to explore its configurational phase space. Thus, the glass transition corresponds to a breakdown of ergodicity when the relaxation time of the system exceeds the timescale of the measurement. Based on this definition, the glass transition depends on both the internal relaxation time and the external observation time. The conventional approach to define a particular glass transition temperature, T_g , is to assign it to a standard relaxation time, typically taken at 100s. The corresponding calorimetric

glass transition temperature is established by the change in heat flow (or heat capacity) as measured by DSC that occurs as the sample in the glassy state is reheated back to the equilibrium supercooled liquid at a standard scan rate of 10K/min.

In order to study the phase behavior and the glass transition in the set of six P_{666,14} ILs in this study, DSC measurements were performed by thermally cycling the samples between a high temperature, where the liquid is the stable equilibrium phase ($T > T_g + 100K$), and a low temperature in the glassy state of the system ($T < T_g - 40K$) at a scan rate of 10K/min on both cooling and heating in hermetically-sealed aluminum Tzero DSC pans using a TA Instruments Discovery DSC system calibrated using a sapphire disk standard. The resulting thermograms showing normalized heat flow, Q [W/g], as a function of temperature, T [K], for the second cooling and heating cycle are shown in Figure 6.1. We note that the step-like change in heat flow corresponding to the glass transition is observed in all of the ILs studied, occurring at around 200K. In addition, the BH₄, Prop, NFP, NFBS, and TFSI samples show an enthalpic peak, appearing at a temperature $T > T_g$. This feature is observed on both heating and cooling, suggesting it is not simply the result of enthalpy recovery (overshoot) often observed on reheating the glass back to the liquid state.[83, 129, 134, 334, 384, 391]. The reversibility of the peak and its appearance above T_g indicates that it corresponds to a type of phase transition. Since no other peaks are observed at higher temperatures in these scans, crystallization or a crystalline polymorphic transition can be ruled out considering that the structural characterization based on wide-angle X-ray scattering (see Chapter 4) revealed no sharp diffraction peaks corresponding to long-range ordering. The peaks observed in these P_{666,14}-based ILs are therefore assigned to a polyamorphic transition between two supercooled liquid phases, i.e. a liquid-liquid transition.

The absence of crystallization at the scan rate of 10K/min is an indication that these fragile IL systems are good glass-formers and therefore, ideally suited for studying the phenomena of the LLT, which occurs in the metastable supercooled liquid state for many systems in which LLT is observed where crystal formation hampers the unambiguous assignment of features related to LLT. Note that the reversible peak is not present in the CS sample, which only shows the step-like change in heat flow corresponding to the glass transition at this scan rate in the temperature range measured.

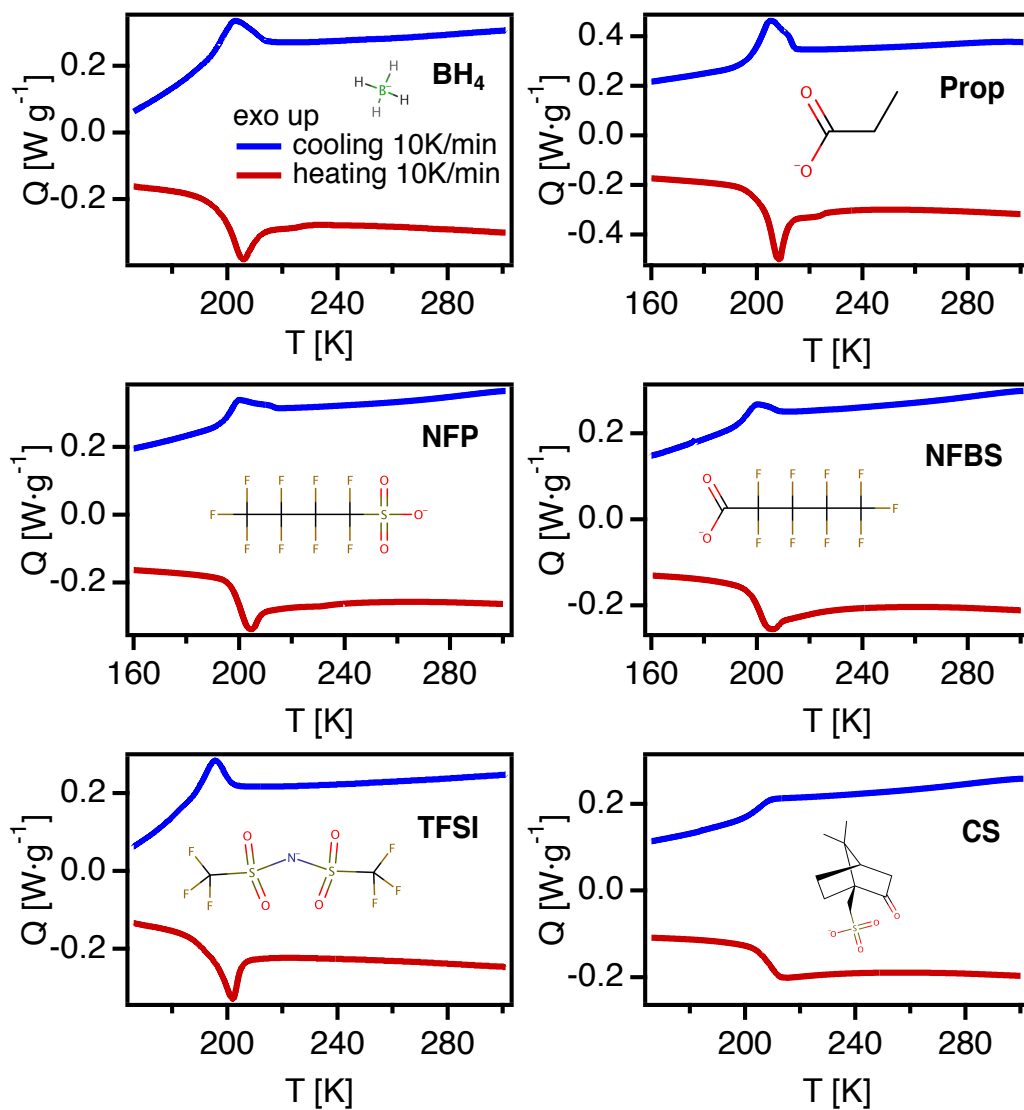


Figure 6.1: DSC thermograms for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop . Middle row, from left to right: NFBS , NFP . Bottom row, from left to right: TFSI , CS .

6.2 Heat Capacity

In this section, we examine the features associated with the glass transition and the LLT in the heat capacity representation as reported by DSC. The heat capacity, C_p , is a thermodynamic property of a material corresponding to the amount of energy that must be supplied to or removed from the system in order to affect a temperature change of 1K per unit (mass or mole) of substance. This quantity is directly related to how the material stores thermal energy at the molecular level. As such, changes in heat capacity are reflective of changes in degrees of freedom associated with molecular mobility. Heat capacity is readily determined from the DSC measurements given by the heat flow, the corresponding scan rate, and the amount of sample measured.

The heat capacities, C_p [J/mol K], of the ionic liquids were determined by the ratio between the heat flow, Q , to the scan rate, dT/dt , using a sapphire disk standard. The samples were measured at a scan rate of 10K/min on both cooling and heating in hermetically-sealed aluminum Tzero DSC pans using a TA Instruments Discovery DSC system. The measured C_p data are shown in Figure 6.2, plotted with respect to T [K] on heating at 10K/min, for the six ILs studied. The enthalpic peak observed for the BH₄, Prop, NFP, NFBS, and TFSI samples presumably arises due the additional energy cost associated with the sudden change in the number of locally favored structures, which occurs upon heating when the amount of thermal energy contained in the system is sufficient to overcome the energy (or entropy) barrier between the ground state of the LFS and the excited state of the NLS. It is clear that the peaks associated with the LLT in these ILs appear broad, spanning 10-30K, and asymmetric, indicative of a time-dependent (kinetic) attribute of the LLT. Furthermore, the asymmetry of the peaks suggests a possible metastable coexistence region where the two liquid states are mixed ending at a spinodal instability on the low temperature side of the LLT. Due to the proximity of the LLT feature to the change in C_p corresponding to dynamic arrest of the glass transition, it is difficult to characterize the heat capacity of the low temperature liquid state, also referred to as liquid II. This proximity is, in some respect, superficial because the glass transition temperature is partially determined by the observation timescale, meaning that, in theory, we can separate the LLT feature from

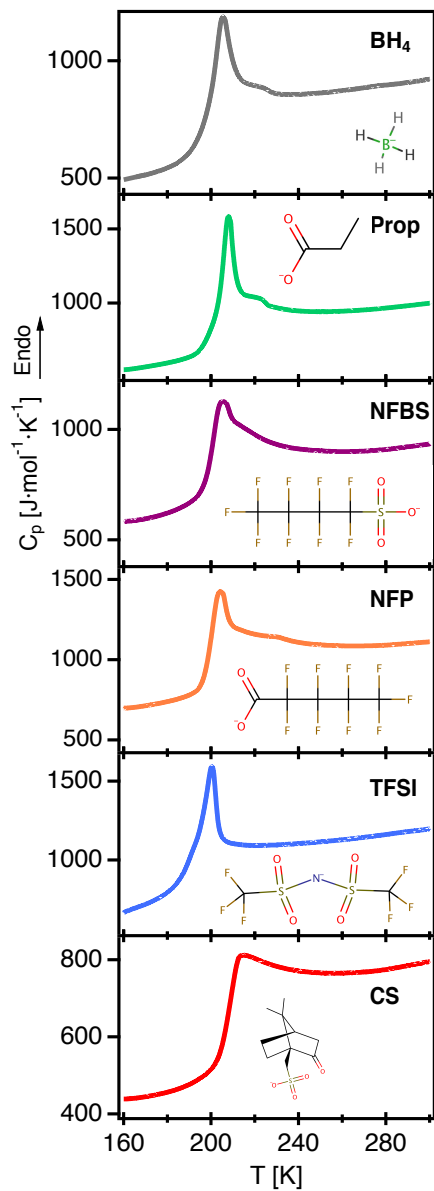


Figure 6.2: Heat capacity of $P_{666,14}$ -based ionic liquids measured on heating at 10K/min . Top to bottom: BH₄, Prop, NFBS, NFP, TFSI, CS.

the glass transition feature by extending the timescale of the measurements, i.e. measuring at a slower scan rate. In practice, reducing the scan rate by an order of magnitude only shifts the measured T_g a few degrees lower since the dynamics of these fragile ILs slow rapidly with decreasing temperature below the LLT, as observed via dielectric spectroscopy (see Chapter 5).

Nevertheless, we can analyze the C_p data to determine the parameters associated with the LLT and the glass transition in these samples. The glass transition can be analyzed by extrapolating the heat capacity of the high temperature liquid state (liquid I) and the glassy state to determine the change in heat capacity, ΔC_p , at the glass transition. The calorimetric glass transition temperature is then determined at the midpoint along the C_p curve. To characterize the LLT feature, we can integrate the peak in C_p to determine the enthalpy change, ΔH_{LL} , associated with the transition and identify the peak temperature, T_p , at the maximum point in C_p . We also obtain the onset temperature of the LLT as the point where C_p returns to the baseline of the high temperature liquid state. These values, determined for both the heating and cooling sides of the thermal cycle, are compiled in Table 6.1. The disparity between the values obtained on heating and cooling reflects the kinetic nature of the transition.

A number of theoretical models of the glass transition ascribe the slowing down of the dynamics approaching the dynamic arrest at T_g to the onset of cooperative motion among the particles of the liquid. As the temperature is decreased, the number of dynamically correlated molecules increases as does the size of the corresponding cooperatively rearranging regions (CRR). A method described by Donth to calculate the number of dynamically correlated molecules at T_g , $N_\alpha(T_g)$, provides an approach to determine the magnitude of the cooperative motion associated with the glass transition.[158, 392] In this approach, the width of the glass transition is related to the size of temperature fluctuations and the change in heat capacity relates to entropy fluctuations associated with the cooperative motion. We can calculate the number of dynamically correlated molecules using the equation:

$$N_\alpha(T_g) = \frac{k_B T_g^2}{M(\delta T)^2} N_A \left(\frac{1}{C_p^{gl}} - \frac{1}{C_p^{liq}} \right) \quad (6.1)$$

Table 6.1: Thermodynamic data from DSC for P_{666,14}-based ILs. A scan rate of 10 K/min was used for all measurements. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	T_g (K)	ΔC_p (J/mol K)	T_p (K)	T_{on} (K)	ΔH_{LL} (kJ/mol)
<i>Heating</i>					
BH ₄	197.0	248	205.7	229.2	2.97
Prop	200.7	280	208.2	229.1	5.26
NFP	198.3	403	204.8	231.6	3.66
NFBS	199.1	290	206.2	231.5	3.32
TFSI	190.5	177	200.7	205.0	3.51
CS	207.9	306	—	—	—
<i>Cooling</i>					
BH ₄	195.8	124	202.6	214.3	2.10
Prop	196.6	195	205.1	214.2	3.22
NFP	195.3	225	199.9	215.3	1.97
NFBS	194.5	128	200.1	215.2	1.01
TFSI	188.9	124	195.5	201.4	2.08
CS	204.5	188	—	—	—

where M is the molar mass of the material, T_g is the glass transition temperature, k_B is the Boltzmann constant, N_A is Avogadro's number, and C_p^{gl} and C_p^{liq} correspond to the extrapolated values of C_p for the glass and liquid states at T_g , respectively. The parameter, δT , is related to the width of the glass transition, i.e. the temperature range over which C_p changes from the liquid behavior to the glassy behavior. Details of this analytic procedure are described by Grzybowska *et al.*[159] Application of this method to the P_{666,14}-based ILs in this work yields the values compiled in Table 6.2. Note that any discrepancy between the values given by this method and those reported earlier are due to differing methods of extrapolation of C_p . The results of these calculations give values for $N_\alpha(T_g)$ in the range of 8 to 30 molecules corresponding to the cooperative regions on the order of 8 to 30nm³. This seems reasonable considering the size of the P_{666,14} cation and degrees of freedom corresponding to the long alkyl chains. The value for $N_\alpha(T_g)$ calculated for the CS sample is 16.5, falling in the middle of the range of values computed for this limited set of samples, suggesting this value is not directly connected to the presence or absence of the LLT. In a recent article by Musiał *et al.*[160], where they analyzed C_p data for over 30 ILs, they concluded that a direct connection between the observation of a dynamic crossover and the value of $N_\alpha(T_g)$ could be drawn. Based on the ILs analyzed in their article, they determined that the dynamic crossover is only observed in ILs having a value of $N_\alpha(T_g) > \sim 100$. Clearly, this is contradicted by the analysis given here, where even the CS sample, which does not exhibit LLT behavior, shows a dynamic crossover. This analysis reveals that the size of the cooperative regions at T_g reflect the relative sizes and interaction strengths of the constituent ions, while having little bearing on the presence of the dynamic crossover or the LLT. Furthermore, the values computed for the volume of the cooperative region fall in a range from about 8 to 55nm³ according to their data. The corresponding values for the ILs in this work are within that range. It may be concluded that this represents a typical range for glass-forming ILs, however, any connection between the value of $N_\alpha(T_g)$ and the presence of a dynamic crossover appears dubious. Failure to establish a connection between the behavior of C_p at T_g and the observed dynamic crossover in cases where LLT is present as well as in its absence means we must search elsewhere for a thermodynamic connection to the dynamic changes that take place above T_g .

Table 6.2: Analysis of the number of dynamically correlated molecules at T_g , $N_\alpha(T_g)$, and the size of the correlated regions, $N_\alpha(T_g) \cdot (\nu_+ + \nu_-)$. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	T_g (K)	ΔC_p (J/mol K)	δT (K)	$N_\alpha(T_g)$	$N_\alpha(T_g) \cdot (\nu_+ + \nu_-)$ (nm ³)
BH ₄	195.1	243.5	3.64	12.4	9.76
Prop	197.3	205.0	2.55	18.9	16.04
NFP	196.9	250.2	1.83	29.9	29.65
NFBS	195.9	168.4	3.50	8.3	8.42
TFSI	187.8	238.8	3.17	8.2	7.83
CS	205.5	216.4	3.70	16.5	15.65

6.3 Configurational Entropy

In this section, we employ the Adam-Gibbs (AG) model of the dynamic glass transition to understand the crossover phenomena in terms of the two order parameter (TOP) model of the liquid state. The Adam-Gibbs model is an approach to understanding the glass transition in terms of the cooperative rearrangement of liquid particles. The AG model predicts that the relaxation time of the system is inversely related to the configurational entropy, $S_c(T)$, more specifically stated as $\log_{10}(\tau_\alpha) \propto (S_c T)^{-1}$.^[157]

Firstly, we define the configurational entropy as the portion of the entropy associated with the number of accessible configurational microstates of the liquid.^[393] At high temperatures, where the dynamics of the liquid are relatively fast and the local structures are governed predominately by the density ordering, the number of accessible configurational states is high. As the temperature of the liquid is decreased, the dynamics slow down accordingly and, in the TOP model, the local arrangement of the ions is increasingly governed by the short-range ordering associated with bond orientation as reflected in the order parameter ψ , corresponding to the fraction of LFS. Thus, the configurational entropy of the system necessarily decreases in accordance with the changes in local structure governed by the presence of LFS. Based on the Adam-Gibbs approach and the predictions of the TOP model, we propose that a direct link can be drawn between the relaxation dynamics reported by dielectric spectroscopy and the configurational entropy, $S_c(T)$, which is readily determined from C_p data as reported by DSC.

We can calculate $S_c(T)$ by the following equation:

$$S_c(T) = S_0 + \int_{T_g}^T \frac{C_p^{liq}(T) - C_p^{gl}(T)}{T} dT \quad (6.2)$$

where T_g denotes the calorimetric glass transition temperature, T is the variable temperature of the system, C_p^{liq} is the measured heat capacity of the liquid state above T_g , C_p^{gl} is the extrapolated heat capacity of the glassy state to temperatures above T_g , and S_0 is the residual configurational entropy of the glass.^[162, 163, 191] The heat capacity of the glass, C_p^{gl} , is extrapolated to high temperatures using a quadratic expansion in T . The value of S_0 is determined by the constraint that the Vogel temperatures, T_0 , obtained from the VFT fits to

the dynamic quantities in Chapter 5 agree with the Kauzmann temperatures determined by extrapolation of $S_c(T)$ to the temperature where $S_c(T_K) = 0$. The temperature dependence of the relaxation times, τ_α , in the AG model is given by:

$$\log_{10}(\tau_\alpha) = \log_{10} \tau_\infty + \frac{C}{S_c(T) \cdot T} \quad (6.3)$$

where τ_∞ is the high temperature limiting value of τ_α , C is a constant parameter, and $S_c(T)$ is the configurational entropy at temperature T . [162, 163, 191] By equating τ_∞ to the corresponding VFT parameter and assuming the Kauzmann temperature, T_K , where $S_c(T)$ vanishes is equal to the Vogel temperature, T_0 , we can write an expression for the temperature dependence of $S_c(T)$ as:

$$S_c(T) = S_\infty \left(1 - \frac{T_K}{T} \right) \quad (6.4)$$

referred to as the VFT-AG equation where S_∞ is the high temperature limit of $S_c(T)$ and T_K denotes the Kauzmann temperature. [162, 163, 191] Since this expression is obtained by the assumption that the VFT equation (Equation 5.8) and the AG equation (Equation 6.3) provide equivalent descriptions of the temperature dependence of the relaxation times, it follows as a consequence that the VFT-AG equation is only valid for a given range of temperatures which can be sufficiently described by a single VFT fit. Hence, we immediately conclude that if the VFT-AG equation suffices to fit the $S_c(T)$ data, we will require two separate fits covering the temperature ranges $T > T_x$ and $T_g < T < T_x$.

Figure 6.3 shows the temperature dependence of S_c for the six P_{666,14}-based ILs included in this work. In these plots, high (above T_x) and low (between T_g and T_x) temperature fits to Equation 6.4 are shown by the dashed and dotted lines, respectively. The fit parameters are compiled in Table 6.3. On the basis of the Adam-Gibbs equation given by Equation 6.3 and the relation $\log_{10}(\tau) \propto (S_c T)^{-1}$ along with the assumption that the VFT description can be equated to the AG description providing the basis for the functional form for $S_c(T)$ given by Equation 6.4, values for $S_c(T)$ can be calculated from the relaxation time data and

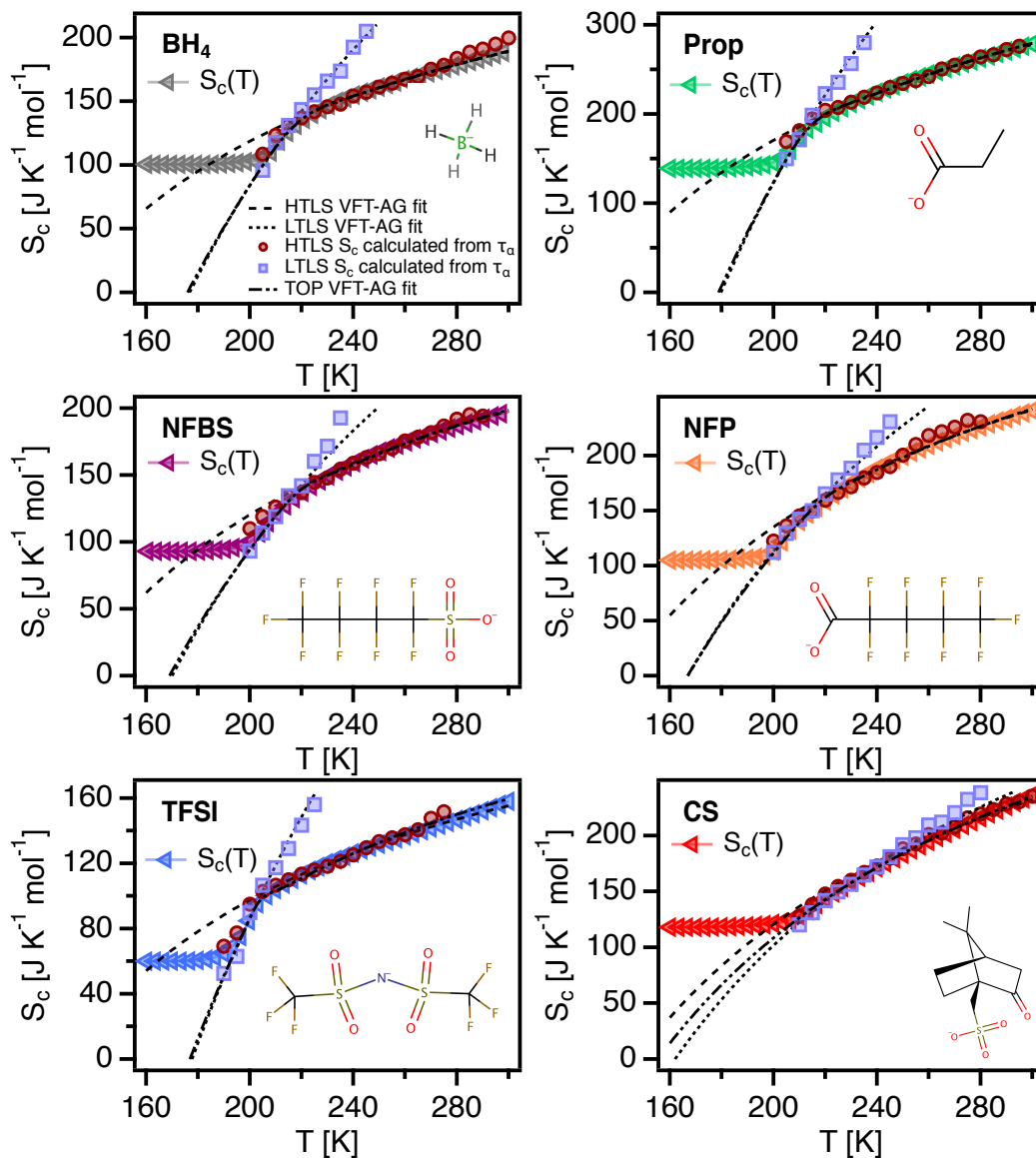


Figure 6.3: Configurational entropy for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , Prop. Middle row, from left to right: NFBS, NFP. Bottom row, from left to right: TFSI, CS.

Table 6.3: Parameters from VFT-AG fits to $S_c(T)$. S_c is given in units of [J/mol K], T is given in units of [K], TS_c is given in units of [kJ/mol]. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	S_∞^H	T_K^H	S_∞^L	T_K^L	T_x	$(TS_c)_x$	S_x/S_∞^H	S_x/S_∞^L
BH ₄	329.9	128.1	723.7	176.8	218.4	29.8	0.41	0.19
Prop	493.5	130.9	1210.1	179.7	213.5	40.8	0.39	0.16
NFP	455.0	140.7	684.0	166.9	219.1	35.7	0.36	0.24
NFBS	353.1	131.9	628.6	170.0	219.1	30.8	0.40	0.22
TFSI	270.8	128.0	772.5	177.7	204.2	20.6	0.37	0.13
CS	454.2	146.9	535.2	162.0	246.5	45.3	0.40	0.34

the parameters corresponding to the VFT and VFT-AG fits using the expression:

$$S_c(T) = \frac{DT_0 S_\infty \cdot \log_{10} e}{[(\log_{10} \tau_\alpha - \log_{10} \tau_\infty) \cdot T]} \quad (6.5)$$

The values computed from this expression are plotted in Figure 6.3 where the values corresponding to the high temperature fits are represented by the red circles and those computed based on the low temperature fits are represented by the blue squares. From these plots, it is evident that the VFT-AG form of $S_c(T)$ given by Equation 6.4 provides a quantitative description of the $S_c(T)$ determined from the DSC results of the heat capacity. Similarly, the corresponding S_c values computed from the relaxation times reported by dielectric spectroscopy are in agreement with the $S_c(T)$ data obtained from the DSC measurements. These results lead to the conclusion that the thermodynamic link to the dynamic crossover is readily obtained from the analysis of the configurational entropy calculated from the heat capacity data. By extension, in the cases that show a LLT at the corresponding crossover temperature, analysis of the change in configurational entropy provides a means of understanding the connection between the structural, dynamic, and thermodynamic behavior related to the LLT.

By analogy to the description of the dynamic behavior in terms of the TOP model given by Equation 5.17, we can write a similar expression for $S_c(T)$ by incorporating the order parameter, ψ . Thus, we propose the following expression to describe the full range of the temperature dependence of S_c from T_g to high temperatures far above T_x :

$$S_c(T) = (1 - \psi)S_\infty^\rho \left(1 - \frac{T_K^\rho}{T}\right) + \psi S_\infty^\psi \left(1 - \frac{T_K^\psi}{T}\right) \quad (6.6)$$

where S_∞^ρ and T_K^ρ are the parameters corresponding to the purely NLS and S_∞^ψ and T_K^ψ are the parameters describing the LFS, with ψ given by the logistic ansatz defined by Equation 5.16. Fits to the data using this equation are shown in the plots in Figure 6.3 by the dash-dot-dot lines. The parameters from these fits are given in Table 6.4. This model is found to yield a quantitative description of the data, and the fit parameters are in close agreement with the fits of the relaxation times. A notable exception to this correspondence is seen in

Table 6.4: Parameters from TOP-VFT-AG fits to $S_c(T)$. S_c is given in units of [J/mol K], T is given in units of [K], TS_c is given in units of [kJ/mol]. The magnitude of the error in the tabulated values corresponds to the magnitude of the last reported digit.

Anion	S_∞^ψ	T_K^ψ	S_∞^ρ	T_K^ρ	T_x	δT	$(TS_c)_x$	S_x/S_∞^ψ	S_x/S_∞^ρ
BH ₄	677.8	176.0	336.7	131.2	218.4	33.0	28.9	0.20	0.39
Prop	1120.9	178.9	509.4	135.4	213.5	29.5	39.2	0.16	0.36
NFP	670.5	166.9	464.5	143.4	219.1	22.2	34.5	0.23	0.34
NFBS	603.8	169.0	363.3	135.8	219.1	22.0	29.7	0.22	0.37
TFSI	738.5	176.9	293.4	136.9	204.2	9.8	19.9	0.13	0.33
CS	469.1	162.0	491.7	146.9	246.5	1500	44.2	0.38	0.37

the CS sample. Fitting of the $S_c(T)$ data using Equation 6.6 for this case gives a width of the crossover more than one order of magnitude greater than what was found from fits to the dynamic quantities obtained via dielectric spectroscopy. The width of the crossover in the dynamics for the CS sample was $\sim 75\text{K}$, while the value corresponding to the configurational entropy was determined to be on the order of $\sim 1500\text{K}$. This suggests that the S_c data for the $\text{P}_{666,14}$ CS sample is best described by a much narrower range for the fraction of LFS, switching from values of ψ just below the critical value ($\psi_c = 1/2$) to values just above the critical value. This discrepancy suggests that, for cases where the LLT is absent, the switching from the normal liquid behavior to the behavior characteristic of the LFS may not be well-defined in the thermodynamic quantities, appearing almost as an average between the two states. This type of mixing behavior in the thermodynamic data may explain why a corresponding thermodynamic signature of the dynamic crossover observed in a variety of glass-forming systems has not been found and is likely related to the absence of the LLT in these systems.

Since the dynamic crossover behavior, in cases exhibiting the LLT and in its absence, is found to be reflected in the configurational entropy of these systems, it is natural to assume a uniqueness of the quantity $(TS_c)_x$ defined in relation to the timescale of the crossover, τ_x . To test the Adam-Gibbs prediction of the proportionality between the relaxation times and the configurational entropy, we plot the inverse of (TS_c) normalized by the crossover value against $\log_{10}(\tau_x/\tau_\alpha)$ in Figure 6.4. These plots show the expected inverse proportionality of these quantities and, by normalizing the data by the crossover values, we see that the slopes change at the crossover reflecting the two state behavior of the $\text{P}_{666,14}$ -based ionic liquids while validating the predictions of the Adam-Gibbs approach to the dynamic glass transition.

6.4 Thermodynamics of the Liquid-Liquid Transition

We are now at a point where the thermodynamic description given by the two order parameter model of the liquid state can be assessed in light of the results obtained from

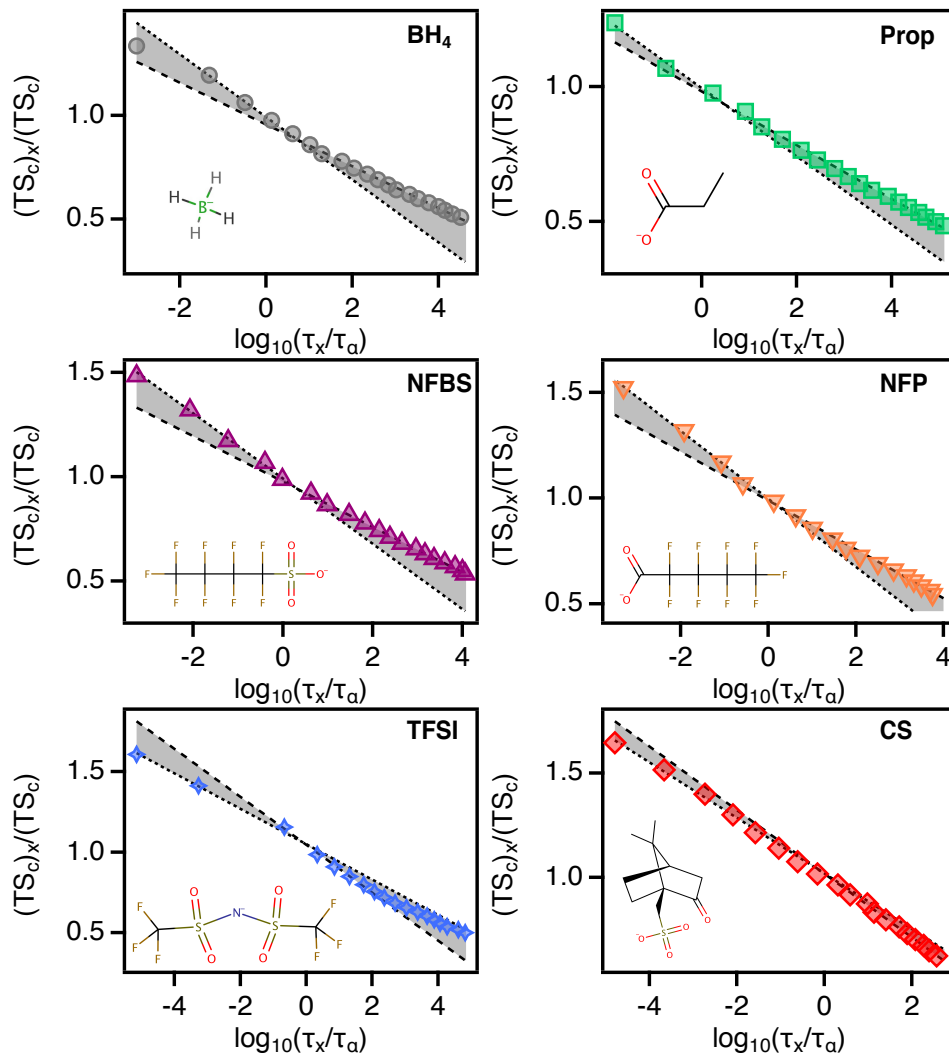


Figure 6.4: The quantity TS_c^{-1} normalized by the crossover value plotted against inverse structural relaxation times normalized by the crossover time for $P_{666,14}$ -based ionic liquids. Top row, from left to right: BH_4 , $Prop$. Middle row, from left to right: $NFBS$, NFP . Bottom row, from left to right: $TFSI$, CS . Dashed and dotted lines with shaded region in between serve as guides for the eye.

the structural analysis (see Chapter 4), the dielectric permittivity and dynamic behavior (see Chapter 5), and the thermodynamic properties described earlier in this chapter. The expression for the mean-field free energy as a function of the fraction of LFS encapsulated in the order parameter, ψ , which is given by Equation 2.9, is defined by the difference in energy, volume, and degeneracy between the two states corresponding to the NLS and LFS. However, in order to describe the liquid state in general, we also need to account for the free energy contributions solely arising from the density order parameter, ρ , contained in the term f_ρ as well as the coupling between the order parameters. The coupling between ρ and ψ is the origin of the density anomaly corresponding to the LLT. However, the most important term in the description of the free energy that gives rise to the phenomena of LLT and the associated liquid-liquid critical point (LLCP) is the cooperative formation of locally favored structures parameterized by the term J in the free energy expression. A prerequisite for the existence of the LLCP and the LLT is a non-zero value of J . We have previously neglected the role of the cooperative formation of LFS in order to simplify the expressions derived from the TOP model for use in the analysis of the experimental data. However, in a complete description of the liquid state in terms of the two order parameters, the influence of the cooperativity term J must be accounted for. We must therefore concede that the analysis of the experimental data presented in this work only amounts to an approximation of the two state behavior exhibited by the P_{666,14}-family of ionic liquids. Despite the explicit absence of the J term in our analysis, its influence is noted by the discontinuities in the structural parameters and the static dielectric permittivities observed for the five ILs included in this work which show undeniable evidence of a transition occurring between amorphous states in the supercooled liquid. It should also be emphasized that the absence of LLT behavior in the case of the CS anion does not prove outright that the cooperativity term J related to this sample is zero. Cases where the cooperative formation of LFS is very weak, but non-zero, correspond to a scenario where the LLCP is hidden below the glass transition, making experimental determination of the LLT a practical impossibility. Even still, since the CS sample exhibits a dynamic crossover above T_g with a concomitant change in the temperature dependence of the effective dipole moment, it is reasonable to conclude that this system does not have a LLCP or LLT. This situation can be accounted for by the parameters associated

with the difference in energy, volume, and entropy of the two states corresponding to differing types of local ordering in the liquid structure. Specifically, the entropy difference of the two states, which is determined by the degeneracies of the corresponding states plays a crucial role in determining the phase behavior of a liquid described by the TOP model. The ground state of the LFS is assumed to have a degeneracy $g_\psi < g_\rho$. However, according to the two state model of Strässler and Kittel[178] upon which the TOP model of the liquid state is built, if the degeneracy of the excited state is not sufficiently larger than that of the ground state, no thermodynamic phase transition can occur, only a continuous crossover between the two states is possible. This scenario is likely what is occurring in the CS case, and is probably quite common for a variety of molecular glass-formers which can be described by the TOP model but show no experimental evidence for the existence of a LLT. In summary, we emphasize that the two state feature related to the formation of LFS is a phenomena that is generalizable to describe local ordering in the condensed liquid and associated glassy states of matter, but the manifestation of the two state behavior in a first-order LLT with an associated LLCP is not assumed to be the norm. It is the authors opinion based on the results contained within this dissertation that the cases where the LLT is present are special cases where the differences between the NLS and the LFS are finely tuned to manifest the second critical point. In addition, these cases are further classified based on the cooperativity term J , where depending on the magnitude of J and the energy difference, ΔE , the LLCP may lie below the glass transition for cases of small J and ΔE . For cases with intermediate values for J and ΔE , the LLT occurs in the supercooled liquid where crystallization may hinder experimental determination of the LLT behavior. Finally, for liquids having large J and ΔE , which may be the case for carbon and phosphorous, the LLT can manifest in the stable liquid state above T_m . [14]

To summarize the key points, the necessary conditions for the LLT are the existence of LFS and the cooperativity of their formation. The TOP model predicts structural changes, including density changes, as the fraction of LFS increases. These changes appear abruptly in cases of first order LLT as well as in the critical region crossing the Widom line. These changes appear smooth and continuous far from the LLCP in the Boltzmann regime as well as in cases where no LLCP exists. In general, the TOP model predicts the existence of

LLT and the LLCP, but only for particular values of the parameters ΔE , Δv , $\Delta\sigma$, and J describing the distinction between the two states, i.e. NLS and LFS. For the vast majority of liquids, the NLS and LFS are possibly close enough leading to the case where no LLT occurs. Additionally, if J is very low, LLT may be possible, but only below T_g . In the $P_{666,14}$ -based ILs in this work, structural and permittivity analysis provide evidence of changes in local coordination and orientational order associated with changes in the relative abundance of the NLS and LFS. This leads to the hypothesis that changes in dynamics are related to the relative abundance of these two types of local structures. This is reflected in the configurational entropy, providing the link between dynamics and thermodynamics. The glass transition itself remains a mystery, but may arise due to frustration resulting from competition between NLS, LFS, and equilibrium crystal structures.

6.5 Conclusions

To conclude this chapter, we summarize the main findings related to the measurement of thermodynamic quantities in $P_{666,14}$ -based ILs as reported by DSC. First and foremost, a reversible enthalpic peak attributed to the LLT was observed in the DSC data above T_g for the ILs containing the BH_4 , Prop, NFP, NFBS, and TFSI anions. A similar peak was not observed in the CS sample. This set of fragile ILs shows only evidence of the LLT and the glass transition in the temperature range of the DSC measurements, indicating good glass-forming behavior in contrast with other ILs where crystallization is an important factor. No direct correlation between the presence of the dynamic crossover and the number of dynamically correlated molecules at T_g could be established. However, the configurational entropy, S_c , reflects the switching observed in dynamic behavior and the relation between the relaxation times and the configurational entropy predicted by the Adam-Gibbs model holds with a change in proportionality at the dynamic crossover in these fragile IL systems. Following a discussion of the general thermodynamic behavior predicted by the two order parameter model of the liquid state, it is argued that LLT can only occur in a subset of liquids despite the two state description being generally applicable to all liquids to an extent.

Chapter 7

Conclusions

The goal of this dissertation is to develop an understanding of the molecular details relevant to the liquid-liquid transition that occurs in certain trihexyltetradecylphosphonium-based ionic liquids. To that aim, I posed a set of questions at the outset whose purpose was to motivate the work in its appropriate context and to focus the scope of the project. In pursuing this matter, I have set out to find answers to these questions and endeavored to uncover further lines of questioning that will surely lead to new discoveries and deeper insight into the fundamental nature of the liquid state. At the conclusion of this dissertation, we can revisit those initial questions and summarize the answers obtained through the studies that were laid out in detail in the previous chapters. Some of the questions we can answer definitively, while others leave us with some insight into future efforts that will help us unravel the complex mysteries of the liquid state.

1. *How does the liquid structure change across the liquid-liquid transition in ionic liquids?*

The general trend in the structural characteristics corresponding to the observed LLT in $P_{666,14}$ -based ILs is manifested in the polarity alternation structure showing a tendency to increase in extension of the apolar domain, while changes in the degree of order in the apolar structure vary with the size of the anion. For the smaller anions, BH_4 and Prop, the order of the apolar domains see an increase across the LLT, while a decrease in order of the apolar is observed for the larger anions, NFP, NFBS, and TFSI. Aspects of the charge alternation structure show a notable trend at the point of

the LLT, specifically showing an overall increase in the degree of charge ordering, with the exception of the NFBS anion. However, the structural parameter that displays the most significant effect emerging from the LLT is the average ion coordination, which increases in dramatic fashion at the LLT for the ILs bearing the BH_4 , Prop, NFP, NFBS, and TFSI anions.

2. *How do the structural changes correlate with the macroscopic dielectric properties of the ionic liquids?*

The key macroscopic property affected by the LLT is the static dielectric permittivity, ϵ_s , showing a step-like increase accompanying the transition, by more than 100% in the $\text{P}_{666,14}$ BH_4 system. The correspondence between ϵ_s and the local ordering of dipoles reflects a direct link between the emergence of increased local order accompanying the increase in the average ion coordination number at the LLT and the macroscopic increase in the static permittivity of the system.

3. *How does the liquid-liquid transition affect the dynamics and transport properties of ionic liquids?*

The dynamics of the $\text{P}_{666,14}$ -based ILs that exhibit LLT shift towards slower timescales as evidenced by a crossover from moderately fragile dynamics above the LLT to more fragile dynamics at the transition.

4. *How is the liquid-liquid transition related to the glass transition?*

The effect of the LLT on the dynamics of the fragile ILs studied results in an apparent increase in the T_g in these systems compared to the values predicted in the absence of LLT.

5. *Is the liquid-liquid transition in these ionic liquids a true first-order phase transition?*

The evidence suggests the LLT in the $\text{P}_{666,14}$ -based ILs in this study is a first-order thermodynamic phase transition. This conclusion is supported by the apparent discontinuous changes in properties with a direct dependence on the order parameter ψ governing LLT behavior, including the average ion coordination number and the

static dielectric permittivity. In addition, a reversible enthalpic peak appears in the heat capacity of the ILs corresponding to the latent heat associated with a first-order phase transition.

6. *What role does the anion play in the liquid-liquid transition?*

The existence of the LLT in $P_{666,14}$ -based ILs is entirely anion-dependent, in that the cation has the ability to display LLT behavior, but will only do so with certain anion pairings. So the characteristics of the anion structure will play the deciding role in the manifestation of LLT behavior in $P_{666,14}$ -based ILs. The types of anions that show evidence of the LLT are typically small in size and very weakly coordinating. No quantitative diagnostic criteria were established from this limited subset of anions demonstrating LLT behavior. More extensive, systematic investigation would be needed. However, the types of anions studied here vary considerably in size and coordination strength, suggesting other anions that lie within the range of properties spanned by this series would display LLT behavior when paired with the $P_{666,14}$ cation.

7. *Can we identify a structural descriptor corresponding to the locally favored structures characterizing the low-temperature liquid state?*

The most we can determine based on the set of experiments performed to study the LLT in this series of $P_{666,14}$ -based ILs is revealed by the trends in the average ion coordination number. The family of $P_{666,14}$ -based ILs are known to possess a filamentous morphology in the high temperature liquid state, which corresponds to a sequential arrangement of alternating charges. This would correspond to a typical ion coordination number of 2. In fact, we see coordination numbers larger than 2 in the high temperature liquid states, an indication of branching in the 3-D, continuously-percolating charge network. The increases in the average ion coordination numbers observed at the LLT indicates a characteristic of the locally favored structures in these fragile ILs is a tendency to maximize the number of ion associations. A more detailed understanding of the symmetries and spatial arrangements adopted by the LFS in $P_{666,14}$ -based ILs would require *ab initio* or atomistic molecular dynamics simulations to parse out the structural descriptor corresponding to the LFS in these systems.

7.1 Outlook

The work presented in this dissertation demonstrates the capability of fragile ionic liquid systems to exist in two distinct liquid phases differing by the type of ordering of the ions on the local level separated by a first-order thermodynamic transition with implications for the macroscopic properties, dynamic behavior, and the glass transition. These relative ease of synthesizing new ionic liquids based on the same cation by swapping the anions means there is a lot of low hanging fruit to be plucked by simply playing with the anion structures and coming up with new systems to study the liquid-liquid transition in ionic liquids. Likewise, it stands to reason, given the exceptionally vast tunability of ionic liquid structures, there should also be other cation systems with a hidden propensity for two-state behavior, waiting to be discovered. If liquid-liquid transitions are possible in trihexyltetradecylphosphonium ionic liquids, why not other quaternary phosphonium systems or, similarly, quaternary ammonium systems?

But if we want to get a deeper understanding of the mechanisms underlying the liquid-liquid transition, it will be necessary to push the boundaries of experimentation to unlock the key to the specific interactions responsible for locally ordered structures that, in turn, fuel the dynamic and macroscopic changes that emerge between the two liquid phases across the transition. Incorporating more powerful techniques, such as Flash DSC to probe kinetics of the phase transition, synchrotron X-ray and neutron scattering techniques to more accurately elucidate structure in finer detail, Raman and Infrared spectroscopy to probe vibrational states sensitive to the local environment, and the advantages of studying dynamics using a combination of techniques that compliment the results of dielectric measurements, will serve to place the confirmation of the liquid-liquid transition in these fragile ionic liquid system on firmer ground and further our understanding of the underlying mechanisms.

Probing deeper in the liquid-liquid transition, demonstrated here for the first time in pure ionic liquid systems, will, for sure, require the use of a wider array of experimental techniques capable of accurately capturing subtleties in the structural, dynamic, and thermodynamic aspects of these systems. Sophisticated computational studies would transform the spark lit by this work into a roaring blaze, casting light capable of illuminating aspects of the

microscopic details of the liquid-liquid transition obscured in the shadow cast by bulk studies alone. Indeed, through a combination of computational simulations of liquid-liquid transitions in ionic liquids with a gamut of experimental tools, the groundwork laid before us opens up into a whole new field at the intersection of efforts to unravel the mysteries of the liquid state manifested in the liquid-liquid transition and the infinite zoo of ionic liquids brimming with technological potential.

To pull back a bit, it is important to recognize the controversy that follows the liquid-liquid transition. In doing so, we must recognize the importance of careful interpretation of data of any kind, whether it originates from a physical experiment or computer code. The conclusions arrived at here regarding the existence of fragile ionic liquids capable of undergoing a liquid-liquid transition are the culmination of countless hours spent verifying analytical procedures so that when the controversy arrives, I know this work will endure the scrutiny, even while knowing full well that no matter how much time is devoted to agonizing over the results of an experiment, the scientific endeavor is focused squarely on uncovering the truth, promising both validation and disappointment along the way. Only the mystery endures.

Bibliography

- [1] Bilin Zhuang and Zhen-Gang Wang. Statistical field theory for polar fluids. *The Journal of Chemical Physics*, 149(12):124108, 2018. [x](#), [xviii](#), [138](#), [139](#), [142](#)
- [2] Bilin Zhuang, Gabriele Ramanauskaite, Zhao Yuan Koa, and Zhen-Gang Wang. Like dissolves like: A first-principles theory for predicting liquid miscibility and mixture dielectric constant. *Science Advances*, 7(7):1–8, 2021. [x](#), [xviii](#), [138](#), [139](#), [142](#), [143](#), [144](#)
- [3] Yizhak Marcus. Ionic and molar volumes of room temperature ionic liquids. *Journal of Molecular Liquids*, 209:289–293, 2015. [x](#), [99](#), [139](#)
- [4] Juan C. Araque, Jeevapani J. Hettige, and Claudio J. Margulis. Modern Room Temperature Ionic Liquids, a Simple Guide to Understanding Their Structure and How It May Relate to Dynamics. *Journal of Physical Chemistry B*, 119(40):12727–12740, 2015. [xii](#), [4](#), [13](#), [14](#), [37](#), [38](#), [76](#), [87](#), [108](#)
- [5] Hajime Tanaka. Liquid–liquid transition and polyamorphism. *The Journal of Chemical Physics*, 153(13):130901, 2020. [xii](#), [1](#), [17](#), [24](#), [25](#), [27](#), [28](#), [29](#), [32](#), [33](#), [34](#), [87](#), [158](#), [160](#), [161](#)
- [6] Matthew A. Harris, Thomas Kinsey, Durgesh V. Wagle, Gary A. Baker, and Joshua Sangoro. Evidence of a liquid–liquid transition in a glass-forming ionic liquid. *Proceedings of the National Academy of Sciences*, 118(11):e2020878118, 2021. [xvii](#), [xviii](#), [31](#), [44](#), [75](#), [78](#), [124](#), [125](#), [127](#), [128](#), [132](#)
- [7] Shuying Shang, Zhengguang Zhu, Zaijun Lu, and Guangzhao Zhang. Liquid-to-liquid relaxation of polystyrene melts investigated by low-frequency anelastic spectroscopy. *Journal of Physics: Condensed Matter*, 19(41):416107, 2007. [1](#)
- [8] Giancarlo Franzese, Gianpietro Malescio, Anna Skibinsky, Sergey V. Buldyrev, and H. Eugene Stanley. Generic mechanism for generating a liquid-liquid phase transition. *Nature*, 409(6821):692–695, 2001. [1](#), [24](#)
- [9] Gianpietro Malescio, Giancarlo Franzese, Giuseppe Pellicane, Anna Skibinsky, Sergey V Buldyrev, and H Eugene Stanley. Liquid-liquid phase transition in one-component fluids. *Journal of Physics: Condensed Matter*, 14(9):2193–2200, 2002. [1](#)

- [10] S. V. Buldyrev, G. Franzese, N. Giovambattista, G. Malescio, M. R. Sadr-Lahijany, A. Scala, A. Skibinsky, and H. E. Stanley. Models for a liquid-liquid phase transition. *Physica A: Statistical Mechanics and its Applications*, 304(1-2):23–42, 2002. [1](#), [24](#)
- [11] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev, and H. E. Stanley. Metastable liquid-liquid phase transition in a single-component system with only one crystal phase and no density anomaly. *Physical Review E*, 66(5):051206, 2002. [1](#), [24](#)
- [12] A. Skibinsky, S. V. Buldyrev, G. Franzese, G. Malescio, and H. E. Stanley. Liquid-liquid phase transitions for soft-core attractive potentials. *Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics*, 69(6):15, 2004. [1](#), [24](#)
- [13] Limei Xu, Pradeep Kumar, S. V. Buldyrev, S. H. Chen, P. H. Poole, F. Sciortino, and H. E. Stanley. Relation between the Widom line and the dynamic crossover in systems with a liquid-liquid phase transition. *Proceedings of the National Academy of Sciences of the United States of America*, 102(46):16558–16562, 2005. [1](#), [24](#), [33](#), [169](#)
- [14] Hajime Tanaka. Bond orientational order in liquids: Towards a unified description of water-like anomalies, liquid-liquid transition, glass transition, and crystallization. *The European Physical Journal E*, 35(10):113, 2012. [1](#), [24](#), [25](#), [27](#), [34](#), [158](#), [160](#), [192](#)
- [15] H. Eugene Stanley, editor. *Liquid Polymorphism*, volume 152 of *Advances in Chemical Physics*. John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013. [1](#)
- [16] Hajime Tanaka. Simple physical model of liquid water. *Journal of Chemical Physics*, 112(2):799–809, 2000. [1](#), [160](#)
- [17] T. A. Kesselring, G. Franzese, S. V. Buldyrev, H. J. Herrmann, and H. E. Stanley. Nanoscale Dynamics of Phase Flipping in Water near its Hypothesized Liquid-Liquid Critical Point. *Scientific Reports*, 2(1):474, 2012. [1](#)
- [18] Rui Shi and Hajime Tanaka. The anomalies and criticality of liquid water. *Proceedings of the National Academy of Sciences*, 117(43):26591–26599, 2020. [1](#), [31](#), [33](#)

- [19] Riccardo Foffi, John Russo, and Francesco Sciortino. Structural and topological changes across the liquid–liquid transition in water. *The Journal of Chemical Physics*, 154(18):184506, 2021. [1](#)
- [20] Srikanth Sastry and C. Austen Angell. Liquid-liquid phase transition in supercooled silicon. *Nature Materials*, 2(11):739–743, 2003. [1](#), [24](#), [31](#)
- [21] Paul F. Mcmillan, Mark Wilson, Dominik Daisenberger, and Denis Machon. A density-driven phase transition between semiconducting and metallic polyamorphs of silicon. *Nature Materials*, 4(9):680–684, 2005. [1](#), [24](#), [31](#)
- [22] M. W. C. Dharma-wardana, Dennis D. Klug, and Richard C. Remsing. Liquid-liquid Phase Transitions in Silicon. *Physical Review Letters*, 125(7):075702, 2020. [1](#)
- [23] Yoshinori Katayama, Takeshi Mizutani, Wataru Utsumi, Osamu Shimomura, Masaaki Yamakata, and Ken Ichi Funakoshi. A first-order liquid-liquid phase transition in phosphorus. *Nature*, 403(6766):170–173, 2000. [1](#), [3](#), [24](#), [32](#)
- [24] G. Monaco, S. Falconi, W. A. Crichton, and M. Mezouar. Nature of the First-Order Phase Transition in Fluid Phosphorus at High Temperature and Pressure. *Physical Review Letters*, 90(25):255701, 2003. [1](#), [24](#), [32](#)
- [25] Alice Ha, Itai Cohen, Xiaolin Zhao, Michelle Lee, and Daniel Kivelson. Supercooled liquids and polyamorphism. *Journal of Physical Chemistry*, 100(1):1–4, 1996. [1](#), [24](#), [33](#)
- [26] Hajime Tanaka, Rei Kurita, and Hiroshi Mataki. Liquid-Liquid Transition in the Molecular Liquid Triphenyl Phosphite. *Physical Review Letters*, 92(2):025701, 2004. [1](#), [24](#), [28](#), [31](#), [34](#)
- [27] Rei Kurita and Hajime Tanaka. Kinetics of the liquid-liquid transition of triphenyl phosphite. *Physical Review B - Condensed Matter and Materials Physics*, 73(10):1–5, 2006. [1](#), [24](#), [34](#), [169](#)

- [28] Rei Kurita, Yuya Shinohara, Yoshiyuki Amemiya, and Hajime Tanaka. Microscopic structural evolution during the liquid–liquid transition in triphenyl phosphite. *Journal of Physics: Condensed Matter*, 19(15):152101, 2007. [1](#), [24](#), [34](#), [169](#)
- [29] Ken Ichiro Murata and Hajime Tanaka. Microscopic identification of the order parameter governing liquid-liquid transition in a molecular liquid. *Proceedings of the National Academy of Sciences of the United States of America*, 112(19):5956–5961, 2015. [1](#), [24](#), [28](#), [31](#), [34](#), [169](#)
- [30] Finlay Walton, John Bolling, Andrew Farrell, Jamie MacEwen, Christopher D. Syme, Mario González Jiménez, Hans M. Senn, Claire Wilson, Gianfelice Cinque, and Klaas Wynne. Polyamorphism Mirrors Polymorphism in the Liquid-Liquid Transition of a Molecular Liquid. *Journal of the American Chemical Society*, 142(16):7591–7597, 2020. [1](#), [34](#), [169](#)
- [31] Maciej Galiński, Andrzej Lewandowski, and Izabela Stepniak. Ionic liquids as electrolytes. *Electrochimica Acta*, 51(26):5567–5580, 2006. [2](#), [35](#)
- [32] José O. Valderrama and Roberto E. Rojas. Critical Properties of Ionic Liquids. Revisited. *Industrial & Engineering Chemistry Research*, 48(14):6890–6900, 2009. [2](#)
- [33] Alexander Kokorin, editor. *Ionic Liquids: Theory, Properties, New Approaches*. InTech, Rijeka, Croatia, 2011. [2](#)
- [34] Alexander Kokorin, editor. *Ionic Liquids: Applications and Perspectives*. InTech, Rijeka, Croatia, 2011. [2](#)
- [35] Tom Welton. Ionic liquids: a brief history. *Biophysical Reviews*, 10(3):691–706, 2018. [2](#), [35](#)
- [36] Jan Langmaier and Zdeněk Samec. Cyclic voltammetry of ion transfer across a room temperature ionic liquid membrane supported by a microporous filter. *Electrochemistry Communications*, 9(10):2633–2638, 2007. [2](#), [35](#)

- [37] Michel Armand, Frank Endres, Douglas R. MacFarlane, Hiroyuki Ohno, and Bruno Scrosati. Ionic-liquid materials for the electrochemical challenges of the future. *Nature Materials*, 8(8):621–629, 2009. [2](#), [35](#)
- [38] Jenel Vatamanu, Liulei Cao, Oleg Borodin, Dmitry Bedrov, and Grant D. Smith. On the Influence of Surface Topography on the Electric Double Layer Structure and Differential Capacitance of Graphite/Ionic Liquid Interfaces. *The Journal of Physical Chemistry Letters*, 2(17):2267–2272, 2011. [2](#), [35](#)
- [39] Katherine L. Van Aken, Majid Beidaghi, and Yury Gogotsi. Formulation of ionic-liquid electrolyte to expand the voltage window of supercapacitors. *Angewandte Chemie - International Edition*, 54(16):4806–4809, 2015. [2](#), [35](#)
- [40] P. Sippel, P. Lunkenheimer, S. Krohns, E. Thoms, and A. Loidl. Importance of liquid fragility for energy applications of ionic liquids. *Scientific Reports*, 5(1):13922, 2015. [2](#), [35](#)
- [41] Anja-Verena Mudring and Sifu Tang. Ionic Liquids for Lanthanide and Actinide Chemistry. *European Journal of Inorganic Chemistry*, 2010(18):2569–2581, 2010. [2](#), [35](#)
- [42] Ning Deng, Min Li, Lijie Zhao, Chengfei Lu, Sergio L. de Rooy, and Isiah M. Warner. Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic liquids for environmental remediation. *Journal of Hazardous Materials*, 192(3):1350–1357, 2011. [2](#), [4](#), [35](#)
- [43] Dongli Zhang, Wei Wang, Yuefeng Deng, Jianping Zhang, He Zhao, and Ji Chen. Extraction and recovery of cerium(IV) and fluorine(I) from sulfuric solutions using bifunctional ionic liquid extractants. *Chemical Engineering Journal*, 179:19–25, 2012. [2](#), [35](#)
- [44] Yinghui Liu, Ji Chen, and Deqian Li. Application and Perspective of Ionic Liquids on Rare Earths Green Separation. *Separation Science and Technology*, 47(2):223–232, 2012. [2](#), [35](#)

- [45] Antonia Pérez De Los Ríos and Francisco José Hernández Fernández, editors. *Ionic Liquids in Separation Technology*. Elsevier, Amsterdam, The Netherlands, 2014. [2](#), [35](#)
- [46] R.B. Gujar, S.A. Ansari, and P.K. Mohapatra. Spectacular enhancements in actinide ion uptake using novel extraction chromatography resins containing TODGA and ionic liquid. *Separation and Purification Technology*, 141:229–234, 2015. [2](#), [35](#)
- [47] Kevin D. Clark, Omprakash Nacham, Jeffrey A. Purslow, Stephen A. Pierson, and Jared L. Anderson. Magnetic ionic liquids in analytical chemistry: A review. *Analytica Chimica Acta*, 934:9–21, 2016. [2](#), [35](#)
- [48] Youzhen Li, Xue Dong, Jianhua Yuan, Ning Pu, Pingping Wei, Taoxiang Sun, Weiqun Shi, Jing Chen, Jianchen Wang, and Chao Xu. Performance and Mechanism for the Selective Separation of Trivalent Americium from Lanthanides by a Tetradentate Phenanthroline Ligand in Ionic Liquid. *Inorganic Chemistry*, 59(6):3905–3911, 2020. [2](#), [35](#)
- [49] Filipe S. Oliveira, João M.M. Araújo, Rui Ferreira, Luís Paulo N. Rebelo, and Isabel M. Marrucho. Extraction of L-lactic, L-malic, and succinic acids using phosphonium-based ionic liquids. *Separation and Purification Technology*, 85:137–146, 2012. [2](#), [35](#)
- [50] Rafal Bogel-Lukasik, editor. *Ionic Liquids in the Biorefinery Concept: Challenges and Perspectives*. The Royal Society of Chemistry, Cambridge, England, 2015. [2](#), [35](#)
- [51] Xiangqian Meng, Julien Devemy, Vincent Verney, Arnaud Gautier, Pascale Husson, and Jean Michel Andanson. Improving Cellulose Dissolution in Ionic Liquids by Tuning the Size of the Ions: Impact of the Length of the Alkyl Chains in Tetraalkylammonium Carboxylate. *ChemSusChem*, 10(8):1749–1760, 2017. [2](#), [35](#)
- [52] Zahoor Ullah, Amir Sada Khan, Nawshad Muhammad, Riaz Ullah, Ali S. Alqahtani, Syed Nasir Shah, Ouahid Ben Ghanem, Mohamad Azmi Bustam, and Zakaria Man. A review on ionic liquids as perspective catalysts in transesterification of different feedstock oil into biodiesel. *Journal of Molecular Liquids*, 266:673–686, 2018. [2](#), [35](#)

- [53] Tyler Cosby, Ashlee Aiello, David P. Durkin, and Paul C. Trulove. Kinetics of ionic liquid-facilitated cellulose decrystallization by Raman spectral mapping. *Cellulose*, 28(3):1321–1330, 2021. [2](#), [35](#)
- [54] Umair Qasim, Sikander Rafiq, Farrukh Jamil, Ashfaq Ahmed, Touqeer Ali, Jaan Kers, M Shahzad Khurram, Murid Hussain, Abrar Inayat, and Young-Kwon Park. Processing of lignocellulose in ionic liquids: A cleaner and sustainable approach. *Journal of Cleaner Production*, 323:129189, 2021. [2](#), [35](#)
- [55] Arash Babai and Anja Verena Mudring. Rare-earth iodides in ionic liquids: Crystal structures of $[\text{bmpyr}]_4[\text{LnI}_6][\text{Tf}_2\text{N}]$ ($\text{Ln}=\text{La}, \text{Er}$). *Journal of Alloys and Compounds*, 418(1-2):122–127, 2006. [2](#), [35](#)
- [56] Chris Hardacre and Vasile Parvulescu, editors. *Catalysis in Ionic Liquids: From Catalyst Synthesis to Application*. Catalysis Series. Royal Society of Chemistry, Cambridge, England, 2014. [2](#), [35](#)
- [57] Rohit L. Vekariya. A review of ionic liquids: Applications towards catalytic organic transformations. *Journal of Molecular Liquids*, 227:44–60, 2017. [2](#), [35](#)
- [58] Nakara Bhawawet, Jeremy B. Essner, Durgesh V. Wagle, and Gary A. Baker. Ionic Liquid Anion Controlled Nanoscale Gold Morphology Grown at a Liquid Interface. *Langmuir*, 33(24):6029–6037, 2017. [2](#), [35](#)
- [59] Amal A. Elgharbawy, Fatimah Azizah Riyadi, Md Zahangir Alam, and Muhammad Moniruzzaman. Ionic liquids as a potential solvent for lipase-catalysed reactions: A review. *Journal of Molecular Liquids*, 251:150–166, 2018. [2](#), [35](#)
- [60] Anja Verena Mudring, Arash Babai, Sven Arenz, Ralf Giernoth, K. Binnemans, Kris Driesen, and Peter Nockemann. Strong luminescence of rare earth compounds in ionic liquids: Luminescent properties of lanthanide(III) iodides in the ionic liquid 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. *Journal of Alloys and Compounds*, 418(1-2):204–208, 2006. [2](#)

- [61] Mihkel Koel. Ionic Liquids in Chemical Analysis. *Critical Reviews in Analytical Chemistry*, 35(3):177–192, 2005. [2](#), [35](#)
- [62] Yanying Wang, Miao Han, Guishen Liu, Xiaodong Hou, Yina Huang, Kangbing Wu, and Chunya Li. Molecularly imprinted electrochemical sensing interface based on in-situ-polymerization of amino-functionalized ionic liquid for specific recognition of bovine serum albumin. *Biosensors and Bioelectronics*, 74:792–798, 2015. [2](#)
- [63] Natalia V. Plechkova and Kenneth R. Seddon. Applications of ionic liquids in the chemical industry. *Chemical Society Reviews*, 37(1):123–150, 2008. [2](#), [35](#)
- [64] Adam J. Greer, Johan Jacquemin, and Christopher Hardacre. Industrial Applications of Ionic Liquids. *Molecules*, 25(21):5207, 2020. [2](#), [35](#)
- [65] Yunxiao Zhang, Joshua B. Marlow, Wade Millar, Zachary M. Aman, Debbie S. Silvester, Gregory G. Warr, Rob Atkin, and Hua Li. Nanostructure, electrochemistry and potential-dependent lubricity of the catanionic surface-active ionic liquid [P_{6,6,6,14}][AOT]. *Journal of Colloid and Interface Science*, 608(2):2120–2130, 2022. [2](#), [4](#), [36](#)
- [66] Wagner Silva, Marcileia Zanatta, Ana Sofia Ferreira, Marta C. Corvo, and Eurico J. Cabrita. Revisiting Ionic Liquid Structure-Property Relationship: A Critical Analysis. *International Journal of Molecular Sciences*, 21(20):7745, 2020. [2](#), [19](#), [35](#)
- [67] S. Zhang, J. Wang, X. Lu, and Q. Zhou, editors. *Structures and Interactions of Ionic Liquids*. Structure and Bonding. Springer-Verlag Berlin Heidelberg, Heidelberg, Germany, 2014. [2](#), [3](#)
- [68] Robert Hayes, Gregory G. Warr, and Rob Atkin. Structure and Nanostructure in Ionic Liquids. *Chemical Reviews*, 115(13):6357–6426, 2015. [2](#), [36](#)
- [69] Rui Shi and Yanting Wang. Dual Ionic and Organic Nature of Ionic Liquids. *Scientific Reports*, 6(1):19644, 2016. [2](#)
- [70] Sandipa Indra and Snehasis Daschakraborty. Nonpolar solvation dynamics for a nonpolar solute in room temperature ionic liquid: a nonequilibrium molecular dynamics simulation study. *Journal of Chemical Sciences*, 130(1):1–14, 2018. [2](#)

- [71] Guang Feng, Ming Chen, Sheng Bi, Zachary A.H. Goodwin, Eugene B. Postnikov, Nikolai Brilliantov, Michael Urbakh, and Alexei A. Kornyshev. Free and Bound States of Ions in Ionic Liquids, Conductivity, and Underscreening Paradox. *Physical Review X*, 9(2):21024, 2019. [2](#), [43](#), [45](#)
- [72] Oscar Nordness and Joan F. Brennecke. Ion Dissociation in Ionic Liquids and Ionic Liquid Solutions. *Chemical Reviews*, 120(23):12873–12902, 2020. [2](#), [3](#), [43](#)
- [73] S. V. Buldyrev, G. Malescio, C. A. Angell, N. Giovambattista, S. Prestipino, F. Saija, H. E. Stanley, and L. Xu. Unusual phase behavior of one-component systems with two-scale isotropic interactions. *Journal of Physics: Condensed Matter*, 21:504106, 2009. [3](#)
- [74] Pieter Naert, Korneel Rabaey, and Christian V. Stevens. Ionic liquid ion exchange: Exclusion from strong interactions condemns cations to the most weakly interacting anions and dictates reaction equilibrium. *Green Chemistry*, 20(18):4277–4286, 2018. [3](#)
- [75] Tamisra Pal and Michael Vogel. On the relevance of electrostatic interactions for the structural relaxation of ionic liquids: A molecular dynamics simulation study. *The Journal of Chemical Physics*, 150(12):124501, 2019. [3](#)
- [76] M. van Thiel and F. H. Ree. High-pressure liquid-liquid phase change in carbon. *Physical Review B*, 48(6):3591–3599, 1993. [3](#), [24](#), [31](#), [32](#)
- [77] Limei Xu, Sergey V. Buldyrev, Nicolas Giovambattista, and H. Eugene Stanley. Liquid-liquid phase transition and glass transition in a monoatomic model system. *International Journal of Molecular Sciences*, 11(12):5184–5200, 2010. [3](#), [24](#), [31](#)
- [78] Shuai Wei, Fan Yang, Jozef Bednarcik, Ivan Kaban, Olga Shuleshova, Andreas Meyer, and Ralf Busch. Liquid-liquid transition in a strong bulk metallic glass-forming liquid. *Nature Communications*, 4(1):2083, 2013. [3](#), [31](#)
- [79] Yezeng He, Hui Li, Yanyan Jiang, Xiongying Li, and Xiufang Bian. Liquid-liquid phase transition and structure inheritance in carbon films. *Scientific Reports*, 4(1):3635, 2015. [3](#), [32](#)

- [80] Francis W. Starr and Francesco Sciortino. “Crystal-Clear” Liquid-Liquid Transition in a Tetrahedral Fluid. *Soft Matter*, 10(47):9413–9422, 2014. [3](#)
- [81] Wei Xu, Magdalena T. Sandor, Yao Yu, Hai-Bo Ke, Hua-Ping Zhang, Mao-Zhi Li, Wei-Hua Wang, Lin Liu, and Yue Wu. Evidence of liquid–liquid transition in glass-forming $\text{La}_{50}\text{Al}_{35}\text{Ni}_{15}$ melt above liquidus temperature. *Nature Communications*, 6(1):7696, 2015. [3](#), [31](#)
- [82] Laura Henry, Mohamed Mezouar, Gaston Garbarino, David Sifré, Gunnar Weck, and Frédéric Datchi. Liquid–liquid transition and critical point in sulfur. *Nature*, 584(7821):382–386, 2020. [3](#), [24](#), [31](#)
- [83] Weidi Zhu, Ozgur Gulbiten, Bruce Aitken, and Sabyasachi Sen. Viscosity, enthalpy relaxation and liquid-liquid transition of the eutectic liquid $\text{Ge}_{15}\text{Te}_{85}$. *Journal of Non-Crystalline Solids*, 554(2021):120601, 2021. [3](#), [174](#), [175](#)
- [84] Rei Kurita and Hajime Tanaka. On the abundance and general nature of the liquid–liquid phase transition in molecular systems. *Journal of Physics: Condensed Matter*, 17(27):L293–L302, 2005. [3](#), [24](#), [28](#), [31](#), [34](#), [169](#)
- [85] H. E. Stanley, P. Kumar, G. Franzese, L. Xu, Z. Yan, M. G. Mazza, S. V. Buldyrev, S. H. Chen, and F. Mallamace. Liquid polyamorphism: Possible relation to the anomalous behaviour of water. *European Physical Journal: Special Topics*, 161(1):1–17, 2008. [3](#), [24](#)
- [86] Joanna Mosses, Christopher D. Syme, and Klaas Wynne. Order parameter of the liquid-liquid transition in a molecular liquid. *Journal of Physical Chemistry Letters*, 6(1):38–43, 2015. [3](#), [24](#), [31](#), [34](#), [169](#)
- [87] Men Zhu, Jun-Qiang Wang, John H. Perepezko, and Lian Yu. Possible existence of two amorphous phases of D-mannitol related by a first-order transition. *The Journal of Chemical Physics*, 142(24):244504, 2015. [3](#), [24](#), [31](#)
- [88] W. Tang and J. H. Perepezko. Polyamorphism and liquid-liquid transformations in D-mannitol. *The Journal of Chemical Physics*, 149(7):074505, 2018. [3](#), [31](#)

- [89] Loni Kringe, Wyatt A. Thornley, Bruce D. Kay, and Greg A. Kimmel. Reversible structural transformations in supercooled liquid water from 135 to 245 K. *Science*, 369(6509):1490–1493, 2020. [3](#)
- [90] L. Pison, J. N. Canongia Lopes, L. P. N. Rebelo, A. A. H. Padua, and M. F. Costa Gomes. Interactions of Fluorinated Gases with Ionic Liquids: Solubility of CF_4 , C_2F_6 , and C_3F_8 in Trihexyltetradecylphosphonium Bis(trifluoromethylsulfonyl)amide. *The Journal of Physical Chemistry B*, 112(39):12394–12400, 2008. [4](#)
- [91] André F. Ferreira, Pedro N. Simões, and Abel G.M. Ferreira. Quaternary phosphonium-based ionic liquids: Thermal stability and heat capacity of the liquid phase. *Journal of Chemical Thermodynamics*, 45(1):16–27, 2012. [4](#)
- [92] A.G.M. Ferreira, P.N. Simões, A.F. Ferreira, M.A. Fonseca, M.S.A. Oliveira, and A.S.M. Trino. Transport and thermal properties of quaternary phosphonium ionic liquids and IoNanofluids. *The Journal of Chemical Thermodynamics*, 64:80–92, 2013. [4](#), [44](#)
- [93] Volkan Balci and Alper Uzun. Understanding Spectroscopic Features of Trihexyltetradecylphosphonium Chloride. *ChemistrySelect*, 1(4):741–747, 2016. [4](#)
- [94] Mohammad Hadi Ghatee and Maryam Bahrami. Emergence of innovative properties by replacement of nitrogen atom with phosphorus atom in quaternary ammonium ionic liquids: Insights from ab initio calculations and MD simulations. *Chemical Physics*, 490:92–105, 2017. [4](#)
- [95] K.K. Thasneema, Mohamed Shahin Thayyil, Tancia Rosalin, K.K. Elyas, T. Dipin, Pramod K. Sahu, N.S. Krishna Kumar, V.C. Saheer, Mouslim Messali, and Taibi Ben Hadda. Thermal and spectroscopic investigations on three phosphonium based ionic liquids for industrial and biological applications. *Journal of Molecular Liquids*, 307:112960, 2020. [4](#), [147](#), [174](#)

- [96] Christine J Bradaric, Andrew Downard, Christine Kennedy, Allan J Robertson, and Yuehui Zhou. Industrial preparation of phosphonium ionic liquids. *Green Chem.*, 5(2):143–152, 2003. [4](#)
- [97] Esther Santos, Jonathan Albo, Andreia Rosatella, Carlos A.M. Afonso, and Ángel Irabien. Synthesis and characterization of Magnetic Ionic Liquids (MILs) for CO₂ separation. *Journal of Chemical Technology & Biotechnology*, 89(6):866–871, 2014. [4](#), [35](#)
- [98] Kevin D. Clark, Omprakash Nacham, Honglian Yu, Tianhao Li, Melissa M. Yamsek, Donald R. Ronning, and Jared L. Anderson. Extraction of DNA by Magnetic Ionic Liquids: Tunable Solvents for Rapid and Selective DNA Analysis. *Analytical Chemistry*, 87(3):1552–1559, 2015. [4](#), [35](#)
- [99] Haiyue Zhou, Yanliang Wang, Xiangguang Guo, Yamin Dong, Xiang Su, and Xiaoqi Sun. The recovery of rare earth by a novel extraction and precipitation strategy using functional ionic liquids. *Journal of Molecular Liquids*, 254:414–420, 2018. [4](#)
- [100] Lorenzo Gontrani, Olga Russina, Fabrizio Lo Celso, Ruggero Caminiti, Gary Annat, and Alessandro Triolo. Liquid Structure of Trihexyltetradecylphosphonium Chloride at Ambient Temperature: An X-ray Scattering and Simulation Study. *The Journal of Physical Chemistry B*, 113(27):9235–9240, 2009. [4](#), [39](#)
- [101] Karina Shimizu, Margarida F. Costa Gomes, Agílio A.H. Pádua, Luís P.N. Rebelo, and José N. Canongia Lopes. Three commentaries on the nano-segregated structure of ionic liquids. *Journal of Molecular Structure: THEOCHEM*, 946(1-3):70–76, 2010. [4](#), [38](#), [39](#), [87](#), [117](#)
- [102] Hemant K. Kashyap, Cherry S. Santos, Harsha V.R. Annapureddy, N. Sanjeeva Murthy, Claudio J. Margulis, and Edward W. Castner. Temperature-dependent structure of ionic liquids: X-ray scattering and simulations. *Faraday Discussions*, 154:133–143, 2012. [4](#), [39](#), [41](#)

- [103] Jeevapani J. Hettige, Hemant K. Kashyap, and Claudio J. Margulis. Communication: Anomalous temperature dependence of the intermediate range order in phosphonium ionic liquids. *Journal of Chemical Physics*, 140(11):1–5, 2014. [4](#), [39](#), [41](#)
- [104] Jeevapani J. Hettige, Juan C. Araque, Hemant K. Kashyap, and Claudio J. Margulis. Communication: Nanoscale structure of tetradecyltrihexylphosphonium based ionic liquids. *The Journal of Chemical Physics*, 144(12):121102, 2016. [4](#), [39](#)
- [105] Shobha Sharma, Aditya Gupta, Debdas Dhabal, and Hemant K. Kashyap. Pressure-dependent morphology of trihexyl(tetradecyl)phosphonium ionic liquids: A molecular dynamics study. *The Journal of Chemical Physics*, 145(13):134506, 2016. [4](#), [39](#)
- [106] Yong-Lei Wang, Bin Li, Sten Sarman, and Aatto Laaksonen. Microstructures and dynamics of tetraalkylphosphonium chloride ionic liquids. *The Journal of Chemical Physics*, 147(22):224502, 2017. [4](#), [39](#)
- [107] Fabrizio Lo Celso, Alessandro Triolo, Lorenzo Gontrani, and Olga Russina. Communication: Anion-specific response of mesoscopic organization in ionic liquids upon pressurization. *Journal of Chemical Physics*, 148(21):1–5, 2018. [4](#)
- [108] Sten Sarman, Yong Lei Wang, Patrick Rohlmann, Sergei Glavatskih, and Aatto Laaksonen. Rheology of phosphonium ionic liquids: A molecular dynamics and experimental study. *Physical Chemistry Chemical Physics*, 20(15):10193–10203, 2018. [4](#), [36](#)
- [109] Klaus A. Gernoth and Manfred L. Ristig. Scattering from Condensed Matter: A Brief Introduction. In Klaus A. Gernoth and Manfred L. Ristig, editors, *Particle Scattering, X-Ray Diffraction, and Microstructure of Solids and Liquids*, pages 1–5. Springer-Verlag Berlin Heidelberg, Heidelberg, Germany, 2003. [10](#), [11](#), [12](#), [13](#), [73](#)
- [110] Jean-Louis Barrat and Jean-Pierre Hansen. *Basic Concepts for Simple and Complex Liquids*. Cambridge University Press, 2003. [10](#), [11](#)

- [111] Jean-Pierre Hansen and I.R. McDonald. *Theory of Simple Liquids: with applications to soft matter*. Academic Press, Amsterdam, The Netherlands, 4th revised edition, 2013. [10](#), [11](#)
- [112] Paola Gallo and Mauro Rovere. *Physics of Liquid Matter*. Soft and Biological Matter. Springer International Publishing, Cham, Switzerland, 2021. [10](#), [11](#), [12](#), [13](#), [23](#), [77](#)
- [113] Dabir S. Viswanath, Tushar K. Ghosh, Dasika H.L. Prasad, Nidamarty V.K. Dutt, and Kalipatnapu Y. Rani. *Viscosity of Liquids: Theory, Estimation, Experiment, and Data*. Springer, Dordrecht, The Netherlands, 2007. [10](#)
- [114] C. A. Angell. Perspective on the glass transition. *Journal of Physics and Chemistry of Solids*, 49(8):863–871, 1988. [10](#), [18](#), [20](#), [22](#)
- [115] M. D. Ediger, C. A. Angell, and Sidney R. Nagel. Supercooled liquids and glasses. *Journal of Physical Chemistry*, 100(31):13200–13212, 1996. [10](#), [22](#), [174](#)
- [116] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin. Relaxation in glassforming liquids and amorphous solids. *Journal of Applied Physics*, 88(6):3113–3157, 2000. [10](#), [166](#), [174](#)
- [117] Friedrich Kremer and Andreas Schönhals, editors. *Broadband Dielectric Spectroscopy*. Springer, New York, 2003. [10](#), [15](#), [16](#), [17](#), [20](#), [22](#), [49](#), [50](#), [51](#), [52](#), [55](#), [56](#), [57](#), [59](#), [60](#), [61](#), [62](#), [64](#), [65](#), [66](#), [69](#)
- [118] Z. Chen, C. A. Angell, and R. Richert. On the dynamics of liquids in their viscous regime approaching the glass transition. *The European Physical Journal E*, 35(7):65, 2012. [10](#)
- [119] G. G. Harvey. X-ray diffraction in liquid ethyl alcohol. *The Journal of Chemical Physics*, 7(10):878–880, 1939. [13](#)
- [120] Author W H Flygare, A D Buckingham, M R Battaglia, H A Posch, Physical Sciences, and Light Scattering. The structure of simple organic liquids. *Philosophical*

- Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 293(1402):277–285, 1979. [13](#)
- [121] M. Descamps, V. Legrand, Y. Guinet, A. Amazzal, C. Alba, and J. Dore. “Pre-Peak” in the Structure Factor of Simple Molecular Glass Formers. *Progress of Theoretical Physics Supplement*, 126(126):207–212, 1997. [13](#)
- [122] James P. Mithen and Richard P. Sear. State between Liquid and Crystal: Locally Crystalline but with the Structure Factor of a Liquid. *Crystal Growth & Design*, 16(6):3049–3053, 2016. [13](#)
- [123] Hajime Tanaka. Importance of many-body orientational correlations in the physical description of liquids. *Faraday Discussions*, 167:9, 2013. [15](#), [22](#)
- [124] Pascal Richet, Reinhard Conradt, Akira Takada, and Joël Dyon, editors. *Encyclopedia of Glass Science, Technology, History, and Culture*. John Wiley & Sons, Inc., Hoboken, New Jersey, 2021. [15](#), [16](#), [17](#), [18](#), [20](#), [22](#), [24](#), [33](#), [34](#)
- [125] F. Stickel, E. W. Fischer, and R. Richert. Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric relaxation data. *The Journal of Chemical Physics*, 102(15):6251–6257, 1995. [16](#), [22](#), [147](#), [149](#)
- [126] A. V. Granato. A derivation of the Vogel-Fulcher-Tammann relation for supercooled liquids. *Journal of Non-Crystalline Solids*, 357(2):334–338, 2011. [16](#), [17](#)
- [127] Masahiro Ikeda and Masaru Aniya. Understanding the Vogel-Fulcher-Tammann law in terms of the bond strength-coordination number fluctuation model. *Journal of Non-Crystalline Solids*, 371-372:53–57, 2013. [16](#), [17](#), [147](#)
- [128] Frank H. Stillinger. Relaxation and flow mechanisms in “fragile” glass-forming liquids. *The Journal of Chemical Physics*, 89(10):6461–6469, 1988. [16](#)
- [129] C.A. Angell. Relaxation in liquids, polymers and plastic crystals — strong/fragile patterns and problems. *Journal of Non-Crystalline Solids*, 131-133:13–31, 1991. [16](#), [174](#), [175](#)

- [130] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek. Nonexponential relaxations in strong and fragile glass formers. *The Journal of Chemical Physics*, 99(5):4201–4209, 1993. [16](#), [65](#)
- [131] Li-Min Wang, V. Velikov, and C. A. Angell. Direct determination of kinetic fragility indices of glassforming liquids by differential scanning calorimetry: Kinetic versus thermodynamic fragilities. *The Journal of Chemical Physics*, 117(22):10184–10192, 2002. [16](#), [174](#)
- [132] Wu Xu, Emanuel I Cooper, and C. Austen Angell. Ionic Liquids: Ion Mobilities, Glass Temperatures, and Fragilities. *The Journal of Physical Chemistry B*, 107(25):6170–6178, 2003. [16](#), [18](#)
- [133] Li-Min Wang and John C. Mauro. An upper limit to kinetic fragility in glass-forming liquids. *The Journal of Chemical Physics*, 134(4):044522, 2011. [16](#)
- [134] Qiuju Zheng, Yanfei Zhang, Maziar Montazerian, Ozgur Gulbiten, John C. Mauro, Edgar D. Zanutto, and Yuanzheng Yue. Understanding Glass through Differential Scanning Calorimetry. *Chemical Reviews*, 119(13):7848–7939, 2019. [16](#), [17](#), [80](#), [81](#), [174](#), [175](#)
- [135] L. S. Garca-Coln, L. F. del Castillo, and Patricia Goldstein. Theoretical basis for the Vogel-Fulcher-Tammann equation. *Physical Review B*, 40(10):7040–7044, 1989. [17](#)
- [136] R. R. Nigmatullin, S. I. Osokin, and G. Smith. New approach in the description of dielectric relaxation phenomenon: correct deduction and interpretation of the Vogel–Fulcher–Tamman equation. *Journal of Physics: Condensed Matter*, 15(20):3481–3503, 2003. [17](#)
- [137] Nouredine Metatla and Armand Soldera. The Vogel-Fulcher-Tamman Equation Investigated by Atomistic Simulation with Regard to the Adam-Gibbs Model. *Macromolecules*, 40:9680–9685, 2007. [17](#)
- [138] Masahiro Ikeda and Masaru Aniya. Bond strength-coordination number fluctuation model of viscosity: An alternative model for the Vogel-Fulcher-Tammann equation and

- an application to bulk metallic glass forming liquids. *Materials*, 3(12):5246–5262, 2010. [17](#), [147](#)
- [139] Wolfgang Götze. *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory*. Oxford University Press, Oxford, England, 2009. [17](#), [20](#), [166](#)
- [140] Peter G. Wolynes and Vassiliy Lubchenko, editors. *Structural Glasses and Supercooled Liquids*. John Wiley & Sons, Inc., Hoboken, NJ, USA, 2012. [17](#), [20](#), [46](#)
- [141] Misaki Ozawa, Giorgio Parisi, and Ludovic Berthier. Configurational entropy of polydisperse supercooled liquids. *The Journal of Chemical Physics*, 149(15):154501, 2018. [17](#)
- [142] Giulio Biroli, Chiara Cammarota, Gilles Tarjus, and Marco Tarzia. Random field Ising-like effective theory of the glass transition. II. Finite-dimensional models. *Physical Review B*, 98(17):174206, 2018. [17](#), [166](#)
- [143] Giulio Biroli, Chiara Cammarota, Gilles Tarjus, and Marco Tarzia. Random-field Ising-like effective theory of the glass transition. I. Mean-field models. *Physical Review B*, 98(17):174205, 2018. [17](#), [166](#)
- [144] Walter Kauzmann. The Nature of the Glassy State and the Behavior of Liquids at Low Temperatures. *Chemical Reviews*, 43(2):219–256, 1948. [17](#)
- [145] J Perez. Theories of liquid-glass transition. *Journal of Food Engineering*, 22(1-4):89–114, 1994. [18](#)
- [146] Marc Mézard and Giorgio Parisi. Statistical physics of structural glasses. *Journal of Physics: Condensed Matter*, 12(29):6655–6673, 2000. [18](#)
- [147] Hajime Tanaka. Possible resolution of the Kauzmann paradox in supercooled liquids. *Physical Review E*, 68(1):011505, 2003. [18](#)
- [148] V.I. Dimitrov. The liquid–glass transition – is it a fourth order phase transition? *Journal of Non-Crystalline Solids*, 351(30-32):2394–2402, 2005. [18](#)

- [149] V.I. Dimitrov. Theory of fluidity of liquids, glass transition, and melting. *Journal of Non-Crystalline Solids*, 352(3):216–231, 2006. [18](#)
- [150] Ryan Soklaski, Vy Tran, Zohar Nussinov, K. F. Kelton, and Li Yang. A locally preferred structure characterises all dynamical regimes of a supercooled liquid. *Philosophical Magazine*, 96(12):1212–1227, 2016. [18](#), [24](#), [45](#), [158](#)
- [151] C. Patrick Royall, Francesco Turci, and Thomas Speck. Dynamical phase transitions and their relation to structural and thermodynamic aspects of glass physics. *The Journal of Chemical Physics*, 153(9):090901, 2020. [18](#), [19](#), [174](#)
- [152] Austen Angell. Liquid landscape. *Nature*, 393(6685):521–523, 1998. [18](#)
- [153] David J. Wales, Mark A. Miller, and Tiffany R. Walsh. Archetypal energy landscapes. *Nature*, 394(6695):758–760, 1998. [18](#), [158](#)
- [154] David J. Wales and Jonathan P. K. Doye. Dynamics and thermodynamics of supercooled liquids and glasses from a model energy landscape. *Physical Review B*, 63(21):214204, 2001. [18](#)
- [155] Patrick Charbonneau, Jorge Kurchan, Giorgio Parisi, Pierfrancesco Urbani, and Francesco Zamponi. Fractal free energy landscapes in structural glasses. *Nature Communications*, 5(1):3725, 2014. [18](#)
- [156] Yue Fan, Takuya Iwashita, and Takeshi Egami. Energy landscape-driven non-equilibrium evolution of inherent structure in disordered material. *Nature Communications*, 8(1):15417, 2017. [18](#), [174](#)
- [157] Gerold Adam and Julian H. Gibbs. On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids. *The Journal of Chemical Physics*, 43(1):139–146, 1965. [18](#), [183](#)
- [158] E. Donth. The size of cooperatively rearranging regions at the glass transition. *Journal of Non-Crystalline Solids*, 53(3):325–330, 1982. [19](#), [179](#)

- [159] K. Grzybowska, A. Grzybowski, Z. Wojnarowska, J. Knapik, and M. Paluch. Ionic liquids and their bases: Striking differences in the dynamic heterogeneity near the glass transition. *Scientific Reports*, 5(1):16876, 2015. [19](#), [181](#)
- [160] Małgorzata Musiał, Shinian Cheng, Zaneta Wojnarowska, and Marian Paluch. Magnitude of Dynamically Correlated Molecules as an Indicator for a Dynamical Crossover in Ionic Liquids. *Journal of Physical Chemistry B*, 125(16):4141–4147, 2021. [19](#), [151](#), [181](#)
- [161] Misaki Ozawa, Camille Scalliet, Andrea Ninarello, and Ludovic Berthier. Does the Adam-Gibbs relation hold in simulated supercooled liquids? *The Journal of Chemical Physics*, 151(8):084504, 2019. [19](#)
- [162] S. Cheng, M. Musiał, Z. Wojnarowska, and M. Paluch. The relation between molecular dynamics and configurational entropy in room temperature ionic liquids: Test of Adam–Gibbs model. *The Journal of Chemical Physics*, 152(9):091101, 2020. [19](#), [183](#), [184](#)
- [163] S. Cheng, Z. Wojnarowska, M. Musiał, and M. Paluch. Correlation between configurational entropy, excess entropy, and ion dynamics in imidazolium-based ionic liquids: Test of the Adam–Gibbs model. *The Journal of Chemical Physics*, 154(4):044502, 2021. [19](#), [183](#), [184](#)
- [164] Mark D Ediger. Spatially Heterogeneous Dynamics in Supercooled Liquids. *Annual Review of Physical Chemistry*, 51(1):99–128, 2000. [19](#), [65](#), [166](#)
- [165] Yong-Lei Wang, Bin Li, Sten Sarman, Francesca Mocci, Zhong-Yuan Lu, Jiayin Yuan, Aatto Laaksonen, and Michael D. Fayer. Microstructural and Dynamical Heterogeneities in Ionic Liquids. *Chemical Reviews*, 120(13):5798–5877, 2020. [19](#), [35](#), [36](#)
- [166] Mauro Merolle, Juan P. Garrahan, and David Chandler. Space-time thermodynamics of the glass transition. *Proceedings of the National Academy of Sciences*, 102(31):10837–10840, 2005. [19](#)

- [167] Hajime Tanaka. Two-order-parameter model of the liquid-glass transition. II. Structural relaxation and dynamic heterogeneity. *Journal of Non-Crystalline Solids*, 351(43-45):3385–3395, 2005. [19](#), [20](#), [160](#)
- [168] Takeshi Kawasaki, Takeaki Araki, and Hajime Tanaka. Correlation between Dynamic Heterogeneity and Medium-Range Order in Two-Dimensional Glass-Forming Liquids. *Physical Review Letters*, 99(21):215701, 2007. [19](#)
- [169] C. Cammarota, A. Cavagna, I. Giardina, G. Gradenigo, T. S. Grigera, G. Parisi, and P. Verrocchio. Phase-Separation Perspective on Dynamic Heterogeneities in Glass-Forming Liquids. *Physical Review Letters*, 105(5):055703, 2010. [19](#)
- [170] Ludovic Berthier. Dynamic Heterogeneity in Amorphous Materials. *Physics*, 4(42), 2011. [19](#)
- [171] Takeshi Kawasaki and Hajime Tanaka. Structural signature of slow dynamics and dynamic heterogeneity in two-dimensional colloidal liquids: glassy structural order. *Journal of Physics: Condensed Matter*, 23(19):194121, 2011. [19](#)
- [172] K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, and M. Paluch. Effects of dynamic heterogeneity and density scaling of molecular dynamics on the relationship among thermodynamic coefficients at the glass transition. *The Journal of Chemical Physics*, 143(2):024502, 2015. [19](#)
- [173] Joan Manuel Montes de Oca, Sebastián R. Accordino, Gustavo A. Appignanesi, Philip H. Handle, and Francesco Sciortino. Size dependence of dynamic fluctuations in liquid and supercooled water. *The Journal of Chemical Physics*, 150(14):144505, 2019. [19](#)
- [174] Hyun Woo Cho, Mauro L. Mugnai, T. R. Kirkpatrick, and D. Thirumalai. Fragile-to-strong crossover, growing length scales, and dynamic heterogeneity in Wigner glasses. *Physical Review E*, 101(3):032605, 2020. [19](#)
- [175] Arthur K. Doolittle. Studies in Newtonian Flow. II. The Dependence of the Viscosity of Liquids on Free-Space. *Journal of Applied Physics*, 22(12):1471–1475, 1951. [19](#)

- [176] Morrel H. Cohen and G. S. Grest. Liquid-glass transition, a free-volume approach. *Physical Review B*, 20(3):1077–1098, 1979. [19](#)
- [177] M. Paluch, R. Casalini, and C. M. Roland. Cohen-Grest model for the dynamics of supercooled liquids. *Physical Review E*, 67(2):021508, 2003. [19](#), [166](#)
- [178] S. Strässler and C. Kittel. Degeneracy and the Order of the Phase Transformation in the Molecular-Field Approximation. *Physical Review*, 139(3A):A758–A760, 1965. [20](#), [25](#), [192](#)
- [179] Hajime Tanaka. Two-order-parameter description of liquids. I. a general model of glass transition covering its strong to fragile limit. *Journal of Chemical Physics*, 111(7):3163–3174, 1999. [20](#), [24](#), [45](#), [158](#)
- [180] Hajime Tanaka. Two-order-parameter description of liquids. II. Criteria for vitrification and predictions of our model. *Journal of Chemical Physics*, 111(7):3175–3182, 1999. [20](#), [24](#)
- [181] Hajime Tanaka. Two-order-parameter model of the liquid-glass transition. I. Relation between glass transition and crystallization. *Journal of Non-Crystalline Solids*, 351(43-45):3371–3384, 2005. [20](#), [22](#), [158](#)
- [182] Hajime Tanaka. Two-order-parameter model of the liquid-glass transition. III. Universal patterns of relaxations in glass-forming liquids. *Journal of Non-Crystalline Solids*, 351(43-45):3396–3413, 2005. [20](#), [22](#)
- [183] Wolfgang Götze and Lennart Sjögren. Relaxation processes in supercooled liquids. *Reports on Progress in Physics*, 55(3):241–376, 1992. [20](#), [153](#), [166](#)
- [184] Wolfgang Götze. Recent tests of the mode-coupling theory for glassy dynamics. *Journal of Physics: Condensed Matter*, 11(10A):A1–A45, 1999. [20](#), [153](#), [166](#)
- [185] Giorgio Parisi. Slow dynamics of glassy systems. In *Complex Behaviour of Glassy Systems*, pages 111–121. Springer Berlin Heidelberg, 2008. [20](#), [166](#), [174](#)

- [186] Abhishek Jaiswal, Stephanie O’Keeffe, Rebecca Mills, Andrey Podlesynak, Georg Ehlers, Wojciech Dmowski, Konstantin Lokshin, Joseph Stevick, Takeshi Egami, and Yang Zhang. Onset of Cooperative Dynamics in an Equilibrium Glass-Forming Metallic Liquid. *Journal of Physical Chemistry B*, 120(6):1142–1148, 2016. [21](#), [169](#)
- [187] Ranko Richert. Scaling vs. Vogel–Fulcher-type structural relaxation in deeply supercooled materials. *Physica A: Statistical Mechanics and its Applications*, 287(1-2):26–36, 2000. [21](#)
- [188] F. Mallamace, C. Corsaro, H. E. Stanley, and S. H. Chen. The role of the dynamic crossover temperature and the arrest in glass-forming fluids. *European Physical Journal E*, 34(9):94, 2011. [21](#), [151](#), [169](#)
- [189] Claudio Bonati, Massimo D’Elia, and Ettore Vicari. Universal scaling effects of a temperature gradient at first-order transitions. *Physical Review E*, 89(6):062132, 2014. [21](#)
- [190] Hajime Tanaka. A simple physical model of liquid - glass transition: intrinsic fluctuating interactions and random fields hidden in glass-forming liquids. *Journal of Physics: Condensed Matter*, 10(14):L207–L214, 1998. [22](#), [23](#), [24](#)
- [191] R. Richert and C. A. Angell. Dynamics of glass-forming liquids. V. On the link between molecular dynamics and configurational entropy. *The Journal of Chemical Physics*, 108(21):9016–9026, 1998. [22](#), [168](#), [169](#), [183](#), [184](#)
- [192] Julio Cesar Martinez-Garcia, Jorge Martinez-Garcia, Sylwester J. Rzoska, and Jürg Hulliger. The new insight into dynamic crossover in glass forming liquids from the apparent enthalpy analysis. *The Journal of Chemical Physics*, 137(6):064501, 2012. [22](#), [151](#), [154](#), [169](#)
- [193] Hajime Tanaka. Relation between Thermodynamics and Kinetics of Glass-Forming Liquids. *Physical Review Letters*, 90(5):4, 2003. [22](#), [174](#)
- [194] Rei Kurita and Hajime Tanaka. Control of the fragility of a glass-forming liquid using the liquid-liquid phase transition. *Physical Review Letters*, 95(6):1–4, 2005. [22](#)

- [195] Hajime Tanaka. Role of many-body correlation in slow dynamics of glass-forming liquids: intrinsic or perturbative. *Journal of Statistical Mechanics: Theory and Experiment*, 2020(3):034003, 2020. [22](#), [158](#)
- [196] Masahiro Ikeda and Masaru Aniya. Linking the glass-forming ability to the Arrhenius crossover of structural relaxation. *Journal of Non-Crystalline Solids*, 555(August 2020):120617, 2021. [22](#), [151](#), [169](#)
- [197] Peter H Poole, Francesco Sciortino, Ulrich Essmann, and H Eugene Stanley. Phase behaviour of metastable water. *Nature*, 360(6402):324–328, 1992. [23](#), [33](#)
- [198] Yoshinori Katayama, Yasuhiro Inamura, Takeshi Mizutani, Masaaki Yamakata, Wataru Utsumi, and Osamu Shimomura. Macroscopic separation of dense fluid phase and liquid phase of phosphorus. *Science*, 306(5697):848–851, 2004. [24](#)
- [199] Itai Cohen, Alice Ha, Xiaolin Zhao, Michelle Lee, Thomas Fischer, M. Jane Strouse, and Daniel Kivelson. A low-temperature amorphous phase in a fragile glass-forming substance. *Journal of Physical Chemistry*, 100(20):8518–8526, 1996. [24](#), [33](#), [169](#)
- [200] Rei Kurita and Hajime Tanaka. Phase-ordering kinetics of the liquid-liquid transition in single-component molecular liquids. *The Journal of Chemical Physics*, 126(20):204505, 2007. [24](#), [34](#)
- [201] Mika Kobayashi and Hajime Tanaka. The reversibility and first-order nature of liquid–liquid transition in a molecular liquid. *Nature Communications*, 7(1):13438, 2016. [24](#), [34](#)
- [202] Men Zhu and Lian Yu. Polyamorphism of D-mannitol. *The Journal of Chemical Physics*, 146(24):244503, 2017. [24](#), [31](#)
- [203] Yu D. Fomin, V. N. Ryzhov, and E. E. Tareyeva. Generalized van der Waals theory of liquid-liquid phase transitions. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 74(4):1–7, 2006. [24](#)

- [204] Mariano López de Haro, Álvaro Rodríguez-Rivas, Santos B. Yuste, and Andrés Santos. Structural properties of the Jagla fluid. *Physical Review E*, 98(1):012138, 2018. [24](#)
- [205] Paul F McMillan, Mark Wilson, Martin C Wilding, Dominik Daisenberger, Mohamed Mezouar, and G Neville Greaves. Polyamorphism and liquid–liquid phase transitions: challenges for experiment and theory. *Journal of Physics: Condensed Matter*, 19(41):415101, 2007. [24](#)
- [206] Hideki Tanaka. Fluctuation of local order and connectivity of water molecules in two phases of supercooled water. *Physical Review Letters*, 80(1):113–116, 1998. [24](#)
- [207] Hajime Tanaka. Simple physical explanation of the unusual thermodynamic behavior of liquid water. *Physical Review Letters*, 80(26):5750–5753, 1998. [24](#)
- [208] Hajime Tanaka. Two-order-parameter description of liquids: critical phenomena and phase separation of supercooled liquids. *Journal of Physics: Condensed Matter*, 11(15):L159–L168, 1999. [24](#), [45](#)
- [209] Rei Kurita and Hajime Tanaka. Critical-like phenomena associated with liquid-liquid transition in a molecular liquid. *Science*, 306(5697):845–848, 2004. [28](#), [31](#), [34](#), [169](#)
- [210] P.C. Hohenberg and A.P. Krekhov. An introduction to the Ginzburg–Landau theory of phase transitions and nonequilibrium patterns. *Physics Reports*, 572:1–42, 2015. [28](#)
- [211] Jingxiang Guo and Jeremy C. Palmer. Fluctuations near the liquid-liquid transition in a model of silica. *Physical Chemistry Chemical Physics*, 20(39):25195–25202, 2018. [28](#), [31](#)
- [212] Xun Liu, Shiyu Liu, Enyi Chen, Liang Peng, and Yao Yu. First-Order Liquid–Liquid Transition without Density Discontinuity in Molten Sodium Acetate Trihydrate and Its Influence on Crystallization. *The Journal of Physical Chemistry Letters*, 10(15):4285–4290, 2019. [31](#)
- [213] Rui Shi, John Russo, and Hajime Tanaka. Origin of the emergent fragile-to-strong transition in supercooled water. *Proceedings of the National Academy of Sciences of the United States of America*, 115(38):9444–9449, 2018. [31](#), [160](#), [161](#)

- [214] Nicholas J. Hestand and J. L. Skinner. Perspective: Crossing the Widom line in no man’s land: Experiments, simulations, and the location of the liquid-liquid critical point in supercooled water. *The Journal of Chemical Physics*, 149(14):140901, 2018. [31](#), [33](#), [160](#), [161](#)
- [215] V V Brazhkin and A G Lyapin. High-pressure phase transformations in liquids and amorphous solids. *Journal of Physics: Condensed Matter*, 15(36):6059–6084, 2003. [31](#)
- [216] W. Dmowski, S. Gierlotka, Z. Wang, Y. Yokoyama, B. Palosz, and T. Egami. Pressure Induced Liquid-to-Liquid Transition in Zr-based Supercooled Melts and Pressure Quenched Glasses. *Scientific Reports*, 7(1):1–8, 2017. [31](#)
- [217] C.A. Angell, S. Borick, and M. Grabow. Glass transitions and first order liquid-metal-to-semiconductor transitions in 4-5-6 covalent systems. *Journal of Non-Crystalline Solids*, 205-207(2):463–471, 1996. [31](#)
- [218] Y. Kajihara, M. Inui, K. Matsuda, T. Nagao, and K. Ohara. Density fluctuations at the continuous liquid-liquid phase transition in chalcogen systems. *Physical Review B*, 86(21):214202, 2012. [31](#)
- [219] Pierre Lucas, Shuai Wei, and C. Austen Angell. Liquid-liquid phase transitions in glass-forming systems and their implications for memory technology. *International Journal of Applied Glass Science*, 11(2):236–244, 2020. [31](#), [158](#)
- [220] Hermann Weingärtner, M. Kleemeier, S. Wiegand, and W. Schröer. Coulombic and non-Coulombic contributions to the criticality of ionic fluids. An experimental approach. *Journal of Statistical Physics*, 78(1-2):169–196, 1995. [31](#), [44](#)
- [221] Monika Wagner, Olimpiu Stanga, and Wolfram Schröer. Critical viscosity near the liquid-liquid phase transition in the solution of the ionic liquid 1-methyl-3-hexylimidazolium tetrafluoroborate in 1-pentanol. *Physical Chemistry Chemical Physics*, 6(8):1750–1757, 2004. [31](#), [44](#)
- [222] Annamaria Butka, Vlad Romeo Vale, Dragos Saracsan, Cornelia Rybarsch, Volker C. Weiss, and Wolfram Schröer. Liquid-liquid phase transition in solutions of ionic liquids

- with halide anions: Criticality and corresponding states. *Pure and Applied Chemistry*, 80(7):1613–1630, 2008. [31](#), [44](#)
- [223] W. Schröer. A Short History of Phase Transitions in Ionic Fluids. *Contributions to Plasma Physics*, 52(1):78–88, 2012. [31](#)
- [224] Sander Woutersen, Bernd Ensing, Michiel Hilbers, Zuofeng Zhao, and C. Austen Angell. A liquid-liquid transition in supercooled aqueous solution related to the HDA-LDA transition. *Science*, 359(6380):1127–1131, 2018. [31](#), [44](#)
- [225] Marisa A.A. Rocha, Daniela Kerlé, Johannes Kiefer, Wolfram Schröer, and Bernd Rathke. Liquid–Liquid Phase Behavior of Solutions of 1,3-Diethylimidazolium Bis((trifluoromethyl)sulfonyl)amide in n-Alkyl Alcohols. *Journal of Chemical & Engineering Data*, 65(3):1345–1357, 2020. [31](#), [44](#)
- [226] Luca M. Ghiringhelli, Jan H. Los, Evert Jan Meijer, A. Fasolino, and Daan Frenkel. High-pressure diamondlike liquid carbon. *Physical Review B*, 69(10):100101, 2004. [32](#)
- [227] Kyung Hwan Kim, Katrin Amann-Winkel, Nicolas Giovambattista, Alexander Späh, Fivos Perakis, Harshad Pathak, Marjorie Ladd Parada, Cheolhee Yang, Daniel Mariedahl, Tobias Eklund, Thomas J. Lane, Seonju You, Sangmin Jeong, Matthew Weston, Jae Hyuk Lee, Intae Eom, Minseok Kim, Jaeku Park, Sae Hwan Chun, Peter H. Poole, and Anders Nilsson. Experimental observation of the liquid-liquid transition in bulk supercooled water under pressure. *Science*, 370(6519):978–982, 2020. [33](#)
- [228] Hajime Tanaka. A new scenario of the apparent fragile-to-strong transition in tetrahedral liquids: water as an example. *Journal of Physics: Condensed Matter*, 15(45):L703–L711, 2003. [33](#)
- [229] Pradeep Kumar, S. V. Buldyrev, S. R. Becker, P. H. Poole, F. W. Starr, and H. E. Stanley. Relation between the Widom line and the breakdown of the Stokes-Einstein relation in supercooled water. *Proceedings of the National Academy of Sciences*, 104(23):9575–9579, 2007. [33](#)

- [230] Rui Shi and Hajime Tanaka. Direct Evidence in the Scattering Function for the Coexistence of Two Types of Local Structures in Liquid Water. *Journal of the American Chemical Society*, 142(6):2868–2875, 2020. [33](#)
- [231] Denis G. Golovanov, Konstantin A. Lyssenko, Mikhail Yu Antipin, Yakov S. Vygodskii, Elena I. Lozinskaya, and Alexander S. Shaplov. Long-awaited polymorphic modification of triphenyl phosphite. *CrystEngComm*, 7:465–468, 2005. [34](#)
- [232] Rei Kurita and Hajime Tanaka. Drastic enhancement of crystal nucleation in a molecular liquid by its liquid–liquid transition. *Proceedings of the National Academy of Sciences of the United States of America*, 116(50):24949–24955, 2019. [34](#), [169](#)
- [233] Hajime Tanaka. Roles of bond orientational ordering in glass transition and crystallization. *Journal of Physics Condensed Matter*, 23:284115, 2011. [34](#)
- [234] Ken-ichiro Murata and Hajime Tanaka. Link between molecular mobility and order parameter during liquid–liquid transition of a molecular liquid. *Proceedings of the National Academy of Sciences*, 116(15):7176–7185, 2019. [34](#)
- [235] Ken ichiro Murata and Hajime Tanaka. Link between molecular mobility and order parameter during liquid–liquid transition of a molecular liquid. *Proceedings of the National Academy of Sciences of the United States of America*, 116(15):7176–7185, 2019. [34](#), [169](#)
- [236] M. S. Beasley, B. J. Kasting, M. E. Tracy, A. Guiseppi-Elie, R. Richert, and M. D. Ediger. Physical vapor deposition of a polyamorphic system: Triphenyl phosphite. *Journal of Chemical Physics*, 153(12), 2020. [34](#), [35](#), [169](#)
- [237] Stephen F. Swallen, Kenneth L. Kearns, Marie K. Mapes, Yong Seol Kim, Robert J. McMahon, M D Ediger, Tian Wu, Lian Yu, and Sushil Satija. Organic glasses with exceptional thermodynamic and kinetic stability. *Science*, 315(5810):353–356, 2007. [34](#)
- [238] Simona Capponi, Simone Napolitano, and Michael Wübbenhorst. Supercooled liquids with enhanced orientational order. *Nature Communications*, 3(1):1233, 2012. [34](#)

- [239] Birte Riechers, A. Guiseppi-Elie, M. D. Ediger, and Ranko Richert. Ultrastable and polyamorphic states of vapor-deposited 2-methyltetrahydrofuran. *The Journal of Chemical Physics*, 150(21):214502, 2019. [34](#)
- [240] Werner Kunz and Katharina Häckl. The hype with ionic liquids as solvents. *Chemical Physics Letters*, 661:6–12, 2016. [35](#)
- [241] Rico E. Del Sesto, T. Mark McCleskey, Anthony K. Burrell, Gary A. Baker, Joe D. Thompson, Brian L. Scott, John S. Wilkes, and Peg Williams. Structure and magnetic behavior of transition metal based ionic liquids. *Chemical Communications*, 8(4):447–449, 2002. [35](#)
- [242] Masanari Okuno, Hiro O. Hamaguchi, and Satoshi Hayashi. Magnetic manipulation of materials in a magnetic ionic liquid. *Applied Physics Letters*, 89(13):1–3, 2006. [35](#)
- [243] Bert Mallick, Benjamin Balke, Claudia Felser, and Anja Verena Mudring. Dysprosium room-temperature ionic liquids with strong luminescence and response to magnetic fields. *Angewandte Chemie - International Edition*, 47(40):7635–7638, 2008. [35](#)
- [244] Aida Branco, Luís C. Branco, and Fernando Pina. Electrochromic and magnetic ionic liquids. *Chemical Communications*, 47(8):2300–2302, 2011. [35](#)
- [245] I. De Pedro, D. P. Rojas, Jesús A. Blanco, and J. Rodríguez Fernández. Antiferromagnetic ordering in magnetic ionic liquid Emim[FeCl₄]. *Journal of Magnetism and Magnetic Materials*, 323(10):1254–1257, 2011. [35](#)
- [246] Paul Brown, Craig P. Butts, Julian Eastoe, Eduardo Padrón Hernández, Fernando Luis De Araujo Machado, and Rodrigo J. de Oliveira. Dication magnetic ionic liquids with tuneable heteroanions. *Chemical Communications*, 49(27):2765, 2013. [35](#)
- [247] E. Santos, J. Albo, and A. Irabien. Magnetic ionic liquids: Synthesis, properties and applications. *RSC Advances*, 4(75):40008–40018, 2014. [35](#)
- [248] María J. Trujillo-Rodríguez, Omprakash Nacham, Kevin D. Clark, Verónica Pino, Jared L. Anderson, Juan H. Ayala, and Ana M. Afonso. Magnetic ionic liquids

- as non-conventional extraction solvents for the determination of polycyclic aromatic hydrocarbons. *Analytica Chimica Acta*, 934:106–113, 2016. [35](#)
- [249] Kaige Wu and Xinghai Shen. Designing a new type of magnetic ionic liquid: a strategy to improve the magnetic susceptibility. *New Journal of Chemistry*, 43(40):15857–15860, 2019. [35](#)
- [250] Khashayar Ghandi. A review of ionic liquids, their limits and applications. *Green and Sustainable Chemistry*, 04(01):44–53, 2014. [35](#)
- [251] Kai Richter, Paul S. Campbell, Tobias Baecker, Agnes Schimitzek, Damla Yaprak, and Anja Verena Mudring. Ionic liquids for the synthesis of metal nanoparticles. *Physica Status Solidi (B) Basic Research*, 250(6):1152–1164, 2013. [35](#)
- [252] Marjanul Manjum, Nobuyuki Serizawa, Adriana Ispas, Andreas Bund, and Yasushi Katayama. Electrochemical preparation of cobalt-samarium nanoparticles in an aprotic ionic liquid. *Journal of The Electrochemical Society*, 167(4):042505, 2020. [35](#)
- [253] Zhifei Yan, Dawei Meng, Xiuling Wu, Xiaolong Zhang, Weiping Liu, and Kaihua He. Two-dimensional ordering of ionic liquids confined by layered silicate plates via molecular dynamics simulation. *Journal of Physical Chemistry C*, 119(33):19244–19252, 2015. [36](#)
- [254] R. Capozza, A. Benassi, A. Vanossi, and E. Tosatti. Electrical charging effects on the sliding friction of a model nano-confined ionic liquid. *The Journal of Chemical Physics*, 143(14):144703, 2015. [36](#)
- [255] Chengjin Huang, Jianling Li, and Mu Li. Performance measurement and evaluation of an ionic liquid electrospray thruster. *Chinese Journal of Aeronautics*, 2021. [36](#)
- [256] Kanta Suzuki, Masayoshi Nagao, Yongxun Liu, Katsuhisa Murakami, Sommawan Khumpuang, Shiro Hara, and Yoshinori Takao. Fabrication of nano-capillary emitter arrays for ionic liquid electrospray thrusters. *Japanese Journal of Applied Physics*, 60:SCCF07, 2021. [36](#)

- [257] Jinrui Zhang, Guobiao Cai, Aamir Shahzad, Xuhui Liu, and Weizong Wang. Ionic liquid electrospray behavior in a hybrid emitter electrospray thruster. *International Journal of Heat and Mass Transfer*, 175:121369, 2021. [36](#)
- [258] Wei Sun, Zhiwen Wu, Zhenning Sun, Yuntao Guo, Tiankun Huang, Guorui Sun, Jingran Xue, and Ningfei Wang. Study on the control of propellant flow by electric field in ionic liquid electrospray thruster. *International Journal of Heat and Mass Transfer*, 183:121926, 2022. [36](#)
- [259] Weijie Zheng, Xuhui Liu, Jinrui Zhang, Yufeng Cheng, and Weizong Wang. Molecular dynamics simulation of ionic liquid electrospray: Microscopic presentation of the effects of mixed ionic liquids. *International Journal of Heat and Mass Transfer*, 182:121983, 2022. [36](#)
- [260] Christopher Hardacre, John D. Holbrey, Mark Nieuwenhuyzen, and Tristan G.A. Youngs. Structure and solvation in ionic liquids. *Accounts of Chemical Research*, 40(11):1146–1155, 2007. [36](#)
- [261] Olga Russina, Fabrizio Lo Celso, Natalia V. Plechkova, and Alessandro Triolo. Emerging evidences of mesoscopic-scale complexity in neat ionic liquids and their mixtures. *The Journal of Physical Chemistry Letters*, 8(6):1197–1204, 2017. [36](#)
- [262] Alessandro Triolo, Olga Russina, Hans Jurgen Bleif, and Emanuela Di Cola. Nanoscale segregation in room temperature ionic liquids. *Journal of Physical Chemistry B*, 111(18):4641–4644, 2007. [38](#)
- [263] Olga Russina, Alessandro Triolo, Lorenzo Gontrani, Ruggero Caminiti, Dong Xiao, Larry G. Hines, Richard A. Bartsch, Edward L. Quitevis, Natalia Plechkova, and Kenneth R. Seddon. Morphology and intermolecular dynamics of 1-alkyl-3-methylimidazolium bis{(trifluoromethane)sulfonyl}amide ionic liquids: Structural and dynamic evidence of nanoscale segregation. *Journal of Physics Condensed Matter*, 21:424121, 2009. [38](#)

- [264] Harsha V. R. Annapureddy, Hemant K. Kashyap, Pablo M. De Biase, and Claudio J. Margulis. What is the Origin of the Prepeak in the X-ray Scattering of Imidazolium-Based Room-Temperature Ionic Liquids? *The Journal of Physical Chemistry B*, 114(50):16838–16846, 2010. [38](#)
- [265] Christopher Hardacre, John D. Holbrey, Claire L. Mullan, Tristan G. A. Youngs, and Daniel T. Bowron. Small angle neutron scattering from 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids ($[C_n\text{mim}][\text{PF}_6]$, $n=4, 6$, and 8). *The Journal of Chemical Physics*, 133(7):074510, 2010. [38](#)
- [266] Fumiya Nemoto, Maiko Kofu, Michihiro Nagao, Kazuki Ohishi, Shin Ichi Takata, Jun Ichi Suzuki, Takeshi Yamada, Kaoru Shibata, Takeshi Ueki, Yuzo Kitazawa, Masayoshi Watanabe, and Osamu Yamamuro. Neutron scattering studies on short- and long-range layer structures and related dynamics in imidazolium-based ionic liquids. *Journal of Chemical Physics*, 149(5), 2018. [38](#), [44](#)
- [267] Cherry S. Santos, N. Sanjeeva Murthy, Gary A. Baker, and Edward W. Castner. Communication: X-ray scattering from ionic liquids with pyrrolidinium cations. *The Journal of Chemical Physics*, 134(12):121101, 2011. [38](#)
- [268] H. K. Kashyap and C. J. Margulis. (Keynote) Theoretical Deconstruction of the X-ray Structure Function Exposes Polarity Alternations in Room Temperature Ionic Liquids. *ECS Transactions*, 50(11):301–307, 2013. [38](#)
- [269] Alexander M. Smith, Kevin R.J. Lovelock, Nitya Nand Gosvami, Peter Licence, Andrew Dolan, Tom Welton, and Susan Perkin. Monolayer to bilayer structural transition in confined pyrrolidinium-based ionic liquids. *Journal of Physical Chemistry Letters*, 4(3):378–382, 2013. [38](#)
- [270] Wenkang Tu, Grzegorz Szklarz, Karolina Adrjanowicz, Katarzyna Grzybowska, Justyna Knapik-Kowalczyk, and Marian Paluch. Effect of Cation n -Alkyl Side-Chain Length, Temperature, and Pressure on the Glass-Transition Dynamics and Crystallization Tendency of the $[C_nC_1\text{Pyrr}]^+[\text{Tf}_2\text{N}]^-$ Ionic Liquid Family. *Journal of Physical Chemistry C*, 123(20):12623–12637, 2019. [38](#)

- [271] Olga Russina, Alessandro Triolo, Lorenzo Gontrani, and Ruggero Caminiti. Mesoscopic structural heterogeneities in room-temperature ionic liquids. *Journal of Physical Chemistry Letters*, 3(1):27–33, 2012. [38](#)
- [272] Olga Russina and Alessandro Triolo. New experimental evidence supporting the mesoscopic segregation model in room temperature ionic liquids. *Faraday Discuss.*, 154:97–109, 2012. [38](#)
- [273] Valerio Causin and Giacomo Saielli. Ionic liquid crystals. *Green Solvents II: Properties and Applications of Ionic Liquids*, pages 79–118, 2012. [38](#)
- [274] Henning Weiss, Julian Mars, Hailong Li, Gunnar Kircher, Oxana Ivanova, Artem Feoktystov, Olaf Soltwedel, Markus Bier, and Markus Mezger. Mesoscopic correlation functions in heterogeneous ionic liquids. *Journal of Physical Chemistry B*, 121(3):620–629, 2017. [38](#)
- [275] Utkarsh Kapoor and Jindal K. Shah. Globular, Sponge-like to Layer-like Morphological Transition in 1- n -Alkyl-3-methylimidazolium Octylsulfate Ionic Liquid Homologous Series. *The Journal of Physical Chemistry B*, 122(1):213–228, 2018. [38](#)
- [276] Fabrizio Lo Celso, Alessandro Triolo, Lorenzo Gontrani, and Olga Russina. Communication: Anion-specific response of mesoscopic organization in ionic liquids upon pressurization. *The Journal of Chemical Physics*, 148(21):211102, 2018. [38](#)
- [277] Karel Goossens, Kathleen Lava, Peter Nockemann, Kristof Van Hecke, Luc Van Meervelt, Phil Pattison, Koen Binnemans, and Thomas Cardinaels. Pyrrolidinium ionic liquid crystals with pendant mesogenic groups. *Langmuir*, 25(10):5881–5897, 2009. [38](#), [44](#)
- [278] Kathleen Lava, Koen Binnemans, and Thomas Cardinaels. Piperidinium, piperazinium and morpholinium ionic liquid crystals. *Journal of Physical Chemistry B*, 113(28):9506–9511, 2009. [38](#), [44](#)
- [279] Kirill V. Axenov and Sabine Laschat. Thermotropic Ionic Liquid Crystals. *Materials*, 4(1):206–259, 2011. [38](#), [44](#)

- [280] Yumeng Ji, Rui Shi, Yanting Wang, and Giacomo Saielli. Effect of the chain length on the structure of ionic liquids: From spatial heterogeneity to ionic liquid crystals. *Journal of Physical Chemistry B*, 117(4):1104–1109, 2013. [38](#), [44](#)
- [281] Mei Yang, Kathrin Stappert, and Anja Verena Mudring. Bis-cationic ionic liquid crystals. *Journal of Materials Chemistry C*, 2(3):458–473, 2014. [38](#), [44](#)
- [282] Kathrin Stappert, Derya Ünal, Bert Mallick, and Anja Verena Mudring. New triazolium based ionic liquid crystals. *Journal of Materials Chemistry C*, 2(37):7976–7986, 2014. [38](#), [44](#), [174](#)
- [283] Shen Li and Yanting Wang. Percolation Phase Transition from Ionic Liquids to Ionic Liquid Crystals. *Scientific Reports*, 9(1):1–8, 2019. [38](#), [44](#), [117](#)
- [284] Tanja Pott and Philippe Méléard. New insight into the nanostructure of ionic liquids: A small angle X-ray scattering (SAXS) study on liquid tri-alkyl-methyl-ammonium bis(trifluoromethanesulfonyl)amides and their mixtures. *Physical Chemistry Chemical Physics*, 11(26):5469–5475, 2009. [39](#)
- [285] Cherry S. Santos, Harsha V. R. Annapureddy, N. Sanjeeva Murthy, Hemant K. Kashyap, Edward W. Castner, and Claudio J. Margulis. Temperature-dependent structure of methyltributylammonium bis(trifluoromethylsulfonyl)amide: X ray scattering and simulations. *The Journal of Chemical Physics*, 134(6):064501, 2011. [39](#)
- [286] Jeevapani J. Hettige, Juan Carlos Araque, and Claudio J. Margulis. Bicontinuity and multiple length scale ordering in triphilic hydrogen-bonding ionic liquids. *Journal of Physical Chemistry B*, 118(44):12706–12716, 2014. [39](#)
- [287] Tyler Cosby, Zachariah Vicars, Maximilian F. Heres, Katsuhiko Tsunashima, and Joshua Sangoro. Dynamic and structural evidence of mesoscopic aggregation in phosphonium ionic liquids. *The Journal of Chemical Physics*, 148(19):193815, 2018. [39](#), [43](#), [69](#), [73](#), [133](#)

- [288] Hongjun Liu and Stephen J. Paddison. Direct calculation of the X-ray structure factor of ionic liquids. *Physical Chemistry Chemical Physics*, 18(16):11000–11007, 2016. [39](#)
- [289] J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich, and F. Kremer. Universal scaling of charge transport in glass-forming ionic liquids. *Physical Chemistry Chemical Physics*, 11(6):913–916, 2009. [42](#), [43](#), [149](#)
- [290] Joshua R. Sangoro and Friedrich Kremer. Charge transport and glassy dynamics in ionic liquids. *Accounts of Chemical Research*, 45(4):525–532, 2012. [42](#), [43](#)
- [291] F.G. Thomas. The interpretation of ionic conductivity in liquids. *Chemical Geology*, 35(1-2):179–180, 1982. [42](#)
- [292] Philip Griffin, Alexander L. Agapov, Alexander Kisliuk, Xiao-Guang Sun, Sheng Dai, Vladimir N. Novikov, and Alexei P. Sokolov. Decoupling charge transport from the structural dynamics in room temperature ionic liquids. *The Journal of Chemical Physics*, 135(11):114509, 2011. [42](#)
- [293] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, and F. Kremer. Charge transport and mass transport in imidazolium-based ionic liquids. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 77(5):4–7, 2008. [43](#), [147](#)
- [294] J. Sangoro, C. Iacob, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, A. Stoppa, J. Hunger, R. Buchner, and F. Kremer. Electrical conductivity and translational diffusion in the 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. *Journal of Chemical Physics*, 128(21), 2008. [43](#), [149](#)
- [295] J. R. Sangoro, C. Iacob, S. Naumov, R. Valiullin, H. Rexhausen, J. Hunger, R. Buchner, V. Strehmel, J. Kärger, and F. Kremer. Diffusion in ionic liquids: The interplay between molecular structure and dynamics. *Soft Matter*, 7(5):1678–1681, 2011. [43](#)
- [296] J. R. Sangoro, M. Mierzwa, C. Iacob, M. Paluch, and F. Kremer. Brownian dynamics determine universality of charge transport in ionic liquids. *RSC Advances*, 2(12):5047–5050, 2012. [43](#), [149](#)

- [297] Joshua R. Sangoro. Charge transport and dipolar relaxations in an alkali metal oligoether carboxylate ionic liquid. *Colloid and Polymer Science*, 292(8):1933–1938, 2014. [43](#)
- [298] Philip J. Griffin, Adam P. Holt, Katsuhiko Tsunashima, Joshua R. Sangoro, Friedrich Kremer, and Alexei P. Sokolov. Ion transport and structural dynamics in homologous ammonium and phosphonium-based room temperature ionic liquids. *Journal of Chemical Physics*, 142(8), 2015. [43](#), [147](#)
- [299] Tyler Cosby, Zachariah Vicars, Yangyang Wang, and Joshua Sangoro. Dynamic-Mechanical and Dielectric Evidence of Long-Lived Mesoscale Organization in Ionic Liquids. *Journal of Physical Chemistry Letters*, 8(15):3544–3548, 2017. [43](#), [69](#), [133](#)
- [300] Tyler Cosby, Zachariah Vicars, Emmanuel Urandu Mapesa, Katsuhiko Tsunashima, and Joshua Sangoro. Charge transport and dipolar relaxations in phosphonium-based ionic liquids. *Journal of Chemical Physics*, 147(23), 2017. [43](#), [147](#), [149](#)
- [301] S. Cheng, M. Musiał, Z. Wojnarowska, and M. Paluch. The relation between molecular dynamics and configurational entropy in room temperature ionic liquids: Test of Adam-Gibbs model. *Journal of Chemical Physics*, 152(9), 2020. [43](#)
- [302] Douglas R. MacFarlane, Maria Forsyth, Ekaterina I. Izgorodina, Andrew P. Abbott, Gary Annat, and Kevin Fraser. On the concept of ionicity in ionic liquids. *Physical Chemistry Chemical Physics*, 11(25):4962–4967, 2009. [43](#)
- [303] Tyler Cosby, Utkarsh Kapoor, Jindal K. Shah, and Joshua Sangoro. Mesoscale Organization and Dynamics in Binary Ionic Liquid Mixtures. *Journal of Physical Chemistry Letters*, 10(20):6274–6280, 2019. [43](#), [69](#), [133](#)
- [304] Florian Pabst, Zaneta Wojnarowska, Marian Paluch, and Thomas Blochowicz. On the temperature and pressure dependence of dielectric relaxation processes in ionic liquids. *Physical Chemistry Chemical Physics*, 23(26):14260–14275, 2021. [43](#), [149](#)

- [305] Katsuhiko Tsunashima and Masashi Sugiya. Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electrolytes. *Electrochemistry Communications*, 9(9):2353–2358, 2007. [44](#), [174](#)
- [306] Hongjun Liu, Edward Maginn, Ann E. Visser, Nicholas J. Bridges, and Elise B. Fox. Thermal and Transport Properties of Six Ionic Liquids: An Experimental and Molecular Dynamics Study. *Industrial & Engineering Chemistry Research*, 51(21):7242–7254, 2012. [44](#)
- [307] Joseph J. Fillion, Han Xia, M. Aruni Desilva, Mauricio Quiroz-Guzman, and Joan F. Brennecke. Phase transitions, decomposition temperatures, viscosities, and densities of phosphonium, ammonium, and imidazolium ionic liquids with aprotic heterocyclic anions. *Journal of Chemical and Engineering Data*, 61(8):2897–2914, 2016. [44](#)
- [308] Alessandro Triolo, Andrea Mandanici, Olga Russina, Virginia Rodriguez-Mora, Maria Cutroni, Christopher Hardacre, Mark Nieuwenhuyzen, Hans Jurgen Bleif, Lukas Keller, and Miguel Angel Ramos. Thermodynamics, structure, and dynamics in room temperature ionic liquids: The case of 1-Butyl-3-methyl imidazolium hexafluorophosphate ([bmim][PF₆]). *Journal of Physical Chemistry B*, 110(42):21357–21364, 2006. [44](#)
- [309] Hui Jin, Bernie O’Hare, Jing Dong, Sergei Arzhantsev, Gary A. Baker, James F. Wishart, Alan J. Benesi, and Mark Maroncelli. Physical properties of ionic liquids consisting of the 1-butyl-3-methylimidazolium cation with various anions and the bis(trifluoromethylsulfonyl)imide anion with various cations. *Journal of Physical Chemistry B*, 112(1):81–92, 2008. [44](#)
- [310] Ana I.M.C. Lobo Ferreira, Ana S.M.C. Rodrigues, Miguel Villas, Emília Tojo, Luís Paulo N. Rebelo, and Luís M.N.B.F. Santos. Crystallization and Glass-Forming Ability of Ionic Liquids: Novel Insights into Their Thermal Behavior. *ACS Sustainable Chemistry and Engineering*, 7(3):2989–2997, 2019. [44](#), [174](#)
- [311] Denis Prodius and Anja Verena Mudring. Rare earth metal-containing ionic liquids. *Coordination Chemistry Reviews*, 363:1–16, 2018. [44](#)

- [312] Hajime Tanaka. Simple view of waterlike anomalies of atomic liquids with directional bonding. *Physical Review B - Condensed Matter and Materials Physics*, 66(6):1–8, 2002. [45](#)
- [313] Hajime Tanaka. Roles of local icosahedral chemical ordering in glass and quasicrystal formation in metallic glass formers. *Journal of Physics: Condensed Matter*, 15(31):L491–L498, 2003. [45](#), [158](#)
- [314] Hiroshi Shintani and Hajime Tanaka. Frustration on the way to crystallization in glass. *Nature Physics*, 2(3):200–206, 2006. [45](#)
- [315] M. D. Ediger and Peter Harrowell. Perspective: Supercooled liquids and glasses. *The Journal of Chemical Physics*, 137(8):080901, 2012. [45](#), [158](#)
- [316] Mikhail Yu Ivanov, Sergey A. Prikhod'Ko, Nicolay Yu Adonin, Igor A. Kirilyuk, Sergey V. Adichtchev, Nikolay V. Surovtsev, Sergei A. Dzuba, and Matvey V. Fedin. Structural Anomalies in Ionic Liquids near the Glass Transition Revealed by Pulse EPR. *Journal of Physical Chemistry Letters*, 9(16):4607–4612, 2018. [45](#)
- [317] James Clerk Maxwell. *The Electrical Researches of the Honourable Henry Cavendish*. Cambridge University Press, Cambridge, England, 1879. [49](#)
- [318] John Ambrose Fleming. Electricity. In Hugh Chisholm, editor, *The Encyclopædia Britannica: A Dictionary of Arts , Sciences , Literature and General Information*, volume IX, pages 179–193. Cambridge University Press, Cambridge, England, 11th edition, 1911. [49](#)
- [319] Peter Debye. *Polar Molecules*. Lancaster Press, Inc., Lancaster, PA, 1929. [49](#)
- [320] P. Debye. Part I. Dielectric constant. Energy absorption in dielectrics with polar molecules. *Transactions of the Faraday Society*, 30:679, 1934. [49](#)
- [321] P Debye. Methods to determine the electrical and geometrical structure of molecules. In *Nobel Lectures, Chemistry 1922-1941*, pages 383–401. Elsevier Publishing Company, Amsterdam, The Netherlands, 1966. [49](#), [69](#), [70](#), [72](#)

- [322] P. Debye. Dielectric Properties of Pure Liquids. *Chemical Reviews*, 19(3):171–182, 1936. [49](#)
- [323] J. W. Williams. *Biographical Memoirs*. National Academies Press, Washington, D.C., 1975. [49](#), [69](#), [70](#), [71](#), [72](#)
- [324] David J Griffiths. *Introduction to Electrodynamics*. Pearson, Boston, MA, 4th edition, 2013. Re-published by Cambridge University Press in 2017. [49](#), [50](#)
- [325] Lars Onsager. Electric Moments of Molecules in Liquids. *Journal of the American Chemical Society*, 58(8):1486–1493, 1936. [61](#)
- [326] Lars Onsager. Initial recombination of ions. *Phys. Rev.*, 54:554–557, 1938. [61](#)
- [327] P Bordewijk. On the derivation of the Kirkwood-Fröhlich equation. *Physica*, 69(2):422–432, 1973. [61](#), [62](#)
- [328] P. Bordewijk. On the relationship between the Kirkwood correlation factor and the dielectric permittivity. *The Journal of Chemical Physics*, 73(1):595–597, 1980. [61](#), [62](#)
- [329] Wolfram Schröer. Generalization of the Kirkwood-Fröhlich theory of dielectric polarization for ionic fluids. *Journal of Molecular Liquids*, 92(1-2):67–76, 2001. [61](#), [62](#)
- [330] K. L. Ngai. Relation between some secondary relaxations and the α relaxations in glass-forming materials according to the coupling model. *The Journal of Chemical Physics*, 109(16):6982–6994, 1998. [65](#)
- [331] K. L. Ngai. An extended coupling model description of the evolution of dynamics with time in supercooled liquids and ionic conductors. *Journal of Physics: Condensed Matter*, 15(11):S1107–S1125, 2003. [65](#)
- [332] Md Kamrul Haque, Kiyoshi Kawai, and Toru Suzuki. Glass transition and enthalpy relaxation of amorphous lactose glass. *Carbohydrate Research*, 341(11):1884–1889, 2006. [65](#), [174](#)

- [333] M. Ikeda and M. Aniya. Correlation between fragility and cooperativity in bulk metallic glass-forming liquids. *Intermetallics*, 18(10):1796–1799, 2010. [65](#), [147](#)
- [334] Zeming Chen, Linran Zhao, Wenkang Tu, Zijing Li, Yanqin Gao, and Li-Min Wang. Dependence of calorimetric glass transition profiles on relaxation dynamics in non-polymeric glass formers. *Journal of Non-Crystalline Solids*, 433:20–27, 2016. [65](#), [174](#), [175](#)
- [335] Jeppe C. Dyre. The random free-energy barrier model for ac conduction in disordered solids. *Journal of Applied Physics*, 64(5):2456–2468, 1988. [67](#)
- [336] Thomas B. Schröder and Jeppe C. Dyre. Scaling and Universality of ac Conduction in Disordered Solids. *Physical Review Letters*, 84(2):310–313, 2000. [67](#)
- [337] A. Hunt. Frequency-dependent conductivity in glasses. *Journal of Physics: Condensed Matter*, 2(46):9055–9063, 1990. [67](#), [149](#)
- [338] Thomas B. Schröder and Jeppe C. Dyre. ac Hopping Conduction at Extreme Disorder Takes Place on the Percolating Cluster. *Physical Review Letters*, 101(2):025901, 2008. [67](#)
- [339] C. Schröder, M. Haberler, and O. Steinhauser. On the computation and contribution of conductivity in molecular ionic liquids. *Journal of Chemical Physics*, 128(13), 2008. [67](#)
- [340] Wilhelm Conrad Röntgen. On a New Kind of Rays. *Nature*, 53(1369):274–276, 1896. [69](#)
- [341] André Guinier and Gérard Fournet. *Small-Angle Scattering of X-Rays*. John Wiley & Sons, Inc., New York, 1955. [69](#), [70](#), [73](#), [75](#)
- [342] Paul Peter Ewald. Max von Laue, 1879-1960. *Biographical Memoirs of Fellows of the Royal Society*, 6:134–156, 1960. [69](#)

- [343] C. J. Humphreys. The significance of Bragg’s law in electron diffraction and microscopy, and Bragg’s second law. *Acta Crystallographica Section A Foundations of Crystallography*, 69(1):45–50, 2013. [70](#)
- [344] John Meurig Thomas. The birth of X-ray crystallography. *Nature*, 491(7423):186–187, 2012. [70](#)
- [345] E. S Watson and M. J O’Neill. Differential Microcalorimeter, U.S. Patent No. 3,263,484. United States Patent Office. 2 Aug. 1966. [80](#)
- [346] M. Teubner and R. Strey. Origin of the scattering peak in microemulsions. *The Journal of Chemical Physics*, 87(5):3195–3200, 1987. [98](#)
- [347] Henning Weiss, Julian Mars, Hailong Li, Gunnar Kircher, Oxana Ivanova, Artem Feoktystov, Olaf Soltwedel, Markus Bier, and Markus Mezger. Mesoscopic correlation functions in heterogeneous ionic liquids. *Journal of Physical Chemistry B*, 121(3):620–629, 2017. [98](#), [105](#)
- [348] Christopher J. Orendorff, Michael W. Ducey, and Jeanne E. Pemberton. Quantitative correlation of Raman spectral indicators in determining conformational order in alkyl chains. *Journal of Physical Chemistry A*, 106(30):6991–6998, 2002. [124](#), [126](#)
- [349] Kåre Larsson and R. P. Rand. Detection of changes in the environment of hydrocarbon chains by raman spectroscopy and its application to lipid-protein systems. *Biochimica et Biophysica Acta (BBA)/Lipids and Lipid Metabolism*, 326(2):245–255, 1973. [124](#)
- [350] Rolf W. Berg. Raman spectroscopy and ab-initio model calculations on ionic liquids. *Monatshefte fur Chemie*, 138(11):1045–1075, 2007. [124](#)
- [351] Tyler Cosby, Adam Holt, Philip J. Griffin, Yangyang Wang, and Joshua Sangoro. Proton Transport in Imidazoles: Unraveling the Role of Supramolecular Structure. *The Journal of Physical Chemistry Letters*, 6(19):3961–3965, 2015. [133](#)
- [352] Guodong Liu, Dongmei Zhao, and Yang Zuo. Modified Adam-Gibbs models based on free volume concept and their application in the enthalpy relaxation of glassy polystyrene. *Journal of Non-Crystalline Solids*, 417-418:52–59, 2015. [147](#)

- [353] J. Ross Macdonald. Universality, the Barton Nakajima Namikawa relation, and scaling for dispersive ionic materials. *Physical Review B - Condensed Matter and Materials Physics*, 71(18):1–12, 2005. [149](#)
- [354] Christos Tsonos, Athanasios Kanapitsas, Aristides Kechriniotis, and Nicholas Petropoulos. AC and DC conductivity correlation: The coefficient of Barton-Nakajima-Namikawa relation. *Journal of Non-Crystalline Solids*, 358(14):1638–1643, 2012. [149](#)
- [355] V. N. Novikov and A. P. Sokolov. Universality of the dynamic crossover in glass-forming liquids: A “magic” relaxation time. *Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics*, 67(3):6, 2003. [151](#), [153](#), [166](#), [168](#), [169](#)
- [356] Riccardo Casalini, Marian Paluch, and C. Michael Roland. Dynamic crossover in supercooled liquids induced by high pressure. *Journal of Chemical Physics*, 118(13):5701–5703, 2003. [151](#), [153](#), [168](#), [169](#)
- [357] Philip J. Griffin, Joshua R. Sangoro, Yangyang Wang, Adam P. Holt, Vladimir N. Novikov, Alexei P. Sokolov, Zaneta Wojnarowska, Marian Paluch, and Friedrich Kremer. Dynamic crossover and the Debye-Stokes-Einstein relation in liquid N,N-diethyl-3-methylbenzamide (DEET). *Soft Matter*, 9(43):10373–10380, 2013. [151](#), [169](#)
- [358] Martin Goldstein. Viscous Liquids and the Glass Transition: A Potential Energy Barrier Picture. *The Journal of Chemical Physics*, 51(9):3728–3739, 1969. [151](#)
- [359] E N C Phil. Supercooling of liquids. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 215(1120):43–46, 1952. [158](#)
- [360] R.Bruce King. The icosahedron in inorganic chemistry. *Inorganica Chimica Acta*, 198-200(C):841–861, 1992. [158](#)
- [361] Hajime Tanaka. Relationship among glass-forming ability, fragility, and short-range bond ordering of liquids. *Journal of Non-Crystalline Solids*, 351(8-9):678–690, 2005. [158](#)

- [362] John Russo and Hajime Tanaka. The microscopic pathway to crystallization in supercooled liquids. *Scientific Reports*, 2(1):505, 2012. [158](#)
- [363] N. A. Mauro, M. Blodgett, M. L. Johnson, A. J. Vogt, and K. F. Kelton. A structural signature of liquid fragility. *Nature Communications*, 5:1–7, 2014. [158](#)
- [364] T. Egami. How to characterize disorder. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 374:2–7, 2016. [158](#)
- [365] Jean Bellissard and Takeshi Egami. Simple theory of viscosity in liquids. *Physical Review E*, 98(6):063005, 2018. [158](#)
- [366] Rui Shi and Hajime Tanaka. Impact of local symmetry breaking on the physical properties of tetrahedral liquids. *Proceedings of the National Academy of Sciences of the United States of America*, 115(9):1980–1985, 2018. [160](#)
- [367] Lokendra P. Singh, Bruno Issenmann, and Frédéric Caupin. Pressure dependence of viscosity in supercooled water and a unified approach for thermodynamic and dynamic anomalies of water. *Proceedings of the National Academy of Sciences of the United States of America*, 114(17):4312–4317, 2017. [160](#)
- [368] D. L. Sidebottom, B. V. Rodenburg, and J. R. Changstrom. Connecting structure and dynamics in glass forming materials by photon correlation spectroscopy. *Physical Review B - Condensed Matter and Materials Physics*, 75(13):1–4, 2007. [166](#)
- [369] F. Caltagirone, U. Ferrari, L. Leuzzi, G. Parisi, F. Ricci-Tersenghi, and T. Rizzo. Critical Slowing Down Exponents of Mode Coupling Theory. *Physical Review Letters*, 108(8):085702, 2012. [166](#)
- [370] Navneet Singh, A. K. Sood, and Rajesh Ganapathy. Cooperatively rearranging regions change shape near the mode-coupling crossover for colloidal liquids on a sphere. *Nature Communications*, 11(1), 2020. [166](#)
- [371] A. Schönhal. Evidence for a universal crossover behaviour of the dynamic glass transition. *Europhysics Letters*, 56(6):815–821, 2001. [169](#)

- [372] E. Brezin, G. Parisi, and F. Ricci-Tersenghi. The Crossover Region Between Long-Range and Short-Range Interactions for the Critical Exponents. *Journal of Statistical Physics*, 157(4-5):855–868, 2014. [169](#)
- [373] Abhishek Jaiswal, Takeshi Egami, K. F. Kelton, Kenneth S. Schweizer, and Yang Zhang. Correlation between fragility and the Arrhenius crossover phenomenon in metallic, molecular, and network liquids. *Physical Review Letters*, 117(20):1–6, 2016. [169](#)
- [374] Ken Ichiro Murata and Hajime Tanaka. Surface-wetting effects on the liquid-liquid transition of a single-component molecular liquid. *Nature Communications*, 1(2):4–6, 2010. [169](#)
- [375] Ito Kaori, Moynihan CT, and CA Angell. Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water. *Nature*, 398:492–495, 1999. [174](#)
- [376] Mousa M.A. Imran, Deepika Bhandari, and N.S. Saxena. Enthalpy recovery during structural relaxation of $\text{Se}_{96}\text{In}_4$ chalcogenide glass. *Physica B: Condensed Matter*, 293(3-4):394–401, 2001. [174](#)
- [377] C. Austen Angell. Glass transition dynamics in water and other tetrahedral liquids: ‘Order-disorder’ transitions versus ‘normal’ glass transitions. *Journal of Physics Condensed Matter*, 19(20), 2007. [174](#)
- [378] Li-Min Wang and Ranko Richert. Glass Transitions in Viscous Monohydroxy Alcohols: Calorimetry Versus Dielectric Relaxation. *International Journal of Thermophysics*, 29(6):2055–2061, 2008. [174](#)
- [379] Emmerich Wilhelm and Trevor M Letcher, editors. *Heat Capacities*. The Royal Society of Chemistry, Cambridge, 2010. [174](#)
- [380] Matthew D. Green, Christian Schreiner, and Timothy E. Long. Thermal, rheological, and ion-transport properties of phosphonium-based ionic liquids. *Journal of Physical Chemistry A*, 115(47):13829–13835, 2011. [174](#)

- [381] M. Hilder, G. M.A. Girard, K. Whitbread, S. Zavorine, M. Moser, D. Nucciarone, M. Forsyth, D. R. MacFarlane, and P. C. Howlett. Physicochemical characterization of a new family of small alkyl phosphonium imide ionic liquids. *Electrochimica Acta*, 2016. [174](#)
- [382] Iolanda S. Klein and C. Austen Angell. Excess thermodynamic properties of glassforming liquids: The rational scaling of heat capacities, and the thermodynamic fragility dilemma resolved. *Journal of Non-Crystalline Solids*, 451:116–123, 2016. [174](#)
- [383] Emmerich Wilhelm and Trevor Letcher, editors. *Enthalpy and Internal Energy*. Royal Society of Chemistry, Cambridge, 2017. [174](#)
- [384] Tobias K. Bechgaard, John C. Mauro, Mathieu Bauchy, Yuanzheng Yue, Lisa A. Lamberson, Lars R. Jensen, and Morten M. Smedskjaer. Fragility and configurational heat capacity of calcium aluminosilicate glass-forming liquids. *Journal of Non-Crystalline Solids*, 461:24–34, 2017. [174](#), [175](#)
- [385] Li-Min Wang, Yongjun Tian, Riping Liu, and Ranko Richert. Calorimetric versus kinetic glass transitions in viscous monohydroxy alcohols. *The Journal of Chemical Physics*, 128(8):084503, 2008. [174](#)
- [386] Timur V. Tropin, Jörn W.P. Schmelzer, and Christoph Schick. On the dependence of the properties of glasses on cooling and heating rates: I. Entropy, entropy production, and glass transition temperature. *Journal of Non-Crystalline Solids*, 357(4):1291–1302, 2011. [174](#)
- [387] Trond S. Ingebrigtsen, Jeppe C. Dyre, Thomas B. Schrøder, and C. Patrick Royall. Crystallization Instability in Glass-Forming Mixtures. *Physical Review X*, 9(3):031016, 2019. [174](#)
- [388] Giorgio Parisi. On the replica approach to glasses. *ACS Symposium Series*, 676(1):110–121, 1997. [174](#)
- [389] Peter H Poole, Tor Grande, C Austen Angell, and Paul F. McMillan. Polymorphic Phase Transitions in Liquids and Glasses. *Science*, 275(5298):322–323, 1997. [174](#)

- [390] Yael S. Elmatad, Robert L. Jack, David Chandler, and Juan P. Garrahan. Finite-temperature critical point of a glass transition. *Proceedings of the National Academy of Sciences*, 107(29):12793–12798, 2010. [174](#)
- [391] G.P Johari and J.G Shim. Enthalpy recovery on thermal cycling within the non-equilibrium state of a glass. *Journal of Non-Crystalline Solids*, 261(1-3):52–66, 2000. [175](#)
- [392] Ernst-Joachim Donth. *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials*. Springer Berlin Heidelberg, Berlin, Heidelberg, 2001. [179](#)
- [393] Ludovic Berthier, Misaki Ozawa, and Camille Scalliet. Configurational entropy of glass-forming liquids. *Journal of Chemical Physics*, 150(16), 2019. [183](#)

List of Publications

1. Harris, M. A., Kinsey, T., Wagle, D. V., Baker, G. A., and Sangoro, J. Evidence of a Liquid-liquid Transition in a Glass-forming Ionic Liquid. *Proceedings of the National Academy of Sciences*, 2021, 118 (11), e2020878118
2. Mapesa, E. U., Cantillo, N. M., Hamilton, S. T., Harris, M. A., Zawodzinski, T. A., Park, A. A., and Sangoro, J. Localized and Collective Dynamics in Liquid-like Polyethylenimine-Based Nanoparticle Organic Hybrid Materials. *Macromolecules*, 2021, 54 (5), 2296-2305
3. Mapesa, E., Chen, M., Heres, M., Harris, M. A., Wang, Y., Long, T., Lokitz, B., and Sangoro, J. R. Charge Transport in Imidazolium-Based Homo- and Tri-block Poly(Ionic Liquid)s. *Macromolecules*, 2019, 52 (2), 620-628.
4. Harris, M. A., Heres, M., Coote, J., Wenda, A., Strehmel, V., Stein, G. E., and Sangoro, J. R. Ion Transport and Interfacial Dynamics in Disordered Block Copolymers of Ammonium-based Polymerized Ionic Liquids. *Macromolecules*, 2018, 51(9), 3477–3486.
5. Secor, J., Harris, M. A., Zhao, L., Deng, H., Raoux, S., Krusin-Elbaum, L. Phonon renormalization and Raman spectral evolution through amorphous to crystalline transitions in Sb₂Te₃ thin films. *Applied Physics Letters*, 2014, 104(221908), 1-4.

List of Conference Proceedings

1. APS March Meeting 2021, 15th-19th March 2021, Virtual. Two Liquids in One: Liquid-liquid Transition in Ionic Liquids.
2. ACS National Meeting 2020, 22nd-26th March 2020, Philadelphia, PA, USA (Virtual). Using Dielectric Spectroscopy to Probe Mesoscale Dynamics in Binary Mixtures of Pyrrolidinium-based Ionic Liquids.
3. APS March Meeting 2019, 4th-8th March 2019, Boston, MA, USA. Charge Transport and Electrode Polarization in Phosphonium Ionic Liquids Bearing Sulfonate and Carboxylate Anions.
4. GRC Ionic Liquids, 12th-17th August 2018, Newry, ME, USA. Ion Transport and Interfacial Dynamics in Disordered Block Copolymers of Ammonium-Based Polymerized Ionic Liquids.
5. APS March Meeting 2017, 13th-17th March 2017, New Orleans, LA, USA. Charge Transport and Ion Dynamics in Copolymers Containing Ammonium-based Polymerized Ionic Liquids.
6. APS March Meeting 2016, 14th-18th March 2016, Baltimore, MD, USA. Charge Transport and Ion Dynamics in Copolymers Containing Ammonium-based Polymerized Ionic Liquids.

Vita

Matthew Albert Harris was born in New York City and grew up in Queens, NY and the Catskill Mountains. From a young age, he was curious about science and how things worked. Eager to explore the world beyond the confines of a public education in a small town in upstate New York, Matthew left high school at the age of 16 to begin college at Bard College at Simon's Rock, where he received his first associate's degree, an A.A. in liberal arts, in 2007. He subsequently attended SUNY Delhi, a small technical college in his hometown, earning two associate's degrees simultaneously, an A.S. in chemistry and an A.A.S. in applied welding technology, in 2010. He spent the following year working at an art foundry learning the process of lost-wax casting. Matthew returned to academic pursuits in 2011, enrolling at the City College of New York to study chemical engineering. He graduated from CCNY magna cum laude with a bachelor's of engineering degree in chemical engineering, with minors in mathematics and physics, in 2015. Matthew spent the summer of 2015 as a researcher at KTH in Stockholm studying corrosion mechanisms in aluminum alloys, before entering the University of Tennessee, Knoxville to pursue a Ph.D. in the Department of Chemical and Biomolecular Engineering. He joined Dr. Joshua Sangoro's lab that autumn to study fundamental questions in the physics of soft matter, focusing on ionic liquids and their polymeric derivatives. After completing his Ph.D., Matthew plans to pursue a career in industry with a keen interest in working in the fields of either glass technology or applications of ionic liquids.