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I am submitting herewith a thesis written by Hung-Chih Li entitled "A Generalized Quartic Equation of State: Simplification and Performance on Mixtures." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Hank D. Cochran, Major Professor

We have read this thesis and
recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor
and Dean of The Graduate School

A GENERALIZED QUARTIC EQUATION OF STATE : SIMPLIFICATION AND PERFORMANCE ON MIXTURES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Hung-Chih Li

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DEDICATION

This thesis is dedicated to my parents

謹以此論文獻給我的父母

Mr. Tshy-Lang Lee

李次郎先生

and

及

Mrs. Yu-Chih LeeWang

李王玉枝女士

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ABSTRACT

In previous work, a generalized quartic equation of state has been developed (Shah, 1992) and extended to polar fluids (Lin, 1994). The quartic equation of state is a perturbed hard sphere equation of state. Only four pure fluid properties, critical temperature, critical volume, acentric factor, and dipole moment, are needed. However, there are forty general regressed coefficients used in four parameters.

Simplification of the quartic equation of state was done by setting fifteen of those coefficients to zero and obtaining the remaining twenty-five coefficients from regression on the original data base of non-polar and polar fluids used by Shah and Lin. The results of simplification show that the quartic equation of state can achieve similar accuracy with fewer coefficients. The quartic equation of state was tested on thirty-five binary systems and five ternary systems to see the performance of the quartic equation of state on mixtures. Those mixtures contain different types of systems and most of them are high pressure VLE data. Constant temperature bubble point calculations were done, and the results are compared to those from the Peng-Robinson equation of state. The results show that the performance of the quartic equation of state on mixtures is generally comparable to often slightly worse than the Peng-Robinson equation of state.

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NOMENCLATURE

a	parameter of the quartic equation of state, MPa/dm^6
b	van der Waals volume, mol/dm^3
B_v	second virial coefficient, cm^3/mol
c	parameter of the quartic equation of state, MPa/dm^6
e	parameter of the quartic equation of state, mol/dm^3
H_{vap}	enthalpy of vaporization, J/mol
H_r	residual enthalpy, J/mol
k_{ij}	binary interaction parameter
k_0, k_1	quartic equation of state constants
N	number of data points
P	pressure, MPa
R	universal gas constant, $(MPa*dm^3)/(mol*K)$
T	temperature, K
V	molar volume, dm^3/mol
x, y	mole fraction
X_{ij}	quartic equation of state constants
Z	compressibility factor of a fluid
$\alpha(T_r)$	temperature dependence of parameter a
β	hard core volume, dm^3/mol
μ	dipole moment, debyes
ω	acentric factor
$\xi(T_r)$	temperature dependence of parameter c

Superscripts

calc	calculated value
exp	experimental value
*	reduced variable

Subscripts

c	value at the critical temperature or the critical point
g	gas, single phase region
hs	hard-sphere
l	liquid phase
v	vapor phase
r	reduced property or constant
s	saturated, two-phase region
sl	saturated liquid phase
sv	saturated vapor phase

CHAPTER 1

Introduction

1.1 An Equation of State

'Equation of state': an equation used to model the state of a substance. Since an equation of state can describe the state of a substance, it can be used to determine the thermodynamic properties of interest. One of the most important applications of an equation of state is the phase equilibrium calculation. Information of phase equilibrium is very important in chemical industries, especially in separation processes. For example, to design a distillation unit, one needs to know the equilibrium compositions of the vapor and liquid phases, and an equation of state can be used for that.

There are generally two approaches to deal with phase equilibrium calculations. One approach uses an equation of state to model the vapor phase and a liquid model to model the liquid phase. The other approach uses an equation of state for both vapor and liquid phases. To utilize the former approach, an arbitrary standard state needs to be picked for the liquid as a reference, and an activity coefficient model, liquid model, is also needed to describe the deviation from the ideal solution reference state. Many researchers prefer the latter approach to the former one because no arbitrary reference state is needed. However, an equation of state that can model situations far from ideal gas should be developed in order to describe the behavior of liquids well.

An equation of state with sound theoretical basis should not only help us

to describe and predict the state of a particular substance but also help us to understand the substance in detail. However, such an equation of state could be very complex. On the other hand, a purely empirical equation of state could be quite simple and still model the fluid very well within a certain range. It could be risky to use a purely empirical equation for prediction, and such an equation does not provide any information on details about the fluid either. To obtain an equation of state of practical use, a compromise is needed between these two extremes.

As more and more is known about the essence of substances microscopically, an equation of state with stronger theoretical basis yet retaining its simple form might be obtained based on knowledge of which contributions are small enough to be ignored or which contributions should be modeled by specific functional forms. Such an equation of state could model the fluid at its liquid phase more accurately. Therefore, it could be used for both vapor and liquid phases in phase equilibrium calculations, and the arbitrary reference state could be avoided. This is why equations of state are still interesting to researchers, and why a quartic equation of state was developed in previous work and tested on mixtures in this work.

1.2 Literature Review

Because of their usefulness, equations of state have received much attention. Cubic equations of state are the simplest equation of state of practical use. Most equations of state including cubic equations of state separate the contribution to the pressure into attractive and repulsive parts. Hard sphere equations of state provide a theoretically correct foundation for the repulsive part. In a perturbed hard sphere equation of state, the theoretically correct hard sphere

equation of state is combined with an attractive term to give the total equation of state. To make the equation of state able to describe the complicated behavior of real fluids more accurately, additional temperature-dependent parameters are introduced into the equation of state. In this section, all the features above and others will be reviewed.

To apply the equation of state to mixtures, mixing rules that combine the parameters of pure fluids to give the parameters for the mixtures are necessary. Mixing rules will also be reviewed briefly in this section.

1.2.1 Cubic Equations of State

In 1873, van der Waals proposed the first cubic equation of state (Rowlinson, 1988). Most the subsequent cubic equations of state followed the same principle as van der Waals' equation of state. The van der Waals equation of state can be written as follows:

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \tag{1.1}$$

where

P is the pressure of the substance,

T is the absolute temperature of the substance,

V is the molar volume of the substance,

R is the universal gas constant,

a is the parameter for the attractive contribution measuring the intermolecular attractive force, and

b is the parameter for the repulsive contribution measuring the excluded volume of the molecules, van der Waals volume.

The first term of the right hand side is the repulsive term, and the other is the attractive term. The parameters a and b should meet the following conditions at critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c,P_c} = 0 \tag{1.2}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c,P_c} = 0 \tag{1.3}$$

These two features are retained in most of the popular cubic equation of state developed subsequently.

Redlich and Kwong (1949), Soave (1972), and Peng and Robinson (1976) developed their equations of state which are among the most popular equations of state. Their equations of state have the following general form:

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{V^2 + ubV + wb^2} \tag{1.4}$$

For the Redlich-Kwong equation of state, $u = 1$, $w = 0$, and $a(T) = a / T^{0.5}$. Redlich and Kwong introduced the temperature dependence into the parameter a(T). The values of parameter a and b can be determined as those in van der Waals equation of state. The Redlich-Kwong equation of state was widely used in industry at that time.

For the Soave-Redlich-Kwong equation of state, $u = 1$, $w = 0$, and $a(T) = a_c \cdot \alpha(T,\omega)$. In the Soave-Redlich-Kwong equation of state, Soave actually introduced the dependence on the acentric factor, ω, into a(T). The Soave-Redlich-Kwong equation of state can successfully model the systems of

nonpolar mixtures.

For the Peng-Robinson equation of state, $u=2$, $w=-1$, and $a(T)=a_c \cdot \alpha(T,\omega)$. Peng and Robinson followed the same approach used by Soave to introduced the acentric factor, ω, into parameter a. The main difference between them is that Peng and Robinson used data range from boiling point to critical point to determined the coefficients of ω instead of data at $T_r = 0.7$. The Peng-Robinson equation of state might be the most widely used general equation of state to date.

Because of the success of those three cubic equations of state, many modification have been done on them trying to improve their performance. Won and Walker (1979) introduced a polar term into the Soave-Redlich-Kwong equation of state and Yesavage (1986) considered the effects of polarity and the hydrogen bond to extend the equation of state to polar fluids. Stryjek and Vera (1986) proposed an equation of state with modification of the temperature and acentric factor dependence of the parameter a in the Peng-Robinson equation of state.

Abbot (1979) showed that cubic equations of state predicted critical compressibility higher than the actual one in order to achieve better performance in high pressure molar volume along the critical isotherm. Two-parameter equations of state with similar form of $\alpha(T)$ will predict the same critical compressibility for all compounds, which is not the case. To give the substance-dependence of critical compressibility to the equation of state, Usdin and McAuliffe (1976) introduced the critical compressibility factor into the equation of state as the third parameter. Schmidt and Wenzel (1980) modified the van der Waals equation of state by introducing a third parameter to do the same thing. Martin (1979), Harmens and Knapp (1980), Heyen (1981), Patel and Teja (1982), Kubic (1982), and Freze et al. (1983) all used a third parameter in their equations

of state to make the critical compressibility factor depend on the substance and hence make the performance of the equation of state better, especially in the vicinity of the critical point. As a matter of fact, the Patel-Teja equation of state does predict the liquid molar volume more accurately than the Peng-Robinson equation of state.

Other than the three-parameter equations of state above, Adachi, Lu, and Sugie (1983), Guo, Kim, Lin, and Chao (1985), and Trebble, and Bishnoi (1987) proposed their four parameter equations of state. Adachi and Sugie (1986a) and Kumar and Starling (1982) also proposed a five parameter equation of state with all parameters functions of reduced temperature. It is not surprising that as we know more about the essence of the fluids, we might want to introduce more parameters into the equation of state to account for more factors.

Beside the number of the parameter, the temperature dependence of the parameter is another concern. In the Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson equations of state, only the parameter a is dependent on the reduced temperature (and on the acentric factor for the latter two). Yu, Adachi, and Lu (1986) proposed a three parameter equation of state with only one parameter as a function of temperature. Iwai, Margerum, and Lu (1988) extended the equation of state to polar fluids. The temperature dependence was introduced into the parameter b by Heyen (1981), Salerno et al. (1986), and Trebble and Bishnoi (1987). In 1986, Trebble and Bishnoi evaluated the performance of ten equations of state on 75 pure fluids. The results of the Heyen equation of state require that parameter b increases with increasing temperature in the Trebble-Bishnoi equation of state (1987) because the Heyen equation of state would predict negative heat capacity when temperature went above the critical temperature if b decreases as the temperature increases. Salim and Trebble (1991) completely removed this feature in Trebble-Bishnoi equation of

state because it still predicted negative heat capacity at certain range of temperature. Zudkevitch and Joffe (1970) used polynomial functions for the parameter a and b for better performance on vapor pressure and liquid density. Yarborough (1979), Panagiotopoulos and Kumar (1985), and Morris and Turek (1986) applied the same feature in their equations of state. Cisternas (1988) also applied Panagiotopoulos and Kumar's technique to the Usdin-McAuliffe equation of state.

In 1979, Martin proposed that the performance of a cubic equation of state could be improve by a simple volume translation. Peneloux (1982) showed that the volume translation would not affect the result of phase equilibria calculated by the equation of state. This idea was used by Mathias, Naheiri, and Oh (1989) to develop a density correction for Peng-Robinson equation of state.

1.2.2 Hard Sphere and Perturbed Hard Sphere Equation of State

Since the van der Waals equation of state, most equations of state consisted of two terms in the pressure expression, the repulsive and the attractive terms. Rowlinson and Swinton (1982) showed that the repulsive term in the van der Waals equation of state might not be so correct. With the advance in molecular simulation, it is possible to investigate the different contributions of the pressure term separately. Alder and Wainwright (1960) reported the result of molecular dynamic simulation of hard spheres at high pressure. Yao et al. (1982) used Monte Carlo simulation to study the dipolar interaction between particles. The results of simulation make it easier for researchers to propose or modify the equation of state for specific intermolecular interactions. Kanchanakpan (1984) also used statistical mechanics in developing her equation of state.

Carnahan and Starling (1969) proposed an expression for the

compressibility factor for a fluid of hard spheres. The Carnahan-Starling equation of state gave reasonably good agreement with the results from the molecular dynamic simulation and Monte Carlo simulation. However, The Carnahan-Starling equation of state did not agree with the result of molecular dynamic simulation by Alder et al. at high density. Hall (1972) proposed another hard sphere equation of state which gave better agreement with the simulation results from Alder et al. Erpenbeck and Wood (1984) investigated the results of molecular dynamic simulation and proposed an equation of state for hard sphere based on the investigation. Mask and Chao (1984) also proposed an equation based on the research of Yao et al. (1982).

No real particles will have exactly the same behavior as that of hard spheres because of the intermolecular interactions other than repulsive force and the shape of the molecules which are different from sphere. The perturbation theory is necessary to extend the hard sphere equation of state to practical usage.

Gibbons (1969) applied the scaled particle theory to convex bodies, which was shown latter by Gibbons (1970) could not be applied to particles with different shapes. Barker and Henderson (1967) used the part of the Lennard-Jones potential where the energy is positive as the reference potential in their perturbation theory which gave quite good prediction for liquid state. Masuoka et al (1984). applied Barker and Henderson's idea to polar fluids. Weeks, Chandler, and Anderson (1971) proposed another popular reference system which used the part of the potential where the particle separation is smaller than the minimum energy separation. Vera and Prausnitz (1972), Sandler (1985), Lee et al., and Abbott and Prausnitz (1987) also reported their research about the perturbation theory. Chung (1984) showed that a simple reference system could lead to the difficulty in the convergence of the perturbation terms when applied to complicated molecules such as polar fluids. Bryan and Prausnitz (1987)

introduced the temperature dependence into the coefficients of Carnahan-Starling equation to form a new reference system. The reference system was combined with a semiempirical perturbation term to give an equation of state which can be applied to polar fluids. Dohrn and Prausnitz (1990) showed that the effective hard sphere volume should be a function of the density and temperature in order to give an equation of state which can be applied over a wide range of density and temperature.

Boublik (1974), Boublik (1975), and Nezbeda, Pavlicek, and Labik (1979) proposed their hard core equations of state, which can be applied to hard convex bodies. Monson and Rigby (1978) showed that the equations of state by Boublik applied accurately to spherocylinders which had the length to diameter ratio less than 2. In Boublik's and Nezbeda's equations of state, a non-sphericity parameter, α, was used to account for shapes other than spherical. However, Nezbeda and Boublik showed that the convex bodies with the same α could not necessarily be modeled by the same equation of state.

Chien, Greenkorn, and Chao (1983) proposed a chain-of-rotators equation of state which was extended to polar fluids by Masuoka and Chao (1984). Lin, Kim, Guo, and Chao combined the simplified Chien and coworkers' and Carnahan-Starling equation of state to form a cubic chain-of-rotators equation of state (CCOR). The CCOR equation of state was extended to mixtures by Guo (1985) and Kim (1986). Trebble and Bishnoi (1986) showed that the CCOR equation of state could not model the behavior of ammonia at low reduced temperature well enough. Leet, Lin, and Chao replaced the acentric factor in the CCOR equation of state with the critical compressibility factor, and Ciric and Paunovic (1994) readjusted the parameters of the CCOR equation to improve its performance. Pults, Greenkorn, and Chao introduced the group contribution method into the chain-of rotators equation of state whose performance was

improved by Shariat, Dehghany and Moshfeghian (1993) by readjusting the parameters in the equation.

Alder, Young, and Mark (1972) studied the molecular dynamic simulation of square well fluid and proposed a power series of density to express the residual Helmholtz free energy. Chen and Kreglewski (1977) combined the attractive term in Alder et al.'s equation and Boublik's hard core equation to give the BACK equation of state. Lee and Chao (1988) modified the BACK equation to form an equation of state for polar fluids.

In 1975, Beret and Prausnitz proposed the perturbed hard chain theory (PHCT) which including the effect of the density on the rotational and vibrational motions of large molecules. Donohue and Prausnitz (1978) applied the PHCT to polar fluids and mixtures. The PHCT was extended by Gmehling, Lin, and Prausnitz (1979) by considering the dimerization of the components in the system.

Carnahan and Starling (1972) combined their hard sphere equation of state with the attractive term in the Redlich-Kwong equation of state to give the CSRK equation of state, which is a great improvement over the Redlich-Kwong equation of state. It was a popular approach to combine the Carnahan-Starling equation or some other hard core equations of state with a certain attractive term to give the total expression of the equation of state. Bienkowski and Chao (1973) used a truncated virial expansion as the attractive term and combined it with the Carnahan-Starling equation. Oellrich, Knapp, and Prausnitz (1978) combined the Carnahan-Starling equation and the van der Waals equation of state. Svejda and Kohler (1983) used the Boublik's hard core equation with the attractive term in the van der Waals equation of state. Anderson and Prausnitz (1980) and Dimitrekis and Prausnitz (1986) also investigated equations of state composed of a hard core equation and a simple attractive term.

It should be pointed out that all of these perturbed hard sphere equations of state, except the CCOR equation of state and its variants, have substantially more than three roots (often seven or more roots) because the hard sphere equations of state applied in them are usually high order equations. The presence of additional roots can lead to difficulties in choosing the correct root, particularly in automated calculations as are often used in process simulators and oil-field simulators.

1.2.3 Quartic Equation of State

Kubic (1986) proposed the first quartic equation of state for the chain like molecules. Kubic used a simple hard sphere equation based on the work of Beret and Prausnitz (1975) with an empirical attractive term. Latter, Kubic (1986) extended his four parameter quartic equation of state to mixtures by applying the van der Waals one fluid mixing rule on the parameter, a, in the attractive term and linear combination for other parameters. Soave (1990) also proposed a quartic equation of state for pure compounds.

1.2.4 Mixing Rules

To extend an equation of state to systems of mixtures, a set of mixing rules is necessary to combine the parameters of the pure fluids to give the parameters for the mixture. The mixing rules play an important role and have great effect on the performance of the equation of state on mixtures. The simplest and most commonly used mixing rules are: the linear combination and the van der Waals one fluid mixing rules. The van der Waals one fluid mixing rule is shown as follows:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{1.5}$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{1.6}$$

where

a_m is the attractive parameter for the mixture,

x_i is the mole fraction of the component i,

a_{ij} is the attractive parameter for component i interacting with compound j,

b_m is the excluded volume parameter for the mixture, and

b_{ij} is the excluded volume parameter for component i interacting with compound j.

To calculate the parameters a_{ij} and b_{ij} when $i \neq j$, combining rules are used. The most commonly used combining rules are as follows:

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{1.7}$$

$$b_{ij} = \frac{b_i + b_i}{2}\left(1 - m_{ij}\right) \tag{1.8}$$

where

k_{ij} is the binary interaction parameter, and

m_{ij} is the binary interaction parameter.

Since an equation of state usually has repulsive and attractive contributions in its pressure expression, it is natural to use different mixing rules for different contributions. Boublik (1970) and Mansoori et al. (1970) derived a mixing rule for hard sphere equations of state which is essentially the additivity of the hard sphere volume. The Boublik-Mansoori mixing rule is listed as

follows:

Let the hard sphere equation of state be: $Z = f(\xi)$

$$\xi = \sum_{i=1}^{m} \xi_i \tag{1.9}$$

$$\xi_i = \frac{1}{6}\pi\rho d_i^3 x_i \tag{1.10}$$

where

ρ is the number density,

d_i is the hard sphere diameter of the ith component, and

x_i is the mole fraction of the ith component.

For highly nonideal mixtures, van der Waals one fluid mixing rule is not enough. Adachi and Sugie (1986), Panagiotopoulos and Reid (1986a), Sandoval et al. (1989), and Schwartzentruber et al. (1989) introduced composition dependency into the binary interaction parameters to improve the accuracy of equation of state when applied to nonideal mixtures. However, such mixing rules are not based on rigorous statistical mechanics. Panagiotopoulos and Reid (1986b) proposed another mixing rule with density dependency to correct the problem.

Huron and Vidal (1979) proposed another approach to develop mixing rules. They related the mixing rules to the excess Gibbs free energy at infinite pressure from the NRTL liquid model (Renon and Prausnitz 1968). Huron and Vidal assumed that the excess volume at infinite pressure is zero and reached a linear mixing rule for parameter b. Sheng et al. (1992) showed that the assumption was not necessary if the Helmholtz free energy was used instead. Won (1983) used the excess Gibbs free energy at infinite pressure from NRTL with the Soave equation of state. Pandit and Singh (1987) and Tochigi, Kurihara,

and Kojima (1988a, 1988b) used the ASOG group contribution model (Derr and Deal 1969) to obtain the mixing rules that were applied to several equations of state. Gupte (1986) used the modified UNIFAC by Larsen et al. (1987) and NRTL to calculate the excess Gibbs energy at infinite pressure which was used to develop a new mixing rule. Wong and Sandler (1992) proposed a density independent mixing rule which is correct at the low and high density limits. They used the Helmholtz free energy at infinite pressure instead of Gibbs free energy. A local composition model for the van der Waals type equation of state was proposed by Whiting and Prausnitz in 1982. Sandler (1985), Lee Lombardo, and Sandler (1985), Lee, Sandler, and Patel (1986), and Lee and Sandler (1987) reported a series of research on the generalized van der Waals partition function and related it to equations of state.

1.3 Previous Work on the Generalized Quartic Equation of State

Shah (1992) proposed a four parameter perturbed hard sphere quartic equation of state, which was extended to polar fluids by Lin (1994). As pointed out by Rowlinson and Swinton (1982), the van der Waals equation of state is more correct in the attractive term than in the repulsive term. This could be verified by comparing the result of molecular simulation on hard spheres with that predicted by the repulsive term in van der Waals equation of state. As shown in the previous section, most popular cubic equations of state including the Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson equations have the same repulsive term as the van der Waals equation. Therefore, a conclusion could be reach that the success of those cubic equation of state is at least partly due to the error cancellation between the repulsive and the attractive terms.

The hard sphere and hard core equations such as the Carnahan-Starling

equation of state provided better models for the repulsive term. However, Shah (1992) showed most of the perturbed hard sphere equations of state based on several different hard sphere or hard core equations did not give a reasonably accurate prediction of hard sphere volume except for the Dohrn-Prausnitz, CS-vdW, CCOR, and Nezbeda-Aim (1984) equations. It is obviously because the attractive terms were distorted in order to be able work with the repulsive term from van der Waals equation of state.

By comparing with the molecular dynamics simulation result of Alder and Wainwright (1960), it could be shown that the Carnahan-Starling equation can give accurate prediction for the hard sphere compressibility factor up to moderate density. However, the performance is not as good at high density, and the Carnahan-Starling equation is so complex that is can not be used to form a simple equation of state. Therefore, Shah (1992) adopted a simple functional form for the repulsive term and fitted it with the simulation result of Alder and Wainwright (1960). The repulsive term proposed by Shah is given as follows:

$$P_{rep} = \frac{RT}{(V - k_0\beta)} + \frac{\beta\, k_1 RT}{(V - k_0\beta)^2} \qquad (1.11)$$

where

β is the hard sphere molar volume of the fluid, and

k_0 and k_1 are regressed constants.

$k_0 = 1.2864$

$k_1 = 2.8225$

The repulsive term gave a performance which is as good as that of the Carnahan-Starling equation at low and moderate density and better at high density. Most important of all, the repulsive term retained a simple form;

therefore, it could be used with a simple attractive term to give a quartic equation of state.

Shah (1992) applied a practical perturbation approach to develop the attractive term. Shah used real fluid data of argon to provide the actual compressibility factor, Z_{exp}, and the repulsive equation above to calculate the compressibility factor of the hard sphere, Z_{hs}. Equation (1.11) can be rearranged to give the hard sphere compressibility factor:

$$Z_{hs} = \frac{V}{(V - k_0\beta)} + \frac{k_1\beta V}{(V - k_0\beta)^2} \tag{1.12}$$

$$= \frac{1}{(1 - k_0\beta^*\rho^*)} + \frac{k_1\beta^*\rho^*}{(1 - k_0\beta^*\rho^*)^2} \tag{1.13}$$

where

V is the molar volume of argon,

$\rho^* = \frac{\rho}{\rho_c}$ is the reduced density of argon,

ρ_c is the critical density of argon, and

$\beta^* = \beta\rho_c$ is the reduced hard sphere volume of argon.

And the compressibility factor for the attractive part, Z_{att}, could be calculated from:

$$Z_{att} = Z_{exp} - Z_{hs} \tag{1.14}$$

Testing by nonlinear regression was used to choose the functional form of the attractive term and then to obtain the numerical values of the parameters which could give the best fit to the data. The functional form of the attractive

term so obtained is as follows:

$$Z_{att} = -\frac{aV^2 + k_0\beta\, cV}{(V+d)(V+e)(V-k_0\beta)RT} \tag{1.15}$$

where

a and c are temperature and substance dependent parameters, and

d and e are substance dependent parameters, and d is set to zero.

Combining Equation (1.12) and Equation (1.15), and rearranging, the total equation of state could be obtained as an expression of pressure, P:

$$P = \frac{RT}{(V-k_0\beta)} + \frac{\beta\, k_1 RT}{(V-k_0\beta)^2} - \frac{aV + k_0\beta\, c}{V(V+e)(V-k_0\beta)} \tag{1.16}$$

This can be rearranged into a quartic polynomial for volume:

$$V^4 + q_3V^3 + q_2V^2 + q_1V + q_0 = 0 \tag{1.17}$$

where

$$q_3 = \left(-2k_0\beta + e - \frac{RT}{P}\right) \tag{1.18}$$

$$q_2 = \left\{\frac{RT}{P}\left[\beta\,(k_0 - k_1) - e\right] + k_0\beta\,(k_0\beta - 2e)\right\} + \frac{a}{P} \tag{1.19}$$

$$q_1 = e\left[k_0^2\beta^2 + \frac{RT}{P}\beta\,(k_0 - k_1)\right] + \left[\frac{k_0\beta\,(c-a)}{P}\right] \tag{1.20}$$

$$q_0 = -\frac{ck_0^2\beta^2}{P} \tag{1.21}$$

The parameter β is the hard sphere volume of the fluid. Its value at

critical temperature was selected to be $0.165V_c$, where V_c is critical volume of the pure fluid. Temperature dependence was incorporated in β. Shah (1992) used the same form of temperature dependence used by Nezbeda and Aim (1984). The difference is Shah used critical temperature as the reference for the reduced temperature instead of triple point temperature. The complete expression of β is given as follows:

$$\beta = \beta_c \left\{ \exp\left[-0.03125 \ln(T_r) - 0.0054 \left[\ln(T_r) \right]^2 \right] \right\}^3 \tag{1.22}$$

where

$\beta_c = 0.165V_c$ is the hard sphere volume at the critical temperature.

The temperature dependence of parameter a and c is given as follows:

$$a = a_c \alpha(T_r) \tag{1.23}$$

when $T_r \leq 1$

$$\alpha(T_r) = \left[1 + X_2\left(1 - \sqrt{T_r}\right) + X_3\left(1 - \sqrt{T_r}\right)^2 + X_4\left(1 - \sqrt{T_r}\right)^3 \right]^2 \tag{1.24}$$

when $T_r > 1$

$$\alpha(T_r) = \left[1 + X_2\left(1 - \sqrt{T_r}\right) + X_5\left(1 - \sqrt{T_r}\right)^2 + X_6\left(1 - \sqrt{T_r}\right)^3 \right]^2 \tag{1.25}$$

where

a_c is the value of parameter a at the critical temperature of the fluid, and X_2, X_3, X_4, X_5, and X_6 are constants to be determined by regression.

$$c = c_c \xi(T_r) \tag{1.26}$$

$$\xi(T_r) = \left[1 + X_7\left(1 - \sqrt{T_r}\right) \right]^2 \tag{1.27}$$

where

c_c is the value of parameter c at critical temperature of the fluid, and

X_7 is a constant to be determined by regression.

Note that the functional form of the parameter a was chosen such that it is continuous at the critical temperature.

Pitzer's acentric factor ω was introduced into the parameters a_c, c_c, e, and Xs to account for the substance dependence. The expressions for the substance dependence are listed as follows:

$$a_c = \frac{a_r RT_c}{\rho_c} \tag{1.28}$$

$$a_r = a_{r0}\left(1 + a_{r1}\omega + a_{r2}\omega^2\right) \tag{1.29}$$

$$c_c = \frac{c_r RT_c}{\rho_c} \tag{1.30}$$

$$c_r = c_{r0}\left(1 + c_{r1}\omega + c_{r2}\omega^2\right) \tag{1.31}$$

$$e = \frac{e_r}{\rho_c} \tag{1.32}$$

$$e_r = e_{r0}\left(1 + e_{r1}\omega + e_{r2}\omega^2\right) \tag{1.33}$$

$$X_i = X_{i1} + X_{i2}\omega \qquad \text{for i = 2, 3, 4, 5, 6, and 7, and} \tag{1.34}$$

$$\beta_r = \beta_c \rho_c \tag{1.35}$$

where

a_{rj}, c_{rj}, e_{rj}, and X_{ik} for j = 0,1,2 and k = 1,2 are the actual coefficients obtained from regression.

Lin (1994) extended the generalized quartic equation of state for nonpolar fluids to polar fluids by introducing the dipole moment into the regressed

coefficients. The term used to account for the dipole moment is the reduced dipole moment which is defined as follows:

$$\mu^* = \frac{0.3976\mu}{\left(RT_c V_c\right)^{0.5}} \tag{1.36}$$

where

μ is the dipole moment of the polar fluid in debye units.

The revised functions of the constants for regression are listed as follows:

$$a_r = a_{r0}\left(1 + a_{r1}\omega + a_{r2}\omega^2 + a_{r3}\mu^* + a_{r4}\mu^{*2}\right) \tag{1.37}$$

$$c_r = c_{r0}\left(1 + c_{r1}\omega + c_{r2}\omega^2 + c_{r3}\mu^* + c_{r4}\mu^{*2}\right) \tag{1.38}$$

$$X_i = X_{i1} + X_{i2}\omega + X_{i3}\mu^* + X_{i4}\mu^{*2} \text{ for } i = 2, 3, 4, 5, 6, \text{ and } 7. \tag{1.39}$$

Note that Equations (1.37)-(1-39) are physically incorrect, since the terms linear in dipole moment do not enter into any statistical mechanical expression. Replacing Equation (1.29), (1.31), and (1.34) with (1.37), (1.38), and (1.39) in the original equation of state will give the extended equation of state for polar and nonpolar fluids. For nonpolar fluids, the reduced dipole moment goes to zero, and the equation of state returns to its original form. The regressed coefficients for the generalized quartic equation of state are listed in Table 1.1.

The extended generalized quartic equation of state has superior performance over the Peng-Robinson equation of state in calculating many thermodynamic properties such as the vapor pressure, vapor or liquid density, residual enthalpy, and second virial coefficient of both non-polar and polar fluids, especially in the supercritical and compressed liquid region.

Table 1.1: The regressed coefficients for the original generalized quartic equation of state.

Regressed Coefficients		Regressed Coefficients	
a_{r0}	1.847131	X_{31}	-0.32379
a_{r1}	-0.05218	X_{32}	1.84591
a_{r2}	1.06446	X_{33}	0.39338
a_{r3}	-0.02730	X_{34}	-0.25483
a_{r4}	0.02048	X_{41}	0.14833
β_r	0.16500	X_{42}	-3.46693
c_{r0}	1.78336	X_{43}	-0.39170
c_{r1}	-1.29690	X_{44}	-0.01597
c_{r2}	2.78945	X_{51}	0.11048
c_{r3}	0.07000	X_{52}	0.57743
c_{r4}	0.01188	X_{53}	0.41218
e_{r0}	0.63189	X_{54}	-0.10676
e_{r1}	-0.81660	X_{61}	0.02581
e_{r2}	3.25246	X_{62}	-0.02700
k_0	1.28650	X_{63}	0.38327
k_1	2.82250	X_{64}	-0.09008
X_{21}	0.14988	X_{71}	-0.77357
X_{22}	0.97848	X_{72}	-1.45342
X_{23}	-0.01390	X_{73}	-0.04725
X_{24}	0.02928	X_{74}	-0.09669

1.4 Objectives of This Work

As shown in Table 1.1, there are forty regressed coefficients in the extended quartic equation of state. Although it matters little how many coefficients there are in an equation of state if the calculation is done by computer, an equation of state with too many coefficients could make it difficult for users to understand and manipulate it. To show that the quartic equation by Shah (1992) and Lin (1994) could still be accurate with fewer coefficients, the first objective of this work is to test the equation of equation of state with fewer adjustable coefficients during the regression and verify if the performance remain similarly good.

Phase equilibrium calculation is an important application of an equation of state. Most phase equilibria in the chemical industry contain systems of mixtures. Therefore, it is important to show that an equation of state could be applied to mixtures before it will be of any practical use. Lin et al. (1996) proposed that the van der Waals one fluid mixing rule could be used for the attractive term and the Boublik-Mansoori mixing rule could be used for the repulsive term. The second objective of this work is to test the performance of the generalized quartic equation of state on mixtures using the two mixing rules above.

CHAPTER 2

Approach

2.1 Methods of Calculation

To simplify the quartic equation of state, fifteen of the original forty coefficients were set to zero. As proposed by Cummings (1997), eight of the eliminated coefficients are the first order terms of the reduced dipole moment. The other seven coefficients were picked based on a statistical analysis which gave information about the effect of the removal of those coefficients on the ability of the functional expressions of the parameters to fully express the parameters. The remaining twenty five coefficients were determined by a computer program used in previous work (Shah, 1992 and Lin, 1994). This program utilized the Nelder-Mead simplex algorithm (Nelder, 1965 and Nash, 1987) and an adaptive nonlinear least-squares algorithm (Dennis, 1981) to minimize the following objective function:

$$OBJ_1 = \sum_{i=1}^{N_1}\left[\left(\frac{\Delta P_{s,i}}{P_{s,i}}\right)^2 + \left(\frac{\Delta \rho_{sv,i}}{\rho_{sv,i}}\right)^2 + \left(\frac{\Delta \rho_{sl,i}}{\rho_{sl,i}}\right)^2\right] + \sum_{j=1}^{N_2}\left(\frac{\Delta \rho_{g,j}}{\rho_{g,j}}\right)^2$$
$$+ \sum_{k=1}^{N_3}\left(\frac{\Delta H_{r,k}}{H_{r,k}}\right)^2 + \sum_{l=1}^{N_4}\left(\frac{\Delta H_{vap,l}}{H_{vap,l}}\right)^2 + \sum_{m=1}^{N_5}\left(\frac{\Delta B_{v,m}}{B_{v,m}}\right)^2 \qquad (2.1)$$

where

N_1 is the number of saturation data points in the two phase region,

N_2 is the number of gas density data points in the single phase region,

N_3 is the number of residual enthalpy data points,

N_4 is the number of enthalpy of vaporization data points in the two phase region,

N_5 is the number of second virial coefficient data points,

P_s is the saturated vapor pressure,

ρ_{sv} is the saturated vapor density,

ρ_{sl} is the saturated liquid density,

ρ_g is the gas density,

H_r is the residual enthalpy,

H_{vap} is the enthalpy of vaporization,

B_v is the second virial coefficient,

$\Delta P_s = \left(P_s^{calc} - P_s^{exp}\right)$ is the error in the saturated vapor pressure,

$\Delta \rho_{sv} = \left(\rho_{sv}^{calc} - \rho_{sv}^{exp}\right)$ is the error in the saturated vapor density,

$\Delta \rho_{sl} = \left(\rho_{sl}^{calc} - \rho_{sl}^{exp}\right)$ is the error in the saturated liquid density,

$\Delta \rho_g = \left(\rho_g^{calc} - \rho_g^{exp}\right)$ is the error in the gas density,

$\Delta H_r = \left(H_r^{calc} - H_r^{exp}\right)$ is the error in the residual enthalpy,

$\Delta H_{vap} = \left(H_{vap}^{calc} - H_{vap}^{exp}\right)$ is the error in the enthalpy of vaporization, and

$\Delta B_v = \left(B_v^{calc} - B_v^{exp}\right)$ is the error in the second virial coefficient.

In calculations with binary mixtures, only one binary interaction parameter, k_{ij}, was used in each of the three equations of state, Peng-Robinson, original quartic equation of state, and the simplified quartic equation of state. High pressure vapor-liquid phase equilibrium data were used in the regression for

the k_{ij}. The values of k_{ij} were obtained by using the same algorithms above to minimize the following objective function:

$$OBJ_2 = \sum_{n=1}^{N_6}\left[\left(\frac{P_n^{calc} - P_n^{exp}}{P_n^{exp}}\right)^2 + \left(y_n^{calc} - y_n^{exp}\right)^2\right] \tag{2.2}$$

where

N_6 is the number of vapor-liquid phase equilibrium data points,

P^{calc} is the calculated equilibrium pressure,

P^{exp} is the experimental equilibrium pressure,

y^{calc} is the calculated equilibrium vapor phase composition, and

y^{exp} is the experimental equilibrium vapor phase composition.

For the calculations of ternary systems, the respective binary interaction parameters were obtained by the approach above. These values of k_{ij} were then used in bubble-point calculation or dew-point calculation procedures to get the vapor phase or the liquid phase compositions which were compared to the experimental data. It was not necessary to do any regression in the ternary system calculations.

2.2 Studied Systems

Data on sixteen non-polar fluids and thirty polar fluids were used in the regression to obtain the new set of coefficients for the simplified quartic equation of state. Those systems and their critical properties, acentric factor, and dipole moments are listed in Table 2.1 and Table 2.2. The performance of the original and simplified quartic equation of state was tested on thirty-seven binary systems

Table 2.1: Pure non-polar compound physical properties of the fluids used in the regressions (Reid, Prausnitz, and Poling, 1987)

Compound	Critical Temperature (K)	Critical Volume (dm^3/mol)	Acentric Factor	Dipole Moment (debye)
Argon	150.8	0.0749	0.001	0
Krypton	209.4	0.0912	0.005	0
Xenon	289.7	0.1184	0.008	0
Methane	190.4	0.0992	0.011	0
Oxygen	154.6	0.0734	0.025	0
Nitrogen	126.2	0.0898	0.039	0
Ethane	305.4	0.1483	0.099	0
Propane	369.8	0.203	0.153	0
n-Butane	425.2	0.255	0.199	0
Carbon dioxide	304.1	0.0939	0.225	0
n-Pentane	469.7	0.304	0.251	0
n-Hexane	507.5	0.370	0.299	0
n-Octane	568.8	0.492	0.398	0
n-Nonane	594.6	0.548	0.445	0
n-Decane	617.7	0.603	0.489	0
n-Undecane	638.8	0.660	0.535	0

Table 2.2: Pure polar compound physical properties of the fluids used in the regressions (Reid, Prausnitz, and Poling, 1987)

Compound	Critical Temperature (K)	Critical Volume (dm^3/mol)	Acentric Factor	Dipole Moment (debye)
Acetone	508.2	0.209	0.3064	2.880
Carbon monoxide	132.92	0.0931	0.0663	0.112
Carbonyl sulfide	378.8	0.1351	0.1041	0.712
Methyl acetate	506.8	0.228	0.3253	1.679
Ethyl acetate	523.25	0.286	0.3611	1.780
n-Propyl acetate	549.4	0.345	0.3935	1.790
n-Butyl acetate	579.15	0.389	0.4101	1.840
Freon-11(CCl_3F)	471.2	0.248	0.1837	0.450
Freon-13($CClF_3$)	301.96	0.18028	0.18	0.510
Freon-21($CHFCl_2$)	451.58	0.196	0.2069	1.290
Freon-22($CHClF_2$)	369.3	0.166	0.2192	1.420
Freon-23(CHF_3)	298.89	0.1333	0.2672	1.649
Freon-114($C_2Cl_2F_4$)	418.85	0.29368	0.252	0.560
Methyl chloride	416.25	0.139	0.1529	1.870
Methyl fluoride	317.7	0.113	0.2037	1.851

Table 2.2: (cont'd)

Compound	Critical Temperature (K)	Critical Volume (dm^3/mol)	Acentric Factor	Dipole Moment (debye)
Ethyl chloride	460.35	0.200	0.1905	2.050
Chloroform	536.4	0.239	0.2129	1.010
Chlorobenzene	632.35	0.308	0.2505	1.690
Dimethyl ether	400.1	0.170	0.2036	1.300
Diethyl ether	466.7	0.280	0.2846	1.150
Methyl ethyl ether	437.8	0.221	0.2189	1.230
Hydrogen bromide	363.15	0.10026	0.0693	0.820
Hydrogen iodide	423.35	0.12194	0.0381	0.440
Water	647.13	0.05595	0.3449	1.850
Hydrogen sulfide	373.53	0.09849	0.0827	0.970
Methanol	512.58	0.11905	0.5656	1.700
Ammonia	405.65	0.07247	0.2520	1.470
Nitrous oxide	309.57	0.09737	0.1418	0.167
Sulfur dioxide	430.75	0.1220	0.2451	1.630
Acrylonitrile	535	0.212	0.3498	3.870

and four ternary systems against that of the Peng-Robinson equation of state. The studied binary and ternary systems were picked to covered different categories of systems, for example polar-polar, chain-chain, and simple-polar systems. Most of the binary systems are high pressure data because it was hoped that the quartic equation of state would have superior performance over the Peng-Robinson equation of state at high pressure range. Table 2.3 and Table 2.4 shows those binary and ternary systems of mixture used for the regression and calculation respectively.

Table 2.3: Binary systems used for testing the quartic equation of state.

System	System
Acetic acid – n-Octane	1,1-difloroethane – Ethylchloride
Methane – 1-Propanol	Carbon Dioxide – 1-Propanol
Methane – Ethanol	Carbon Dioxide – Ethane
Ethanol – n-Octane	Carbon Dioxide – Ethanol
Propane – Furfural	Nitrogen – n-Hexane
Propylene – Furfural	3-Methyl-2-Butanone – n-Octane
1-Propanol – n-Octane	Argon – Methane
n-Octane – Ethane	Benzene – 1-Propanol
n-Octane – Ethylene	Benzene – Cyclohexane
n-Octane – Carbon Dioxide	Cyclohexane – 1-Propanol
Acetophenone – Ethylene	Cyclohexane – 3-Methyl-2-Butanone
Methyl benzoate – Ethylene	Cyclohexane – n-Heptane
Methanol – Acetone	Cyclohexane – n-Octane
Methane – n-Octane	Nitrogen – Argon
Methane – n-Pentane	Nitrogen – Methane
Chlorodifloromethane – 2-Propanol	n-Hexane – n-Heptane
Chlorodifloromethane – Ethanol	n-Hexane – Cyclohexane
Chlorodifloromethane – n-Hexane	
Chlorodifloromethane – Chloroform	
Chlorodifloromethane – Cyclohexnae	

Table 2.4: Ternary systems used for testing the quartic equation of state.

System
n-Hexane – Cyclohexane – n-Heptane
Cyclohexane – 3-Methyl-2-Butanone – n-Octane
Nitrogen – Argon – Methane
Nitrogen – Carbon Dioxide – Ethane

CHAPTER 3

Results and Discussion

In the original generalized quartic equation of state, there are four parameters, a, and c (which are functions of temperature and depend on the fluid's critical temperature, acentric factor, and dipole moment), β (which is a function of temperature and depends on the fluid's critical temperature and critical volume), and e (which depends on the fluid's critical volume and acentric factor). These four parameters are expressed by polynomial functions of reduced temperature with forty universal coefficients. In this work, fifteen of the original forty coefficients of the generalized quartic equation of state were set to zero, and the other coefficients were obtained by nonlinear regression again. The regression was done on the same sixteen non-polar and thirty polar fluids used in previous work. The new set of coefficients is listed in Table 3.1.

In Table 3.2 and Table 3.3, the performance of both the original and the simplified quartic equations of state is reported on the sixteen non-polar and thirty polar fluids, respectively. Because of some alteration of the database, nonlinear regression was performed again to obtain the coefficients of the original quartic equation of state, and the so obtained coefficients were then used to calculate the various thermodynamic properties. Table 3.2 shows that the performance of the simplified equation on non-polar fluids is generally slightly worse than that of the original equation in most of the calculated properties of various compounds and slightly better in some of them. The overall average performance of the original quartic equation of state is slightly better then that of

Table 3.1: The regressed coefficients for the simplified generalized quartic equation of state.

Regressed Coefficients		Regressed Coefficients	
a_{r0}	1.825716	X_{31}	-0.237932
a_{r1}	0	X_{32}	1.022857
a_{r2}	0.896586	X_{33}	0
a_{r3}	0	X_{34}	0
a_{r4}	0	X_{41}	0.065036
β_r	0.165000	X_{42}	-2.067206
c_{r0}	1.854436	X_{43}	0
c_{r1}	0.596539	X_{44}	0
c_{r2}	-1.946911	X_{51}	0.114614
c_{r3}	0	X_{52}	0.678414
c_{r4}	0.022230	X_{53}	0
e_{r0}	0.622480	X_{54}	0.131914
e_{r1}	0	X_{61}	0.021573
e_{r2}	1.316413	X_{62}	0.029885
k_0	1.28650	X_{63}	0
k_1	2.82250	X_{64}	0.156664
X_{21}	0.143600	X_{71}	-0.853536
X_{22}	0.968548	X_{72}	-0.231363
X_{23}	0	X_{73}	0
X_{24}	0	X_{74}	0

Table 3.2: Comparison of various thermodynamic properties of pure non-polar fluids calculated by original and simplified quartic equations of state.

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Argon	P_s	0.14	0.29	29
	ρ_{sv}	1.89	2.19	29
	ρ_{sl}	4.10	4.83	29
	ρ_g	0.41	0.55	243
	B_{vir}	6.36	4.07	59
	H_r	5.79	8.32	125
Krypton	P_s	0.81	0.67	44
	ρ_{sv}	0.97	1.49	44
	ρ_{sl}	0.42	4.68	44
	ρ_g	1.53	1.58	161
Xenon	P_s	1.72	1.45	30
	ρ_{sv}	0.79	1.84	30
	ρ_{sl}	3.71	4.05	30
	ρ_g	1.47	0.89	120
	B_{vir}	4.50	8.17	71

Table 3.2 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Oxygen	P_s	1.39	0.85	49
	ρ_{sv}	1.28	2.45	49
	ρ_{sl}	6.04	7.12	49
	ρ_g	0.81	1.33	225
	B_{vir}	8.57	7.38	86
	H_r	22.05	21.24	96
Nitrogen	P_s	0.59	0.94	54
	ρ_{sv}	1.42	2.80	54
	ρ_{sl}	4.38	5.73	54
	ρ_g	0.64	1.02	330
	B_{vir}	7.93	5.63	59
	H_r	5.89	12.87	231
Methane	P_s	2.48	2.20	21
	ρ_{sv}	2.30	2.58	21
	ρ_{sl}	4.23	4.87	21
	ρ_g	0.73	0.74	260
	B_{vir}	7.99	6.95	63
	H_r	4.18	2.55	156

Table 3.2 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Ethane	P_s	1.36	0.88	18
	ρ_{sv}	2.34	4.82	18
	ρ_{sl}	3.49	8.34	18
	ρ_g	0.47	0.51	189
	B_{vir}	2.79	2.02	59
	H_r	2.30	1.50	98
Propane	P_s	1.39	1.34	22
	ρ_{sv}	1.34	3.29	22
	ρ_{sl}	3.44	4.42	22
	ρ_g	0.90	1.09	147
	B_{vir}	2.28	1.58	65
	H_r	2.71	2.46	98
n-Butane	P_s	1.60	0.72	25
	ρ_{sv}	1.41	2.96	25
	ρ_{sl}	3.85	4.96	25
	ρ_g	0.84	0.97	98
	B_{vir}	2.92	2.40	55
	H_r	3.06	2.54	98

Table 3.2 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Carbon Dioxide	P_s	1.82	3.24	15
	ρ_{sv}	5.23	7.63	15
	ρ_{sl}	1.95	2.22	15
	ρ_g	0.42	0.48	224
	B_{vir}	11.92	3.83	70
	H_r	3.39	2.73	192
n-Pentane	P_s	4.53	3.58	22
	ρ_{sv}	2.77	2.60	22
	ρ_{sl}	3.21	4.60	22
n-Hexane	P_s	1.53	1.78	25
	ρ_{sv}	1.36	1.76	25
	ρ_{sl}	2.68	2.66	25
n-Octane	P_s	1.22	1.86	25
	ρ_{sv}	2.49	1.26	25
	ρ_{sl}	5.25	4.82	25

Table 3.2 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
n-Nonane	P_s	2.13	3.00	26
	ρ_l	2.07	2.71	28
n-Decane	P_s	4.21	3.75	27
	ρ_l	8.68	7.29	45
n-Undecane	ρ_l	2.39	3.16	49
Overall average	P_s	1.67	1.61	456
	ρ_{sv}	1.72	2.61	403
	ρ_{sl}	4.04	4.78	403
	ρ_g	0.75	0.89	1997
	ρ_l	4.48	4.46	129
	B_{vir}	6.31	4.86	583
	H_r	5.70	6.53	1123

Table 3.3: Comparison of various thermodynamic properties of pure polar fluids calculated by original and simplified quartic equations of state.

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Acetone	P_s	6.76	10.83	22
	ρ_{sl}	2.24	1.54	22
	B_{vir}	4.54	2.28	26
	H_r	2.21	5.03	105
	H_v	2.51	2.43	32
Carbon Monoxide	P_s	3.16	9.29	27
	ρ_{sv}	7.08	13.81	27
	ρ_{sl}	2.70	7.75	27
	ρ_g	1.09	1.82	460
	B_{vir}	1.39	8.62	23
	H_r	6.89	6.96	105
	H_v	4.38	5.81	31
Carbonyl Sulfide	P_s	4.90	1.81	40
	ρ_{sl}	4.30	6.35	40
	B_{vir}	1.79	2.14	45
	H_v	1.60	3.79	43

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Methyl Acetate	P_s	2.95	3.43	48
	ρ_{sl}	3.00	2.56	48
	H_v	1.84	1.84	47
Ethyl Acetate	P_s	2.26	3.68	55
	ρ_{sl}	3.20	3.06	55
	B_{vir}	1.65	2.12	25
	H_v	0.74	0.85	26
n-Propyl Acetate	P_s	1.36	2.29	57
	ρ_{sl}	3.69	3.52	57
	B_{vir}	2.91	1.97	31
	H_v	0.71	0.99	47
n-Butyl Acetate	P_s	1.93	3.32	43
	ρ_{sl}	2.80	3.76	43
	B_{vir}	2.30	2.04	35
	H_v	0.90	0.84	54

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Freon-11 (CCl_3F)	P_s	0.90	1.75	50
	ρ_{sv}	2.11	5.56	50
	ρ_{sl}	3.10	4.70	50
	ρ_l	1.69	3.79	40
	H_r	3.64	3.89	84
	H_v	1.77	3.61	47
Freon-13 ($CClF_3$)	P_s	3.03	5.86	24
	ρ_{sv}	6.10	10.14	24
	ρ_{sl}	3.12	5.10	24
	ρ_g	31.42	33.04	36
	H_r	4.52	9.12	84
	H_v	4.88	5.10	27
Freon-21 ($CHFCl_2$)	P_s	2.44	0.95	41
	ρ_{sv}	2.58	5.59	41
	ρ_{sl}	2.75	4.82	41
	ρ_g	2.15	2.66	36
	ρ_l	2.74	4.48	54
	H_r	2.67	2.98	60
	H_v	2.86	4.04	38

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Freon-22 ($CHClF_2$)	P_s	1.22	0.55	33
	ρ_{sv}	3.19	5.80	33
	ρ_{sl}	1.71	3.11	33
	ρ_g	0.59	0.38	81
	H_r	2.56	2.98	60
	H_v	2.65	2.91	33
Freon-23 (CHF_3)	P_s	0.43	1.55	30
	ρ_{sv}	4.47	3.14	30
	ρ_{sl}	0.66	1.37	30
	ρ_g	0.91	0.70	90
	B_{vir}	3.95	3.54	51
	H_r	6.74	7.14	75
	H_v	3.61	4.09	27
Freon-114 ($C_2Cl_2F_4$)	P_s	2.67	3.24	33
	ρ_{sv}	4.75	6.05	33
	ρ_{sl}	2.95	3.03	33
	ρ_g	0.84	0.54	75
	ρ_l	2.30	3.79	25
	H_r	6.47	5.68	45
	H_v	1.92	2.54	30

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Methyl Chloride	ρ_g	0.93	0.63	80
	B_{vir}	2.49	2.33	25
	H_v	2.97	3.07	37
Methyl Fluoride	P_s	2.64	5.40	34
	ρ_{sl}	3.09	1.80	34
	B_{vir}	1.93	1.98	51
	H_v	3.31	1.81	24
Ethyl Chloride	P_s	2.04	2.82	51
	ρ_{sl}	3.58	2.69	51
	H_v	2.10	2.27	48
Chloroform	P_s	5.27	6.74	28
	ρ_{sl}	2.37	0.70	28
	H_v	0.46	2.01	53
Chloro-benzene	P_s	3.38	1.79	57
	ρ_{sl}	3.08	2.77	57
	B_{vir}	1.10	1.10	47
	H_r	5.03	5.02	75
	H_v	2.00	2.83	51

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Dimethyl Ether	P_s	0.95	1.54	35
	ρ_{sl}	2.31	4.79	35
	H_v	2.97	3.06	40
Diethyl Ether	P_s	3.84	2.88	22
	ρ_{sl}	3.36	3.24	22
	H_r	10.72	11.13	30
	H_v	1.31	2.01	39
Methyl Ethyl Ether	P_s	2.68	0.71	24
	ρ_{sl}	2.66	3.30	24
	H_v	2.48	2.87	11
Hydrogen Bromide	P_s	1.42	4.63	23
	ρ_{sl}	2.91	6.48	23
	H_v	3.53	4.66	28
Hydrogen Iodide	P_s	0.58	2.83	25
	ρ_{sl}	2.99	4.93	25
	H_v	2.75	3.80	33

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Water	P_s	3.85	9.44	35
	ρ_{sv}	4.43	6.82	35
	ρ_{sl}	5.54	5.36	35
	ρ_g	1.13	2.23	100
	B_{vir}	3.43	3.19	25
	H_v	4.39	6.05	31
Hydrogen Sulfide	P_s	1.00	2.61	24
	ρ_{sl}	2.27	3.92	24
	ρ_g	1.32	1.55	48
	H_r	2.29	1.54	45
	H_v	2.60	3.72	32
Methanol	P_s	5.28	9.52	21
	ρ_{sv}	5.95	4.53	21
	ρ_{sl}	7.81	9.63	21
	ρ_g	2.65	293	100
	H_v	2.74	5.07	20

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Ammonia	P_s	5.66	7.00	40
	ρ_{sv}	5.06	4.56	40
	ρ_{sl}	0.89	0.80	40
	ρ_g	0.99	1.23	286
	H_v	4.32	4.96	33
Nitrous Oxide	P_s	0.90	3.29	16
	ρ_{sl}	2.13	4.47	16
	ρ_g	2.58	1.05	108
	B_{vir}	2..45	2.91	42
	H_v	3.82	5.77	22
Sulfur Dioxide	P_s	5.02	4.85	17
	ρ_{sl}	1.19	2.83	17
	ρ_g	1.31	1.02	140
	B_{vir}	3.55	4.61	70
	H_r	2.68	3.01	7
	H_v	3.85	3.82	19
Acrylonitrile	B_{vir}	3.44	3.99	33

Table 3.3 (cont'd)

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Overall average	P_s	2.69	3.75	956
	ρ_{sv}	4.27	6.41	334
	ρ_{sl}	2.99	3.72	956
	ρ_g	1.93	2.14	1640
	ρ_l	2.29	4.10	119
	B_{vir}	2.40	2.76	467
	H_r	4.85	5.52	830
	H_v	2.41	3.11	1003

the simplified equation of state. Table 3.3 shows the same comparison for polar fluids. The comparison shows that the generalized quartic equation of state can achieve similar accuracy with fewer regressed coefficients. Therefore, the conclusion can be reached that the generalized quartic equation of state could be applied with fewer coefficients with only small loss of accuracy.

The extension of the quartic equation of state to mixtures is done by applying the Boublik-Mansoori mixing rule for parameter β and the van der Waals one fluid mixing rule for parameters a, c, and e. In this work, the calculation has been done on thirty-seven binary systems and four ternary systems with the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state. The results are reported in Table 3.4 and Table 3.5 for the binary and ternary mixtures, respectively. Table 3.4 shows that the performance of the simplified equation of state on binary systems is generally slightly worse than that of the original quartic equation, as on pure fluids. The performance of both the original and simplified quartic equations of state is not superior to that of the Peng-Robinson equation of state as had been hoped. It is generally slightly worse than that of the Peng-Robinson equation of state on most of the tested systems and a little worse in some of them. As mentioned previously, the performance of the quartic equation of state on pure fluids is superior to that of the Peng-Robinson equation of state. It is surprising to find that the advantage is not retained upon extension to mixtures. One possible reason might be that the quartic equation of state is more complicated than the Peng-Robinson equation of state, and it would be more difficult to combine the pure fluid parameters with only one binary interaction parameter, k_{ij}. Another reason might be that the quartic equation of state has superior performance when applied to calculations of thermodynamic properties other than the pressure and volumetric properties of pure fluids, and its performance is

Table 3.4: Comparison of vapor-liquid equilibrium calculation results of binary mixtures from the Peng-Robinson, the original, and the simplified quartic equations of state.

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Acetic acid	P (AAPD)	4.74	4.81	4.58	
|	y (AAD)	0.0386	0.0393	0.0788	39
n-Octane	k_{ij}	-0.0006024	-0.012801	0.045839	
Methane	P (AAPD)	12.20	12.49	7.94	
|	y (AAD)	0.0034	0.0024	0.0037	10
1-Propanol	k_{ij}	-0.0005536	-0.030001	0.029234	
Methane	P (AAPD)	10.82	11.62	5.89	
|	y (AAD)	0.0049	0.0034	0.0038	10
Ethanol	k_{ij}	0.008463	-0.025846	0.038795	
Ethanol	P (AAPD)	10.15	10.18	14.66	
|	y (AAD)	0.0574	0.0628	0.0606	23
n-Octane	k_{ij}	0.10295	0.083637	0.071723	
Propane	P (AAPD)	3.44	3.46	2.40	
|	y (AAD)	0.0011	0.0012	0.0023	26
Furfural	k_{ij}	0.02805	0.028933	0.069329	
Propylene	P (AAPD)	2.75	2.70	1.16	
|	y (AAD)	0.0007	0.0009	0.0016	32
Furfural	k_{ij}	0.0057552	0.009391	0.041262	

Table 3.4 (cont'd)

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
1-Propanol	P (AAPD)	5.20	5.23	8.98	
|	y (AAD)	0.0473	0.0541	0.0482	25
n-Octane	k_{ij}	0.10099	0.086432	0.071485	
n-Octane	P (AAPD)	1.88	2.23	1.88	
|	y (AAD)	0.0032	0.0038	0.0020	16
Ethane	k_{ij}	-0.011482	-0.0042953	0.012289	
n-Octane	P (AAPD)	2.10	2.40	1.43	
|	y (AAD)	0.0022	0.0030	0.0008	19
Ethylene	k_{ij}	-0.012685	-0.0056934	0.015308	
n-Octane	P (AAPD)	2.70	2.25	4.04	
|	y (AAD)	0.0013	0.0018	0.0009	18
Carbon Dioxide	k_{ij}	.09008	0.094748	0.12308	
Aceto-phenone	P (AAPD)	8.20	7.07	3.12	
|	y (AAD)	0.0030	0.0028	0.0024	19
Ethylene	k_{ij}	-0.025661	-0.017262	0.02374	
Methyl-benzoate	P (AAPD)	6.79	10.39	5.41	
|	y (AAD)	0.0046	0.0016	0.0010	16
Ethylene	k_{ij}	-0.02997	-0.010536	0.0189336	

Table 3.4 (cont'd)

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Methanol	P (AAPD)	3.78	6.35	1.57	
|	y (AAD)	0.0141	0.0233	0.0082	12
Acetone	k_{ij}	0.003475	-0.028299	-0.0041056	
Methane	P (AAPD)	3.99	4.34	2.18	
|	y (AAD)	0.0064	0.0044	0.0043	31
n-Decane	k_{ij}	0.10683	0.11598	0.0534398	
Methane	P (AAPD)	10.54	8.82	5.65	
|	y (AAD)	0.0018	0.0034	0.0030	9
n-Pentane	k_{ij}	-0.0010501	-0.008217	0.0331086	
Chloro-difluoro-methane	P (AAPD)	2.96	3.48	1.87	
|	y (AAD)	0.0134	0.0150	0.0095	22
2-Propanol	k_{ij}	0.018293	0.0061353	0.012425	
Chloro-difluoro-methane	P (AAPD)	3.82	4.67	3.42	
|	y (AAD)	0.0084	0.0091	0.0068	34
Ethanol	k_{ij}	0.030011	0.011006	0.018317	
Chloro-difluoro-methane	P (AAPD)	1.90	1.71	1.76	
|	y (AAD)	0.0062	0.0079	0.0057	28
n-Hexane	k_{ij}	0.052034	0.053734	0.069616	

Table 3.4 (cont'd)

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Chloro-difluoro-methane	P (AAPD)	2.10	1.75	1.68	
|	y (AAD)	0.0244	0.0221	0.0291	23
Chloroform	k_{ij}	0.010552	0.013884	0.0102916	
Chloro-difluoro-methane	P (AAPD)	2.71	2.38	2.48	
|	y (AAD)	0.0085	0.0108	0.0066	27
Cyclohexane	k_{ij}	0.050659	0.05285	0.0675441	
1,1-Difluoroethane	P (AAPD)	10.60	11.61	7.72	
|	y (AAD)	0.1546	0.1568	0.0999	29
Ethylchloride	k_{ij}	0.10752	0.10515	0.16184	
Carbon Dioxide	P (AAPD)	10.46	11.22	5.91	
|	y (AAD)	0.0022	0.0022	0.0028	15
1-Propanol	k_{ij}	0.066492	0.053201	0.097736	
Carbon Dioxide	P (AAPD)	0.94	1.20	1.06	
|	y (AAD)	0.0090	0.0099	0.0082	44
Ethane	k_{ij}	0.10302	0.11169	0.13525	
Carbon Dioxide	P (AAPD)	6.53	7.27	4.94	
|	y (AAD)	0.0020	0.0027	0.0018	18
Ethanol	k_{ij}	0.079477	0.058756	0.105441	

Table 3.4 (cont'd)

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Nitrogen	P (AAPD)	11.86	11.35	5.92	
|	y (AAD)	0.0233	0.0089	0.0098	39
n-Hexane	k_{ij}	0.087501	0.10989	0.15716	
3-Methyl-2-butanone	P (AAPD)	2.20	3.42	2.26	
|	y (AAD)	0.0128	0.0138	0.0098	39
n-Octane	k_{ij}	0.048967	0.055465	0.06327	
Argon	P (AAPD)	0.57	0.56	0.49	
|	y (AAD)	0.0036	0.0036	0.0040	12
Methane	k_{ij}	0.017875	0.018099	0.0276145	
Benzene	P (AAPD)	1.79	2.87	3.80	
|	y (AAD)	0.0114	0.0190	0.0252	60
1-Propanol	k_{ij}	0.065779	0.06243	0.0778489	
Benzene	P (AAPD)	10.17	10.41	3.50	
|	y (AAD)	0.0155	0.0472	0.0145	71
Cyclohexane	k_{ij}	0.0316	-0.027689	0.007131	
Cyclohexane	P (AAPD)	4.43	6.11	6.38	
|	y (AAD)	0.0290	0.0289	0.0446	56
1-Propanol	k_{ij}	0.08922	0.080462	0.091198	
Cyclohexane	P (AAPD)	0.55	0.90	0.99	
|	y (AAD)	0.0070	0.0074	0.0064	31
3-Methyl-2-butanone	k_{ij}	0.052266	0.052717	0.067533	

Table 3.4 (cont'd)

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Cyclohexane	P (AAPD)	0.53	0.26	0.24	
|	y (AAD)	0.0022	0.0047	0.0046	16
n-Heptane	k_{ij}	-0.011063	-0.0097267	-0.0058872	
Cyclohexane	P (AAPD)	1.00	1.03	0.83	
|	y (AAD)	0.0021	0.0042	0.0034	30
n-Octane	k_{ij}	-0.021573	-0.018557	-0.014377	
Nitrogen	P (AAPD)	0.40	0.85	2.27	
|	y (AAD)	0.0063	0.0074	0.0072	13
Argon	k_{ij}	-0.007696	-0.0033172	-0.0080156	
Nitrogen	P (AAPD)	0.78	1.10	0.83	
|	y (AAD)	0.0018	0.0019	0.0028	10
Methane	k_{ij}	0.01911	0.022846	0.0350966	
n-Hexane	P (AAPD)	0.58	0.61	0.26	
|	y (AAD)	0.0045	0.0066	0.0079	19
n-Heptane	k_{ij}	-0.0003095	-0.0019819	0.0042394	
n-Hexane	P (AAPD)	0.30	0.35	0.31	
|	y (AAD)	0.0027	0.0022	0.0024	17
Cyclohexane	k_{ij}	-0.0061246	-0.0055929	-0.0010708	
Overall	P (AAPD)	4.50	4.90	3.57	958
average	y (AAD)	0.0174	0.0204	0.0183	

Table 3.5: Comparison of vapor-liquid equilibrium calculation results of ternary mixtures from the Peng-Robinson, the original, and the simplified quartic equations of state.

System	Properties	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
n-Hexane | Cyclohexane | n-Heptane	x_2 (AAD) y_1 (AAD) y_2 (AAD)	0.0100 0.0056 0.0076	0.0088 0.0040 0.0076	29
Cyclohexane | 3-Methyl-2-butanone | n-Octane	x_2 (AAD) y_1 (AAD) y_2 (AAD)	0.0196 0.0180 0.0123	0.0147 0.0134 0.0129	39
Nitrogen | Argon | Methane	x_2 (AAD) y_1 (AAD) y_2 (AAD)	0.0144 0.0111 0.0128	0.0089 0.0107 0.0103	9
Nitrogen | Carbon Dioxide | Ethane	x_2 (AAD) y_1 (AAD) y_2 (AAD)	0.0252 0.0083 0.0277	0.0363 0.0186 0.0088	15
Overall	x_2 (AAD) y_1 (AAD) y_2 (AAD)	0.0170 0.0118 0.0134	0.0158 0.0110 0.0103	92

only comparable when applied to the calculations of those properties. Therefore, it is possible that the quartic equation of state might give superior performance when applied to calculation of other properties of mixtures such as heat of mixing. However, this needs to be tested. The results show that the quartic equation of state would need some modification to improve its performance on mixtures in order to compete with the widely used Peng-Robinson equation of state.

Figure 3.1 shows the comparison of the performance of the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state on the chlorodifluoromethane-2-propanol system at 363 K. From Figure 3.1, we find that all three equations of state give about the same results which is very close to the experimental data. Figure 3.2 reports the comparison of the performance of the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state on the 1-propanol-n-octane system at 358.15 K. It can be found from Figure 3.2 that the original and the simplified quartic equation of state have similar performance which is better then that of the Peng-Robinson equation on this system. Figure 3.2 also shows that the original and the simplified quartic equation of state can model systems with an azeotrope reasonably well.

Figure 3.3 shows the performance of the simplified quartic equation of state on the chlorodifluoromethane-n-hexane system at three different temperatures. The results show that the quartic equation of state can model the system at different temperatures with a single binary interaction parameter, k_{ij}.

Although the performance of the original and the simplified quartic equation of state looks good on the figures, the results in the previous tables show that the quartic equation of state does not have superior performance over the Peng-Robinson equation of state for vapor liquid equilibrium calculations.

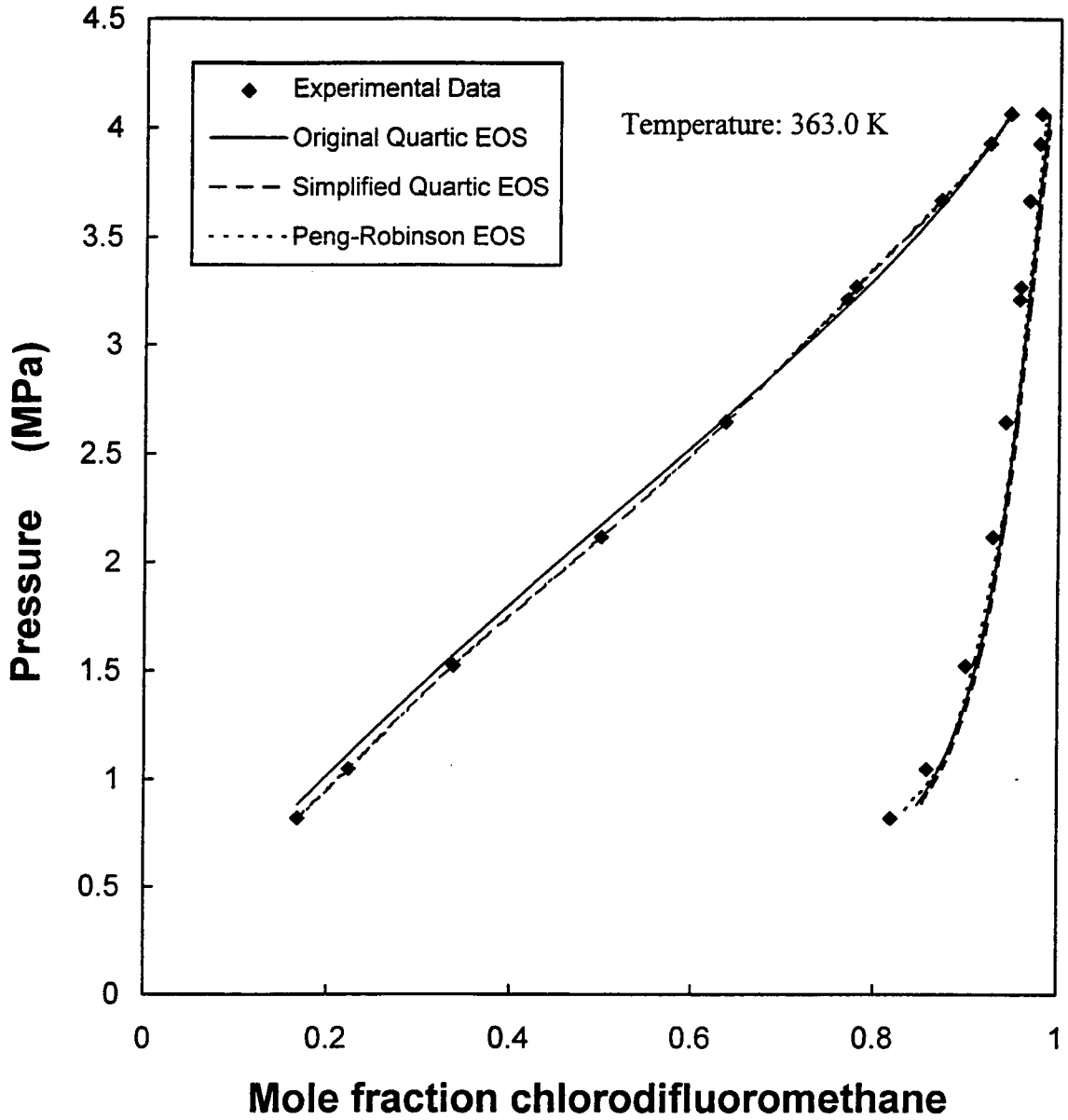

Figure 3.1: Comparison of the performance of the original quartic EOS, simplified quartic EOS, and Peng-Robinson EOS on the chlorodifluoromethane-2-propanol system at 363.0 K.

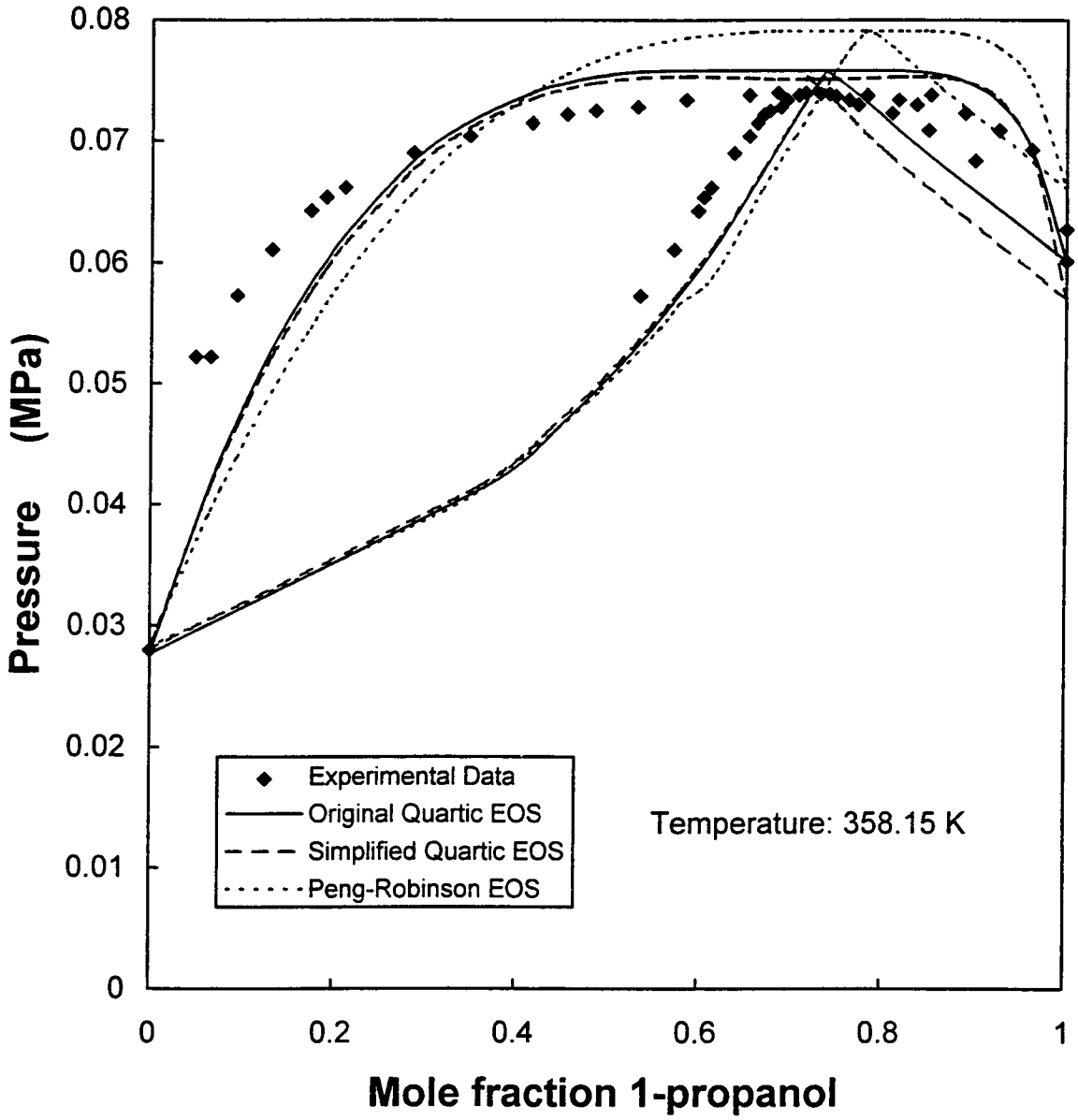

Figure 3.2: Comparison of the performance of the original quartic EOS, simplified quartic EOS, and Peng-Robinson EOS on the 1-propanol-n-octane system at 358.15 K.

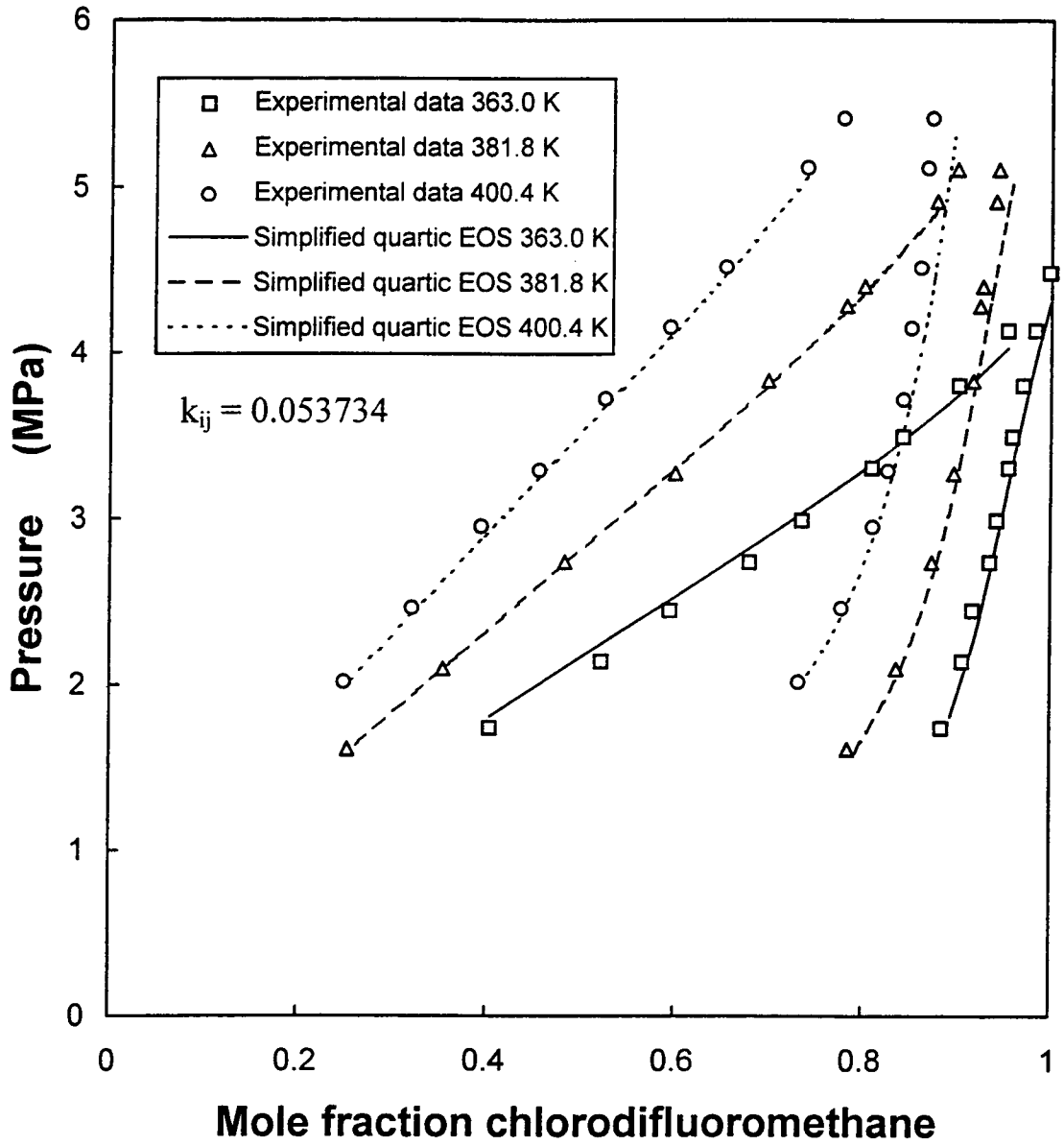

Figure 3.3: Comparison of the performance of the simplified quartic EOS on the chlorodifluoromethane-n-hexane system at 363.0 K, 381.8 K, and 400.4K.

Figure 3.4 reports the comparison of the performance of the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state on the acetophenone-ethylene system at 318.15 K. Figure 3.4 shows that the Peng-Robinson equation of state has better performance than the quartic equations of state in this system, which is the case for some of the tested systems, but for most of the tested systems the performance of the quartic equations of state is close to that of the Peng-Robinson equation of state.

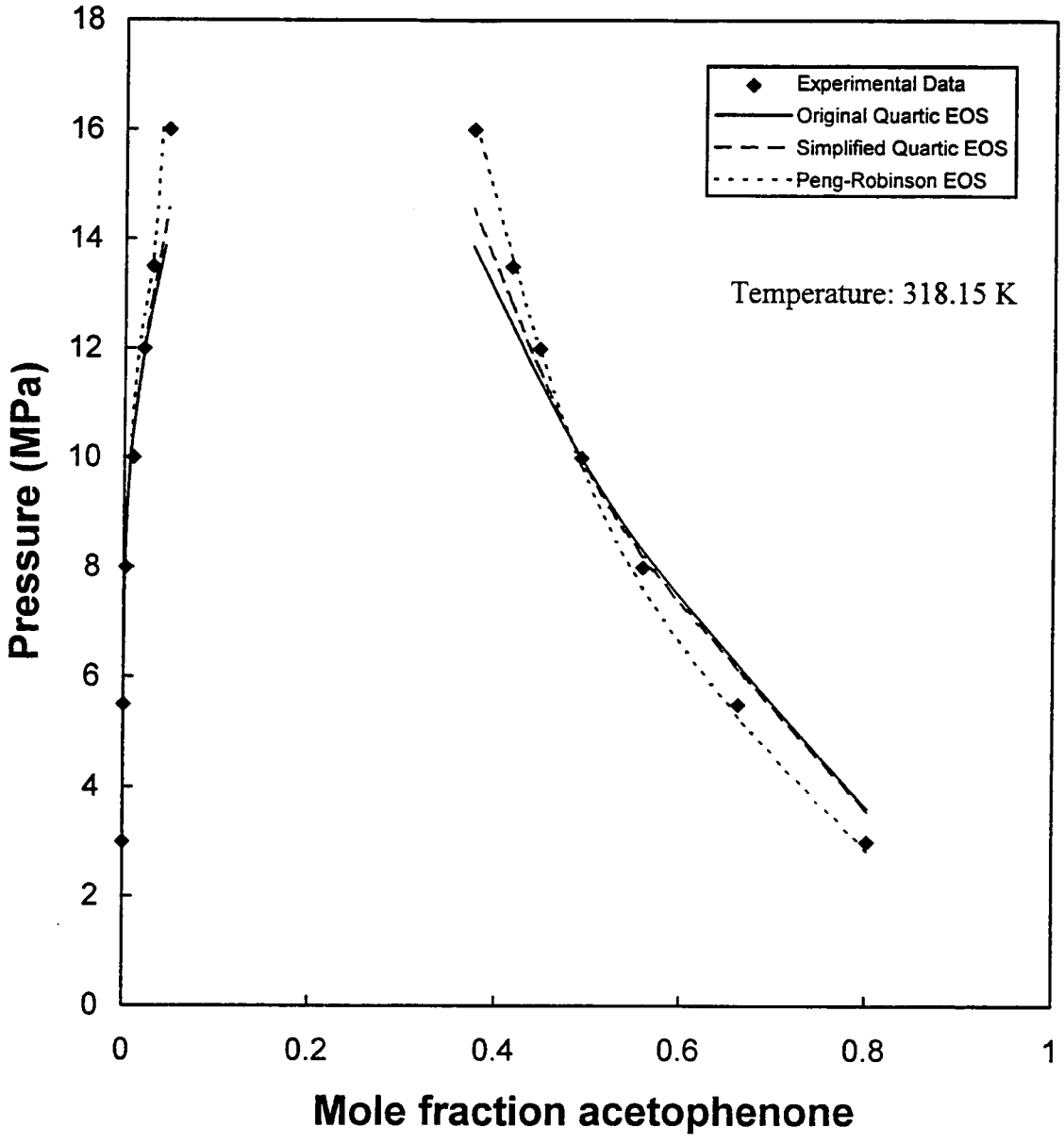

Figure 3.4: Comparison of the performance of the original quartic EOS, simplified quartic EOS, and Peng-Robinson EOS on the acetophenone-ethylene system at 318.15 K.

CHAPTER 4

Conclusions and Recommendations

A generalized quartic equation of state with forty regressed coefficients was previously proved to have superior performance over the Peng-Robinson equation of state over large range of temperature and pressure except for the critical region when applying to pure polar and non-polar fluids. This quartic equation of state was shown to have the two important advantages that cubic equations of state have : analytical solutions and easy specification of the roots. And only four pure fluid properties are needed to model polar fluids.

However, the quartic equation of state looks very complicated with forty coefficients. Although, it matters little how many coefficients an equation of state has when the phase equilibrium calculation is done by computer, too many regressed coefficients does make it difficult for people to understand and accept the equation of state. Besides, almost anything can be modeled with enough adjustable parameters even it is not well understood. Therefore, a new set of coefficients with fifteen fewer than previous work has been obtained to show that a simplified quartic equation of state can model the polar and non-polar fluids about equally well with fewer regressed coefficients. Eight of the eliminated coefficients are the first order terms of the reduced dipole moment. The results from the regression on a data base including sixteen non-polar fluids and thirty polar fluids show that the performance of the quartic equation of state with the new set of twenty-five coefficients is only slightly worse than the original one. It should be noted that twenty-five coefficients is still a lot of coefficients. And

it may be risky to use a model with too many regressed coefficients for extrapolation.

One important application of an equation of state is phase equilibrium calculation for mixtures. Since the performance of the quartic equation of state is superior to the Peng-Robinson equation of state when applying to pure fluids, it was hoped at the beginning that this advantage would remain when extending to mixtures. However, the results show that the performance with mixtures of both the original and simplified quartic equations of state is generally slightly worse than that of the Peng-Robinson equation of state even for systems at high pressure; and the performance of the original quartic equation of state is generally slightly better than that of the simplified one.

Beyond what has been done in this project, some further work concerning the quartic equation of state is recommended as follows:

1. The work on simplification in this project did not really simplify this quartic equation of state. To really simplify it, a new and simple functional form of the attractive term must be proposed. However, it can only be done by trial and error. Analysis on molecular simulation data of simple non-polar, non-polar, and polar fluids might make this easier.
2. The performance of the quartic equation of state on mixtures is not as good as expected. It can be improved by introducing the temperature dependency and/or composition dependency into the binary interaction parameters, using some physical relations to derive mixing rules with more physical meanings, or introducing new binary interaction parameters for parameter c and e. However, all the approaches above will make the quartic equation of state look even more complicated.

3. The quartic equation of state is not predictive for mixtures. To make it predictive for mixtures, a group contribution method could be applied to estimate the binary interaction parameters.
4. One important advantage of the quartic equation of state over the Peng-Robinson equation of state is that the quartic equation of state has much better performance in estimating some properties other than volumetric properties, for example, residual enthalpy (Lin 1994). Therefore, it is reasonable to assume that the performance of the quartic equation of state might be better than that of the Peng-Robinson equation of state in estimating some properties such as heat of mixing for mixtures. This should be tested.

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APPENDIX

Database

Table A.1: Detailed description of the pure non-polar component data used in regressions and their sources.

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Argon	P_s	84-140		29	[1]
	ρ_{sv}	84-140		29	[1]
	ρ_{sl}	84-140		29	[1]
	ρ_g	180-1000	0-100	243	[1]
	B_{vir}	160-740		59	[1]
	H_r	400-1000		125	[1]
Krypton	P_s	116-204		44	[2]
	ρ_{sv}	116-204		44	[2]
	ρ_{sl}	116-204		44	[2]
	ρ_g	250-1000	0-100	161	[2]
Xenon	P_s	164-280		30	[3]
	ρ_{sv}	164-280		30	[3]
	ρ_{sl}	164-280		30	[3]
	ρ_g	289-800	0-100	120	[3]
	B_{vir}	300-1000		71	[4]

Table A.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Oxygen	P_s	56-152		49	[2]
	ρ_{sv}	56-152		49	[2]
	ρ_{sl}	56-152		49	[2]
	ρ_g	180-1000	0-100	225	[2]
	B_{vir}	155-1000		86	[4]
	H_r	400-1000		96	[5]
Nitrogen	P_s	64-117		54	[6]
	ρ_{sv}	64117		54	[6]
	ρ_{sl}	64-117		54	[6]
	ρ_g	150-1000	0-100	330	[6]
	B_{vir}	140-720		59	[4]
	H_r	200-1000		231	[6]
Methane	P_s	100-180		21	[7]
	ρ_{sv}	100-180		21	[7]
	ρ_{sl}	100-180		21	[7]
	ρ_g	200-600	0-100	260	[7]
	B_{vir}	200-820		63	[4]
	H_r	200-600		156	[7]

Table A.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Ethane	P_s	130-300		18	[7]
	ρ_{sv}	130-300		18	[7]
	ρ_{sl}	130-300		18	[7]
	ρ_g	350-600	0-70	189	[7]
	B_{vir}	310-600		59	[4]
	H_r	400-600		98	[7]
Propane	P_s	140-350		22	[7]
	ρ_{sv}	140-350		22	[7]
	ρ_{sl}	140-350		22	[7]
	ρ_g	440-600	0-100	147	[7]
	B_{vir}	380-700		65	[4]
	H_r	400-600		98	[7]
n-Butane	P_s	170-410		25	[7]
	ρ_{sv}	170-410		25	[7]
	ρ_{sl}	170-410		25	[7]
	ρ_g	500-600	0-70	98	[7]
	B_{vir}	430-700		55	[4]
	H_r	500-600		98	[7]

Table A.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Carbon Dioxide	P_s	220-290		15	[8]
	ρ_{sv}	220-290		15	[8]
	ρ_{sl}	220-290		15	[8]
	ρ_g	320-1000	0-60	224	[2]
	B_{vir}	400-1000		70	[4]
	H_r	400-1000		192	[5]
n-Pentane	P_s	250-460		22	[8]
	ρ_{sv}	250-460		22	[8]
	ρ_{sl}	250-460		22	[8]
n-Hexane	P_s	250-490		25	[8]
	ρ_{sv}	250-490		25	[8]
	ρ_{sl}	250-490		25	[8]
n-Octane	P_s	300-540		25	[8]
	ρ_{sv}	300-540		25	[8]
	ρ_{sl}	300-540		25	[8]
n-Nonane	P_s	253-503		26	[2]
	ρ_l	303-573	0-20	28	[2]
n-Decane	P_s	263-523		27	[2]
	ρ_l	313-393	0-10	45	[2]
n-Undecane	ρ_l	303-573	0-100	49	[2]

Table A.2: Detailed description of the pure polar component data used in regressions and their sources.

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Acetone	P_s	400-505		22	[4]
	ρ_{sl}	400-505		22	[4]
	B_{vir}	600-700		26	[5]
	H_r	520-1000	0-100	105	[5]
	H_v	320-475		32	[4]
Carbon Monoxide	P_s	80-132		27	[9]
	ρ_{sv}	80-132		27	[9]
	ρ_{sl}	80-132		27	[9]
	ρ_g	140-1000	0-100	460	[9]
	B_{vir}	140-360		23	[9]
	H_r	200-400	0-100	105	[9]
	H_v	68-128		31	[9]
Carbonyl Sulfide	P_s	180-375		40	[4]
	ρ_{sl}	180-375		40	[4]
	B_{vir}	460-680		45	[4]
	H_v	150-360		43	[4]
Methyl Acetate	P_s	270-505		48	[4]
	ρ_{sl}	270-505		48	[4]
	H_v	250-480		47	[4]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Ethyl Acetate	P_s	250-520		55	[4]
	ρ_{sl}	250-520		55	[4]
	B_{vir}	530-650		25	[4]
	H_v	253-503		26	[4]
n-Propyl Acetate	P_s	260-540		57	[4]
	ρ_{sl}	260-540		57	[4]
	B_{vir}	530-620		31	[4]
	H_v	300-530		47	[4]
n-Butyl Acetate	P_s	360-570		43	[4]
	ρ_{sl}	360-570		43	[4]
	B_{vir}	580-750		35	[4]
	H_v	300-565		54	[4]
Freon-11 (CCl_3F)	P_s	225-470		50	[10]
	ρ_{sv}	225-470		50	[10]
	ρ_{sl}	225-470		50	[10]
	ρ_l	350-450	0-20	40	[10]
	H_r	480-1000	0-50	84	[5]
	H_v	225-455		47	[4]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Freon-13	P_s	180-295		24	[10]
($CClF_3$)	ρ_{sv}	180-295		24	[10]
	ρ_{sl}	180-295		24	[10]
	ρ_g	310-450	0-50	36	[10]
	H_r	340-1000	0-50	84	[5]
	H_v	150-280		27	[10]
Freon-21	P_s	250-450		41	[10]
($CHFCl_2$)	ρ_{sv}	250-450		41	[10]
	ρ_{sl}	250-450		41	[10]
	ρ_g	460-470	0-90	36	[10]
	ρ_l	320-450	1-90	54	[10]
	H_r	600-1000	0-50	60	[5]
	H_v	250-435		38	[10]
Freon-22	P_s	233-361		33	[11]
($CHClF_2$)	ρ_{sv}	233-361		33	[11]
	ρ_{sl}	233-361		33	[11]
	ρ_g	370-560	0-35	81	[10]
	H_r	420-800	0-100	60	[5]
	H_v	180-340		33	[10]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Freon-23	P_s	145-290		30	[10]
(CHF_3)	ρ_{sv}	145-290		30	[10]
	ρ_{sl}	145-290		30	[10]
	ρ_g	300-470	0-58	90	[10]
	B_{vir}	300-550		51	[5]
	H_r	320-600	0-100	75	[5]
	H_v	145-275		27	[10]
Freon-114	P_s	250-410		33	[10]
($C_2Cl_2F_4$)	ρ_{sv}	250-410		33	[10]
	ρ_{sl}	250-410		33	[10]
	ρ_g	420-500	0-20	75	[10]
	ρ_l	300-400	1-20	25	[10]
	H_r	450-600	0-100	45	[5]
	H_v	250-395		30	[10]
Methyl	ρ_g	473-623	0-35	80	[12]
Chloride	B_{vir}	480-600		25	[4]
	H_v	206-386		37	[4]
Methyl	P_s	153-315		34	[4]
Fluoride	ρ_{sl}	153-315		34	[4]
	B_{vir}	700-950		51	[4]
	H_v	168-283		24	[4]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Ethyl Chloride	P_s	200-450		51	[4]
	ρ_{sl}	200-450		51	[4]
	H_v	200-435		48	[4]
Chloroform	P_s	250-514		28	[4]
	ρ_{sl}	250-514		28	[4]
	H_v	250-510		53	[4]
Chloro-benzene	P_s	353-630		57	[4]
	ρ_{sl}	353-630		57	[4]
	B_{vir}	670-900		47	[4]
	H_r	650-900	0-100	75	[5]
	H_v	355-605		51	[4]
Dimethyl Ether	P_s	230-396		35	[4]
	ρ_{sl}	230-396		35	[4]
	H_v	180-375		40	[4]
Diethyl Ether	P_s	260-463		22	[4]
	ρ_{sl}	260-463		22	[4]
	H_r	480-600	0-100	30	[5]
	H_v	255-445		39	[4]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Methyl Ethyl Ether	P_s	320-435		24	[4]
	ρ_{sl}	320-435		24	[4]
	H_v	320-370		11	[4]
Hydrogen Bromide	P_s	250-360		23	[4]
	ρ_{sl}	250-360		23	[4]
	H_v	200-335		28	[4]
Hydrogen Iodide	P_s	300-420		25	[4]
	ρ_{sl}	300-420		25	[4]
	H_v	230-390		33	[4]
Water	P_s	293-633		35	[13]
	ρ_{sv}	293-633		35	[13]
	ρ_{sl}	293-633		35	[13]
	ρ_g	773-1173	0-100	100	[13]
	B_{vir}	660-780		25	[4]
	H_v	300-600		31	[4]
Hydrogen Sulfide	P_s	250-366		24	[4]
	ρ_{sl}	250-366		24	[4]
	ρ_g	453-493	20-170	48	[14]
	H_r	500-900	0-50	45	[5]
	H_v	200-355		32	[4]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Methanol	P_s	300-500		21	[15]
	ρ_{sv}	300-500		21	[15]
	ρ_{sl}	300-500		21	[15]
	ρ_g	640-800	0-70	100	[15]
	H_v	400-495		20	[4]
Ammonia	P_s	200-395		40	[16]
	ρ_{sv}	200-395		40	[16]
	ρ_{sl}	200-395		40	[16]
	ρ_g	450-800	0-100	286	[16]
	H_v	200-360		33	[4]
Nitrous Oxide	P_s	230-305		16	[4]
	ρ_{sl}	230-305		16	[4]
	ρ_g	323-423	0-32	108	[17]
	B_{vir}	315-520		42	[4]
	H_v	190-295		22	[4]

Table A.2 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range (MPa)	No. of Data Points	Data Sources
Sulfur Dioxide	P_s	270-425		17	[4]
	ρ_{sl}	270-425		17	[4]
	ρ_g	448-523	0-32	140	[18]
	B_{vir}	440-560		70	[4]
	H_r	500-900	0-100	7	[5]
	H_v	205-385		19	[4]
Acrylonitrile	B_{vir}	810-970		33	[4]

Table A.3: Detailed description of the binary mixtures data used for testing the quartic equation of state and their sources.

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Acetic acid | n-Octane	323.15 - 343.15	0.0067 - 0.0291	39	[19]
Methane | 1-Propanol	313.4 - 333.4	1.410 - 10.197	10	[20]
Methane | Ethanol	313.4 - 333.4	1.808 - 10.464	10	[20]
Ethanol | n-Octane	343.15	0.0160 - 0.0722	23	[21]
Propane | Furfural	293.15 - 313.15	0.094 - 1.339	26	[22]
Propylene | Furfural	293.15 - 313.15	0.100 - 1.611	32	[22]

Table A.3 (cont'd)

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
1-Propanol | n-Octane	358.15	0.0280 - 0.0628	25	[21]
n-Octane | Ethane	318.15 - 338.15	1.500 - 6.800	16	[23]
n-Octane | Ethylene	318.15 - 338.15	1.500 - 9.500	19	[23]
n-Octane | Carbon Dioxide	313.15 - 348.15	1.500 - 11.350	18	[23]
Aceto-phenone | Ethylene	318.15 - 338.15	3.000 - 19.000	19	[24]
Methyl-benzoate | Ethylene	318.15 - 338.15	2.500 - 15.000	16	[25]
Methanol | Acetone	328.82 - 336.84	0.1013	12	[26]

Table A.3 (cont'd)

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Methane | n-Decane	477.59 - 510.93	0.1379 - 36.192	31	[27]
Methane | n-Pentane	176.21 - 273.16	0 - 4.1367	9	[28]
Chlorodifluoro -methane | 2-Propanol	363.7 - 382.8	0.819 - 5.273	22	[29]
Chlorodifluoro -methane | Ethanol	343.3 - 382.7	0.836 - 5.434	34	[29]
Chlorodifluoro -methane | n-Hexane	363.0 - 400.4	1.614 - 5.412	28	[29]
Chlorodifluoro -methane | Chloroform	364.3 - 383.0	1.485 - 5.379	23	[29]

Table A.3 (cont'd)

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Chlorodifluoro -methane | Cyclohexane	363.3 - 400.6	1.348 - 5.713	27	[29]
1,1- Difluoroethane | Ethylchloride	303.2 323.2	0.466 - 1.047	29	[30]
Carbon Dioxide | 1-Propanol	313.4 - 333.4	0.518 - 10.822	15	[20]
Carbon Dioxide | Ethane	207.00 - 270.00	0.2943 - 3.200	44	[31]
Carbon Dioxide | Ethanol	313.4 - 333.4	0.514 - 10.654	18	[20]
Nitrogen | n-Hexane	310.93 - 444.26	1.7237 - 34.4735	39	[32]

Table A.3 (cont'd)

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
3-Methyl-2-butanone | n-Octane	367.44 - 398.76	0.1013	39	[33]
Argon | Methane	122.89	0.335 - 1.342	12	[34]
Benzene | 1-Propanol	323.15 - 333.15	0.0220 - 0.0567	60	[35]
Benzene | Cyclohexane	323.15 - 333.15	0.0369 - 0.0576	71	[35]
Cyclohexane | 1-Propanol	323.15 - 333.15	0.0279 - 0.0612	56	[35]
Cyclohexane | 3-Methyl-2-butanone	353.87 - 367.44	0.1013	31	[33]
Cyclohexane | n-Heptane	353.79 - 371.45	0.1013	16	[36]

Table A.3 (cont'd)

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Cyclohexane | n-Octane	353.87 - 398.76	0.1013	30	[33]
Nitrogen | Argon	122.89	1.484 - 2.839	13	[34]
Nitrogen | Methane	122.89	0.422 - 2.580	10	[34]
n-Hexane | n-Heptane	341.81 - 371.47	0.1013	19	[36]
n-Hexane | Cyclohexane	341.79 - 353.75	0.1013	17	[36]

Table A.4: Detailed description of the ternary mixtures data used for testing the quartic equation of state and their sources.

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
n-Hexane | Cyclohexane | n-Heptane	345.08 - 363.16	0.1013	29	[36]
Cyclohexane | 3-Methyl-2-butanone | n-Octane	354.41 - 367.01	0.1013	39	[33]
Nitrogen | Argon | Methane	122.89	0.700 - 2.441	9	[34]
Nitrogen | Carbon Dioxide | Ethane	220	0.804	15	[37]

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