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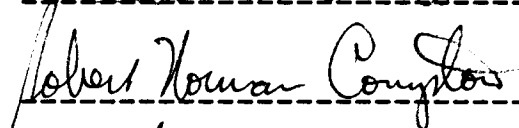
I am submitting herewith a dissertation written by James Patton Downey entitled "A Monte Carlo Study: Dynamic Scaling Properties of Single, Self-Avoiding Polymer Chains as a Function of Temperature or Solvent Quality." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

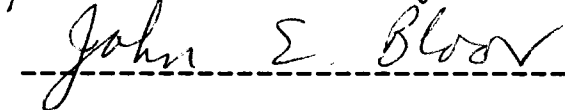


Jeffrey Kovac, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:



Vice Provost and
Dean of the Graduate School

A MONTE CARLO STUDY:
DYNAMIC SCALING PROPERTIES OF SINGLE, SELF-AVOIDING POLYMER
CHAINS AS A FUNCTION OF TEMPERATURE OR SOLVENT QUALITY

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ABSTRACT

Dynamic Monte Carlo simulations of self-avoiding, single polymer chains were performed on body-centered (BCC), face-centered (FCC), and simple cubic (SC) lattices for a variety of chain lengths. A potential energy interaction between the non-bonded nearest-neighbor beads for each lattice was included to simulate the effects of temperature or solvent quality. Scaling exponents relating the relaxation times for the normal modes to the chain length and mode number were determined from the data according to the relations

$$t(L,k) \sim L^{a(k)}$$

and

$$t(L,k) \sim k^{b(L)}$$

where t is the relaxation time, k is mode number, and L is chain length. Even in poor solvent conditions the cross-correlations of the normal modes were found to be statistically equal to zero. The data for the mean square end-to-end distance was fit to the scaling relation below in order to determine 2ν

$$\langle R^2 \rangle \sim L^{2\nu}$$

For extended chains, the scaling exponents of the lattices were approximately equal for a given value of $q \cdot E_r$, where q is the coordination number minus one and $-E_r$ is the minimum of the square-well potential divided by $k_B T$. Within this regime the scaling exponent, $a(1)$, behaved in reasonable

agreement with scaling theory predictions for Bead-Spring models, i.e. $a(1)=2v+1$. The theta point was found to occur at the temperature corresponding to approximately $T=1.75(q*E_r k_B)^{-1}$.

In the poor solvent regime the dynamic scaling exponents for the BCC and FCC lattices were approximately equal for the same value of $q*E_r$. However, the values for the SC lattice were quite different for a given value of $q*E_r$, presumably because the two-bead crankshaft motions required for obtaining reasonable dynamics in the SC lattice are less likely to be performed due to the high bead density within a collapsed chain.

For all three lattices, in all regimes studied, $a(k)$ values increased with increasing k . This dependence became great in poor solvent conditions. In these conditions $b(L)$ decreased with increasing L . The relaxation times in poor solvent conditions were in general consistent with the predictions of Brochard and deGennes for the creation of gel modes.¹ Also, in the collapsed regime $b(L)$ values were found to be highly correlated with coil density.

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LIST OF SYMBOLS

A	The constant for the scaling law relating the relaxation times of the normal modes with the chain length and mode number
$a(k)$	The scaling exponent relating the chain length to the relaxation time of the k 'th mode
B	The Boltzmann factor of a given a state
b	The average of $b(59)$ and $b(71)$
$b(L)$	The scaling exponent relating the mode number to the relaxation time of the normal modes for a chain of length L
C	Concentration
C_D	Coil density
C_M	Center-of-mass coordinate
c_i	Constant
D	Dimension
D_{CM}	The center-of-mass diffusion coefficient
d	derivative
E_d	The energy difference between two states
E_p	The negative of the minimum of the square-well, pair potential
E_r	E_p divided by $k_B T$, the reduced potential
$F_k(t)$	The autocorrelation function of the k ' mode
F_R	The autocorrelation function of R
f_i	The force on bead i
G	Free energy
$g_i(t)$	The displacement of monomer (bead) i at time t
h	The scaling exponent relating the chain length to

	the center-of-mass diffusion constant
i	An index variable
j	An index variable
k	The mode number
k_B	The Boltzmann constant
L	The length of the chain (the number of bonds)
l	The mean end-to-end distance of a segment (spring)
l_i	The vector linking beads i and $i+1$
l_0	Bond length
m_k	The amplitude of mode k
N	The number of beads in the chain
n_i	The number of unoccupied nearest-neighbor sites for bead i
P_i	The probability of event i occurring
Q	Used as an example of a hypothetical function
q	The coordination number of a lattice minus one
R	The end-to-end vector
$\langle R^2 \rangle$	The mean squared end-to-end distance
R_{CM}	The center-of-mass coordinates
R_F	The equilibrium end-to-end distance
R_g	The radius of gyration
R_0	The equilibrium end-to-end distance of an ideal coil (no excluded volume interactions)
r_i	The vector coordinates of bead i
S_i	The entropy associated with the end-to-end distance of the segment between bonds i and $i+1$
$\sum_i$	Summation over i

T	Temperature
T_L	The theta temperature
t_k	The relaxation time of the k 'th normal mode
$t_R(L)$	The relaxation time of the end-to-end vector of a chain of length L
$t(L,k)$	The relaxation time of the k 'th mode of a chain of length L
$U_k(t)$	The normal coordinate of the k 'th mode at time t
u	mobility per monomer
$V(r)$	The value of the pair potential at a separation r
V_m	The volume occupied by a monomer
v	The scaling exponent relating the chain length to the mean end-to-end distance
W	The numerical weighting given a state
w	The scaling exponent relating the chain length to the relaxation time of the end-to-end vector
X	A random number
y	The scaling exponent relating the displacement of a monomer to time
Z	The number of nearest-neighbor contacts in a chain
z_i	The number of nearest-neighbor contacts with non-bonded beads made by a bead or beads after their motion to the position i

INTRODUCTION

The huge size of polymers makes the characterization of their properties one of the most difficult problems in the fields of chemistry and physics. The usefulness of polymers makes understanding their properties one of the most important tasks in these fields at present. Experimental methods for studying many polymer properties are often unavailable, and if there are available methods, they are often expensive and difficult to perform. This is particularly true in the field of polymer dynamics. If polymers were simple enough to be described by straightforward theoretical treatments, then perhaps the difficulty of obtaining experimental data on polymers would not be of much concern. Unfortunately, the large size of polymers makes most theoretical treatments difficult, usually requiring approximations of dubious validity. Another way of gaining insight into polymer behavior is by the use of computer simulations. A computer model of a polymer allows one to conduct a controlled study of a system modeled in a way which is believed to closely resemble an actual polymer.

Most computer simulations involving the studies of polymers are Monte Carlo simulations. The main advantages of Monte Carlo simulations are their simplicity from a computational standpoint and that simulations allow one to study the effect of an individual factor independent of all

others. For example, the effect of excluded volume can be studied by comparing the simulation results for a chain in which excluded volume is ignored and the results for the same chain with the excluded volume condition included. Obviously, this could not be done on a real chain.

There are disadvantages to Monte Carlo studies. One of the most important is that the polymer must be modeled in a physically reasonable way. This is not a trivial task as there are many simulations in the literature which claim to study a given property of real polymer chains, but it is found that the simulation model had a physically unreasonable condition built into it. There is also the very real chance that it will not be possible to judge what is and is not a physically reasonable model. For example, most Monte Carlo simulations describe a polymer chain as a string of connected beads lying on the vertices of a lattice. Restricting the chain to a lattice would not seem reasonable, yet off-lattice studies of equilibrium properties have generally shown no significant differences with equivalent lattice studies. Likewise, the type of lattice used in a study seems to have little, if any, effect on the equilibrium properties observed.

There have been comparatively few Monte Carlo studies of polymer chain dynamics which is the primary focus of this work. It is not known if dynamic properties of polymers would be particularly sensitive to the model selected, but

previous literature has enough conflicts to cause some concern. Therefore, all the simulation models used in this work will be compared with at least one other model in order to verify the universality of the models.

The Monte Carlo model which is the most frequently used to study polymer dynamics consists of a chain of beads confined to the vertices of a simple cubic (SC) lattice. The bonds between the beads are of fixed length and the beads are moved singly or in pairs. An elementary motion involving a bead pair has been proven to be necessary to achieve physically reasonable dynamics. The need for motions involving bead pairs is a great disadvantage at high concentrations, since at high concentrations the odds of finding two empty locations into which the bead pair may be moved are quite low compared to the chance of successfully moving one bead. In effect, the two-bead motions no longer take place.

Crabb saw the need to develop a dynamic simulation in which physically reasonable dynamics were obtained by a model requiring only one-bead motions.² The high-coordination number of the face-centered cubic (FCC) lattice made it the appropriate lattice for developing such a model. This work will attempt to follow the preliminary work of Crabb and to also develop a dynamic simulation using a body-centered cubic (BCC) lattice. These lattices will be used to verify that different lattice models give similar dynamic

scaling behavior. Dynamic scaling behavior of the chains will be investigated by the relaxation times obtained for the chains normal modes. Results will be compared to the well known predictions of bead-spring models and the few previous Monte Carlo studies.

Assuming the data obtained from these two models have been shown to agree with other simulations and theories, more complex models will be developed in which the chains will interact through a square-well potential. This potential will allow the beads of the chain to interact over longer distances and in a more complicated manner than the typical dynamic simulations in which the only self-interaction is due to the excluded-volume condition, i.e. the restriction that no two beads may occupy the same lattice vertex. These pair interactions will allow the simulation of solvent or temperature effects. This is of interest since the dynamics of polymers in thermal solvents has scarcely been studied by simulations, and it is of particular interest to observe how dynamic scaling behavior changes at the theta point, i.e. the temperature at which a chain's attractive self-interactions become great enough to overcome the expansion caused by excluded volume. At the theta point the chain behaves as an ideal chain (a random walk).

In the first chapter of this thesis, previous literature of particular relevance to this work will be

discussed, beginning with a short review of the bead-spring description of polymers in a dilute solution. This is followed by a discussion of the development of a simple cubic lattice model which is used frequently in Monte Carlo studies of polymer dynamics (including in this work). The development of this model is instructive in showing some of the hidden problems which can occur in attempting to develop a simulation model. Also discussed are earlier dynamic simulations of particular interest to this work, simulations to examine static scaling behavior of polymers in a variety of solvent conditions, and pertinent developments in experimental methods of studying polymer dynamics.

In the second chapter, the models used in this work will be discussed in detail. Also, the method of calculating the normal modes of the chain and the relaxation times of these normal modes will be explained. It is primarily by examining the scaling properties of the normal modes that the dynamics of chains will be investigated in this work. The scaling behavior found for the normal modes can be compared to the well known bead-spring models of Rouse,³ Bueche,⁴ and Zimm.^{5,6} The methods with which the data is fit to dynamic scaling exponents is presented in the second chapter as well.

The third chapter contains the results of the simulations performed in this work. The results show that in good and theta solvents, the dynamic scaling observed shows

good agreement with the bead-spring models. The models give approximately the same scaling exponents for a given value of $q \cdot E_r$ where q is the coordination number of the lattice minus one and E_r is the negative of the minimum of the of the square-well potential divided by $k_B T$. E_r will be referred to as the reduced potential and $q \cdot E_r$ will be referred to as the effective potential. This observation indicates that dynamic properties are not sensitive to the coordination number of the lattice even in dense systems.

In the poor solvent regime, the dynamics of the simple cubic model behave differently than the dynamics of the higher coordination number lattices, presumably due to the difficulty of performing two-bead elementary moves in a collapsed chain. In this regime, the dynamics show good agreement with the predictions of Brochard and deGennes for gel modes.¹ The formation of gel modes are predicted to occur if the average lifetime of a pair contact is increased to a value which is approximately of the order of the relaxation time of a mode. When this occurs the relaxation time for that mode should increase dramatically. This is appears to occur for the collapsed chains studied in this research.

CHAPTER I

BACKGROUND

A. The Rouse Model

The classical theory of polymer chain dynamics was developed by works of Rouse³, Bueche⁴, and Zimm^{5,6}. Collectively their works are known as bead-spring models. It was Rouse in 1953 who first simplified the mathematics of the dynamics of an isolated polymer chain into a mathematically tractable form by dividing the polymer chains into segments. These segments were chosen to be long enough so that, to a first approximation, the equilibrium end-to-end distance of these segments obeyed a Gaussian distribution function. In the absence of solvent motion, the motion of the chain would be the result of the Brownian motion of the individual polymer segments as the chain traversed through the equilibrium ensemble of the polymer.

In a paper written approximately one year later, Bueche⁴ modeled a polymer as a chain divided into N segments which interacted with one another through springs obeying Hooke's Law. In the absence of other interactions, the motion of the springs was the result of Brownian forces. Despite the different starting points, the results of Bueche were similar to those of Rouse.³ Zimm^{4,5} soon unified the mathematics of these two models by treating the internal interactions between segments in Rouse's model to be forces

obeying Hooke's Law. Zimm also added a pre-averaged hydrodynamic interaction to the model. This interaction is due to the effect of the flow of the displaced solvent which results from the movement of a chain segment. The resulting motion of the solvent may effect chain segments far along the chain contour from the segment which originally moved. This interaction was not considered in the original Rouse model.

Bead-spring models describe, in a simple manner, the dynamics of polymers in a dilute solution where intermolecular interactions between polymer chains have negligible importance. The model is the standard theory of polymer dynamics in dilute solutions, and there are numerous articles in which it is discussed in great detail. Here, only a brief discussion of Rouse's bead-spring model which follows the description of deGennes⁷ will be presented. In this description and throughout this work, the hydrodynamic interactions are ignored.

The Bead-spring Model may be thought of as a set of N beads at the positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ which are connected by $L=N-1$ springs (bonds) oriented along the vectors $\mathbf{l}_1, \mathbf{l}_2, \dots, \mathbf{l}_L$. (Note: Throughout this work vectors and coordinates will be indicated by bold type.) Since the length of the chain segments are assumed to be Gaussian, the entropy of the chain segment between the beads i and $i+1$ is

$$S_i = 3k_B |\mathbf{l}_i|^2 / 2l^2 \quad (1)$$

$$= (3k_B/2)[(\mathbf{r}_{i+1} - \mathbf{r}_i)/\langle(\mathbf{r}_{i+1} - \mathbf{r}_i)^2\rangle],$$

where $\mathbf{l}_i$ is the end-to-end vector of chain segment between beads i and $i+1$ and l^2 is the mean square end-to-end length of the segment. The pointed brackets $\langle \rangle$ represent ensemble average values whenever they appear in this work. The elastic free energy of the chain is then

$$G = T \sum_i S_i. \quad (2)$$

Next, it is assumed that the force on bead i , $\mathbf{f}_i$ can be written as the sum of forces applied to it from its two neighboring beads,

$$\begin{aligned} \mathbf{f}_i &= dG/d\mathbf{r}_i \\ &= (3k_B T/2l^2)[(\mathbf{r}_{i+1} - \mathbf{r}_i) - (\mathbf{r}_{i-1} - \mathbf{r}_i)], \end{aligned} \quad (3)$$

and that the velocity of the bead is due to a linear combination of these forces

$$d\mathbf{r}_i/dt = u\mathbf{f}_i, \quad (4)$$

where u has the units of mobility per bead segment.

Equations 2 and 3 may be combined to give

$$d\mathbf{r}_i/dt = (3k_B Tu/2l^2)(\mathbf{r}_{i+1} - 2\mathbf{r}_i + \mathbf{r}_{i-1}), \quad (5)$$

which in the continuous limit becomes

$$d\mathbf{r}/dt = (3k_B Tu/2l^2)(d^2\mathbf{r}/di^2). \quad (6)$$

Equation 6 is known as the Rouse equation. At the chain ends the force along the chain's contour drops to zero. This requirement gives the boundary conditions,

$$(d\mathbf{r}/di)_{i=0} = (d\mathbf{r}/di)_{i=N} = 0. \quad (7)$$

The solutions to the Rouse equation are found to be the eigenmodes

$$r_{i,k}(t) = m_k \cos(\pi k i/L) \exp(-t/t_k), \quad (8)$$

where k is the mode number, m_k is the mode amplitude and, t_k is the relaxation time of the k 'th mode given by

$$t_k^{-1} = (3k_B T u / 2l^2) (\pi k/L)^2. \quad (9)$$

The most important predictions of this equation are that the relaxation time of every mode is proportional to the square of the number of bonds in the chain and is inversely proportional to the mode number squared.

The bead-spring model of Rouse is an extremely simple one since it neglects some forces on the chain which would be very difficult to deal with mathematically. One such force is the hydrodynamic interaction. When a bead moves through the solvent, the resulting solvent backflow would effect the motion of beads which may be far along the chain's contour, whereas the Rouse Model assumes that a bead is only affected by forces originating from its neighboring beads. Although the effect of hydrodynamic interactions was added to the model in a simple way by Zimm by a pre-averaging approximation,^{5,6} this effect will be ignored in this work. Another problem with the original model of Rouse is that it assumes that more than one bead of the chain may occupy the same point in space. This ignores the volume which a real polymer chain would occupy. Chains modeled by this assumption are referred to as ideal or phantom chains.

B. Treatment of Excluded Volume

The excluded volume condition which Rouse ignored was of great interest in this work. One of the simplest and most successful treatments of the excluded volume interaction involves Flory's use of Mean Field Theory.⁸ deGennes has simplified these arguments and modified them somewhat.⁹ The mathematical arguments below follow those of Reference 9. They lead to the prediction, shown below, known as the dynamic scaling hypothesis.

$$t_1 \sim L^{1+2\nu}, \quad (10)$$

where 2ν is the scaling exponent relating the mean square end-to-end distance to the chain length. The theoretical arguments from which the value of 2ν is derived are also shown below.

The mathematics of deGennes' argument are fairly straightforward. He starts with the assumption that the polymer chain has the free energy, $G(R)$, of an ideal spring-like coil. Therefore,

$$G(R) = k_B T (c_1 R^2 / R_0^2) = k_B T (c_1 R^2 / l^2 L), \quad (11)$$

where c_1 is a numerical constant, R is the end-to-end distance of the chain, R_0 is the equilibrium end-to-end distance of an ideal coil, and l^2 is the mean square end-to-end distance of a spring. deGennes adds to Equation 11 a repulsive term for L interacting springs, each having an excluded volume V_m , which collectively occupy a volume R^D in a roughly uniform manner, where D is the dimensionality of

the system. This gives

$$G(R) = k_B T [(c_1 R^2 / l^2 L) + (c_2 L^2 v_m / R^D)]. \quad (12)$$

Minimizing $G(R)$ with respect to R yields the equality

$$2c_1 R_F / l^2 L = c_2 D L^2 v_m / R_F^{D+1}, \quad (13)$$

where R_F is the new equilibrium end-to-end distance.

Equation 13 predicts that

$$R_F \sim L^v, \quad (14)$$

where the static scaling exponent v is

$$v = 3 / (D + 2). \quad (15)$$

Therefore in three dimensions

$$R_F = L^{3/5}. \quad (16)$$

For such a simple method the previous arguments' prediction of $v=3/5$ leads to a surprisingly good agreement with computer simulations and experimental results.

To determine the dynamic scaling exponent, deGennes starts with the assumptions that we are dealing with small deviations from equilibrium

$$R - R_F = dR. \quad (17)$$

Using Equation 13 and a Taylor expansion about the equilibrium value of $R=R_F$ deGennes gets

$$\begin{aligned} G(R) - G(R_F) &= (1/2) (d^2 G(R_F) / dR^2) (dR^2) + \dots \\ &= (D + 2) (c_1 k_B T) (dR^2 / l^2 L) \\ &\sim (dR)^2 / L \sim (dR / R_0)^2. \end{aligned} \quad (18)$$

Numerical procedures indicate that the mean field techniques used in Equations 11 (p 11), 12, and 18 overestimate both the attractive and repulsive energies of a three dimensional

chain by a factor of about $L^{0.2}$. (Note that this result does not effect the predictions of Equations 14, 15, and 16 (p 12). Therefore deGennes multiplies the right-hand side of Equation 18 by $L^{0.2}$ and uses Equation 16 to get the corrected energy difference

$$G(R) - G(R_F) \sim (dR/R_F)^2. \quad (19)$$

The rate at which the chain dissipates energy is

$$dG/dt = Lu^{-1}(dR/dt)^2. \quad (20)$$

Equating this to the rate of change of $G(R)$ as is written on the right-hand side of Equation 19 and canceling terms yields

$$Lu^{-1}(dR/dt) \sim dR/R_F^2, \quad (21)$$

which implies

$$t_1 \sim LR_F^2. \quad (22)$$

Substituting L^V for R_F gives the scaling law of Equation 10 (p 11). In three dimensions Equation 10 becomes

$$t_1 \sim L^{2.2}. \quad (23)$$

Equation 23 can be combined with the scaling law relating the relaxation times and mode number predicted by the bead-spring models,

$$t_k \sim k^{b(L)}, \quad (24)$$

where the scaling exponent $b(L)$ is predicted to be equal to 2.0 by the Rouse model. The combination of Equations 23 and 24 lead to the relation,

$$t(L,k) \sim k^{b(L)}L^{2.2}. \quad (25)$$

It is worth noting that these arguments do not predict how

many bead segments in the chain are necessary to achieve asymptotic scaling as described by Equation 25.

Despite their great simplicity, the bead-spring models and deGennes subsequent analysis of excluded volume are the basis of most of the mathematical treatments of the dynamic and static properties of polymers. These models have been quite successful. The comparison between these predictions and experimental results is briefly discussed in Section H, but first a brief review of computer simulation techniques and results will be given in Sections C-G.

C. Monte Carlo Techniques

The use of modern computers has given polymer scientists the ability to simulate and analyze the structure and dynamics of polymers via Monte Carlo methods. One typical Monte Carlo method which is used in this work is a three step process of

- (i) Identifying all states $1, 2, \dots, N$ immediately accessible from the present state 0.
- (ii) Compute the transition probabilities $P_0, P_1, \dots, P_N$ for the movement of the system from the present state 0 to each of the N immediately accessible states using the appropriate (usually Boltzmann) distribution. P_0 is the probability of remaining in the present state.
- (iii) Generate a random number X between 0 and 1 to

determine the next state of the system. If

$$P_0 + P_1 + \dots + P_{j-1} \leq X < P_0 + P_1 + \dots + P_j, \quad (26)$$

then j is selected as the new state of the system.

This process is repeated until a significant number of states have been traversed. Assuming the Monte Carlo method provides a pathway for obtaining every state of the system then, as the number of states generated approaches infinity, the macroscopic properties of the system should approach their ensemble averages.

Another commonly used Monte Carlo method is that of Metropolis et al.¹⁰ The sampling cycle occurs as follows. One of the states immediately accessible from the present state is randomly selected. If the selected state is at a lower energy than the present state, the transition is made to the lower state. On the other hand if the selected state is higher in energy than the present state, then a random number X between 0 and 1 is generated. If E_d , the energy difference between the selected and initial states, satisfies the inequality

$$X < \exp(-E_d/k_B T), \quad (27)$$

the transition to the selected state is made. Otherwise the initial state is kept. This process is continued until a large number of states have been traversed. These selection rules ensure that the Principle of Detailed Balance is obeyed.

The two Monte Carlo methods described above

generated and sampled states in proportion to the Boltzmann factors of the states. Such a process is called simple sampling. All of the data reported in this work were collected by simple sampling procedures. There are other Monte Carlo simulations where all possible states are generated at equal rates without regard to a Boltzmann factor. Such simulations are appropriate for a system which is temperature independent. This implies all allowed states are equally probable. The simulations described in Chapter II, Section A are of this type.

For these methods, the ensemble average is found by calculating weighting factors for the sampled states, then multiplying these weighting factors by the property measured for their respective states, and averaging. If all possible states are generated at the same rate, then the weighting factor of a given state is proportional to the Boltzmann factor of that state. This type of sampling is called biased sampling. A disadvantage of this method is that it may use up computer time without significantly contributing to the ensemble average.

More complicated Monte Carlo methods may even generate states at rates which are neither proportional to their Boltzmann factors nor at equal rates for all possible states. This means a very careful weighting procedure must be used to get correct ensemble averages. An example of this is the polymer chain studies of Mazur and McCrackin.¹¹

For Monte Carlo studies of polymer dynamics such as those cited and performed in this work, it is necessary to define a time scale. The choice of time scale seems obvious. If the polymer chain is at equilibrium then all beads should experience similar Brownian forces over time. These fluctuations are represented in the simulation by attempted bead motions. If we have two chains of N_1 and N_2 beads where N_1 and N_2 attempted bead moves have been performed for the respective chains, then the beads on one chain have the same probability of having undergone an attempted bead movement as the beads on the other. Therefore, for a chain of N beads, the standard time unit will be defined as N attempted bead moves. This definition has been used by most, but not all, researchers in this field.

The greatest disadvantage of a Monte Carlo method is that the only useful information generated comes from ensemble averages, which requires the simulation to generate a large number of representative samples from the ensemble. The advantage of a Monte Carlo method is that it is a simple process and therefore quite fast from a computational viewpoint. Deterministic methods, i.e. molecular dynamics, would be much more complex from a computational view for all but the simplest systems. The huge size of polymers alone makes it unlikely that a deterministic method would be a practical way of modeling dynamic scaling behavior of polymers.

In fact, the only molecular dynamics simulation which investigated dynamic scaling behavior of what could truly be described as a macromolecule is by Gotlib and co-workers.¹² In this simulation a chain and solvent molecules were placed in a tightly packed periodic box. Both the solvent and chain segments interacted through a Lennard-Jones potential, and the bonds were of fixed length. For a chain of 123 segments in a box with four solvent molecules, the authors did report the normal modes to decay exponentially with time. From their figures, it appears that the scaling exponent $b(L)$ was somewhat lower than the Rouse prediction of 2.0.

It is worth noting that occasionally a mixture of Newtonian Dynamics and random fluctuations called Brownian Dynamics is employed. Typically this method is used to simplify solvent effects by treating the solvent as having uniform viscosity and as the source of Brownian forces acting on the chain. The self-interaction of the solute is treated in a deterministic method. Ceperly, et.al.¹³ have performed Brownian Dynamic simulations on polymer chains. The solvent interactions had no effect on dynamic scaling as the authors found that $a=2.2$, which was predicted by the mathematical treatment of excluded volume discussed in Chapter I, Section B.

D. The Monte Carlo Polymer Dynamics Simulations of Verdier

During the 1960's many researchers began to use computers to model polymers and thereby understand polymer properties. At first, computers were used almost exclusively to examine the static properties of polymers since dynamic properties would require much more computer time to simulate. Static properties could be studied by generating a large number of independent samples of polymer contours and averaging the property of interest over the resulting collection. Two of the most well known of these methods are the slithering snake method of Wall¹⁴ and the Rosenbluth walk¹⁵. The results of these simulations of static polymer properties gave results consistent with the Rouse Model in the absence of excluded volume. In the presence of excluded volume the results agreed with the predictions of deGennes.

The first attempt to model the dynamics of polymers was made by Verdier and Stockmayer in 1962.¹⁶ The subsequent refinements of this model have been used in many works, including this one. Therefore, the genesis of this model will be discussed in some detail.

The original model proposed by Verdier and Stockmayer described a polymer chain as a series of N beads located at the vertices of a simple cubic lattice, each bead being separated by a fixed distance from its two nearest-neighbors on the chain contour. This distance was equal to the spacing between lattice points. In units equal to the

lattice spacing, the chain's contour is then of length $L = N-1$. A typical chain contour for simulations with the excluded volume restriction volume is shown in Figure 1 (p 21). The intent of their paper was to examine static properties of a polymer chain, but unlike previous simulations in the literature, the method of generating chain conformations was made by a dynamic process which Verdier and Stockmayer considered to be a reasonable simulation of a polymer chain's motion.

In their model, the beads of the chain are moved by selecting a bead at random. If the bead is an internal bead, the bond vectors between this bead and its neighbors are then exchanged. This means that the bonds remain in the same plane in which they started, and is referred to as a bond vector exchange or in-plane motion. In the presence of excluded volume, this site is then examined to see if it is occupied. If it is, the attempted motion is aborted. Otherwise the bead is moved to this new location. It is worth noting that in the absence of excluded volume that this 'new' location will turn out to be the same as the previous location if the neighboring beads both occupy the same site. The possible motions of an internal bead are shown in Figure 2 (p 22).

If the randomly chosen bead is an end bead, a motion to one of the other five locations which are nearest-neighbors to the next-to-end bead is attempted as is shown

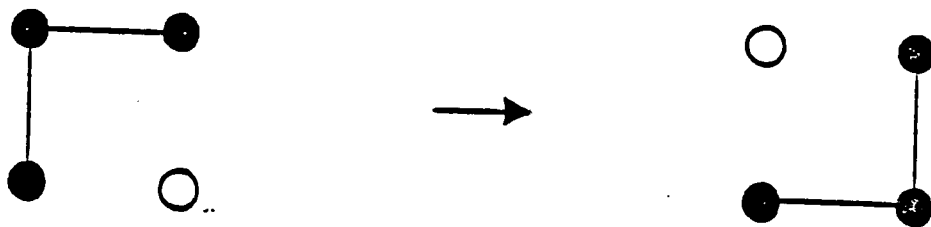


Figure 2. The motion of an internal bead for a chain placed on a SC lattice.

in Figure 3 (p 24). In the presence of excluded volume the attempted move is aborted if the position is already occupied. The attempted motion of a bead (whether or not the attempted motion is aborted) is called a bead cycle, and throughout this work the unit of time will be defined to be N bead cycles.

In the original paper of Verdier and Stockmayer, the authors defined the relaxation time of the mean square end-to-end distance, $\langle R^2 \rangle$, to be the time it took for the quantity to decay to a value of $1/e$ of the difference between its initial and final (equilibrium) values. In the absence of excluded volume the authors found rough agreement with the Rouse Model. In this paper there were also results of simulations in which the excluded volume constraint was included, but the statistical scatter was too great for the results to be meaningful.

In a later paper using this model, Verdier introduced autocorrelation functions to study the dynamics of these chains.¹⁷ The general form for an autocorrelation function of a variable $Q(t)$ is

$$F_Q(t) = [\langle Q(0)Q(t) \rangle - \langle Q(t) \rangle^2] / [\langle Q(t)^2 \rangle - \langle Q(0) \rangle^2]. \quad (28)$$

For a variable with an average value of zero (e.g. a randomly directed vector) the autocorrelation function has the form

$$F_Q(t) = \langle Q(0)Q(t) \rangle / \langle Q(t)^2 \rangle. \quad (29)$$

Throughout this work, the relaxation time data collected

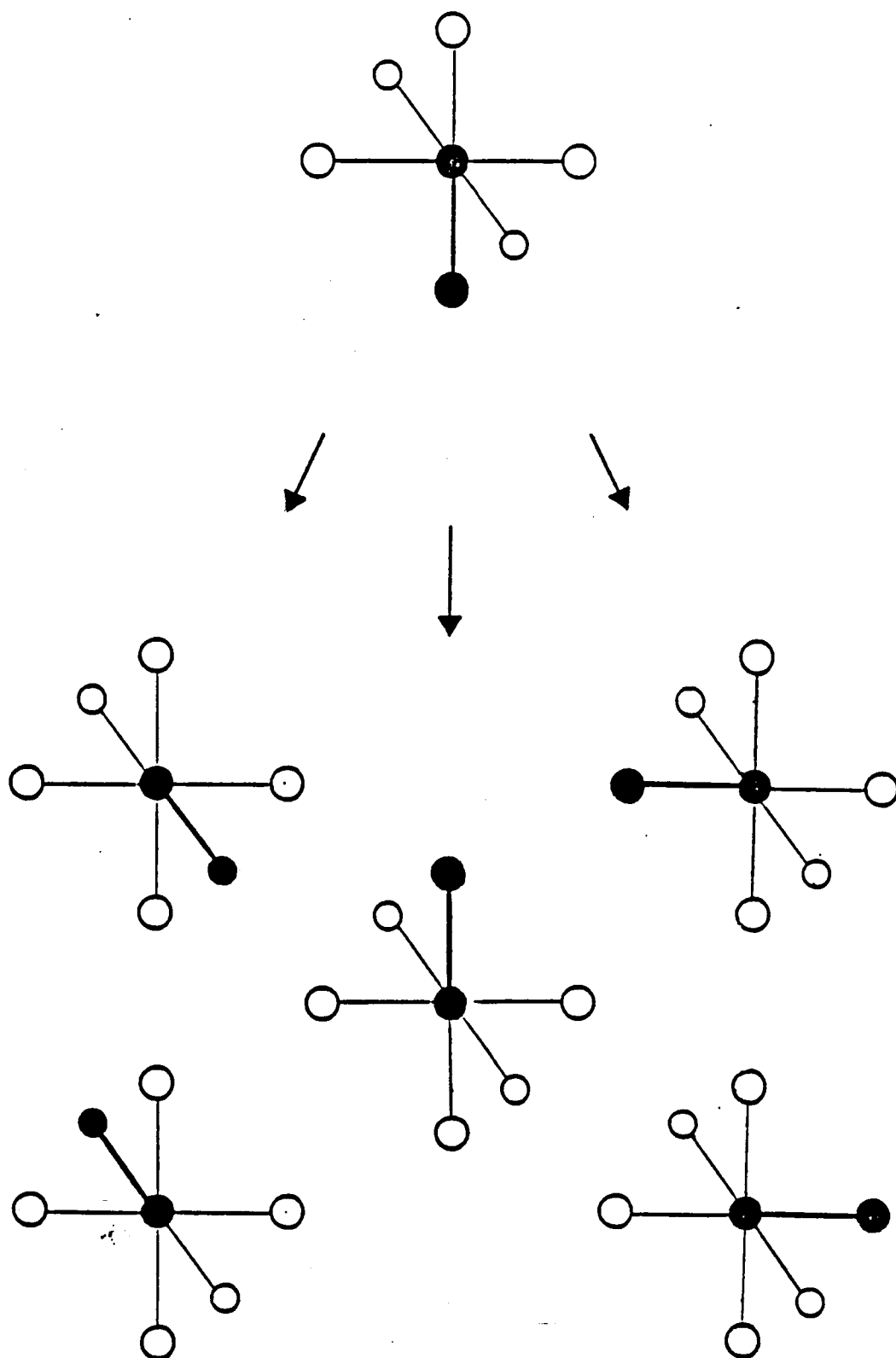


Figure 3. The possible motions of an end bead for a chain placed on a SC lattice.

will be of the form of Equation 29.

Verdier found the decay of the autocorrelation functions of the chains' end-to-end vectors, R , to be exponential at moderately long times, i.e. a semi-log plot of F_R vs. time was found to be linear. At very short times the autocorrelation functions did not decay exponentially. The reason for this is that at short times the relaxation of all modes are contributing to the relaxation of $\langle R^2 \rangle$. At long times the contributions of the faster-relaxing, higher modes die off, and only the first mode contributes to the decay. At very long times, statistical noise prevented meaningful data being collected from which to construct the autocorrelation function. The relaxation times were defined to be the inverse of the negative of the slope of the semi-log plots of the autocorrelation functions. This convention will be followed for all data generated for this work.

In a later paper,¹⁸ Verdier introduced the use of autocorrelation functions to study the relaxations of the eigenmodes (the normal coordinates). A coordinate transformation was used to convert the Cartesian coordinates of the beads, r_j , to normal coordinates, U_k , as is shown in Equation 30.

$$U_k(t) = (2/N)^{1/2} \sum_j r_j(t) \cos[(j-0.5)\pi k/N] \quad (30)$$

The autocorrelation functions for the relaxation of a chain's coordinates were then calculated using Equation 29 (p 23). From the autocorrelation functions, the relaxation

times of the normal modes could be obtained. Most of the dynamic measurements performed in this work are relaxation times obtained from the decay of the autocorrelation functions of the normal modes.

Verdier's first attempt¹⁸ to use the autocorrelation functions of the normal modes gave results which agreed with the Rouse Model in the absence of excluded volume. However, in the presence of excluded volume Verdier found that the autocorrelation functions of the normal modes did not decay exponentially. He concluded that the chains with excluded volume did not possess true normal coordinates. In another work Kranbuehl and Verdier¹⁹ observed that for chains possessing excluded volume, the relaxation times were proportional to the chain length to the 3.2 power. Both these observations were far different from the predictions of the Rouse Model and it was debatable if the inclusion of excluded volume alone could account for this.

Hillhorst and Deutch analyzed the Verdier and Stockmayer Model and arrived at an explanation of why the model gave such unexpected dynamics.²⁰ Qualitatively, their argument was that the local extrema of the chain in the x, y, and z planes could not pass each other using the bead movement rules of the model. Therefore, the only way for the chain's conformation to relax was for these extrema to diffuse out the chain's ends. This corresponds to the one-dimensional diffusion of hard particles and such motion has

a time scale on the order of the number of particles cubed. Hillhorst and Deutch suggested modifying the bead movement rules to include a two-bead, 90° crankshaft motion as shown in Figure 4 (p 28).

Kranbuehl and Verdier responded by constructing a model in which all motions were two-bead motions. The motions were the result of bond vector exchanges between the bonds connecting a two-bead section to the rest of the chain.²¹ In the presence of excluded volume they got results which were essentially the same as before. Boots and Deutch examined this model and determined that there were still traps which prevented structures within the chain from passing each other.²² Therefore, the only way for the chains to relax was for these structures to diffuse from the ends of the chains. Boots and Deutch suggested once again that such problems could be eliminated by a combination of two-bead crankshaft and one-bead motions.

Several authors eventually made use of a model somewhat similar to that suggested by Boots and Deutch. Using a combination of one- and two-bead motion Kranbuehl and Verdier^{23,24} obtained data for which the relaxation times were not proportional to the cube of the chain length but relaxed somewhat faster as chain length increased, although the effect of excluded volume still seemed somewhat larger than was anticipated. Statistical scatter and the varying of the rate and type of two-bead motions made their

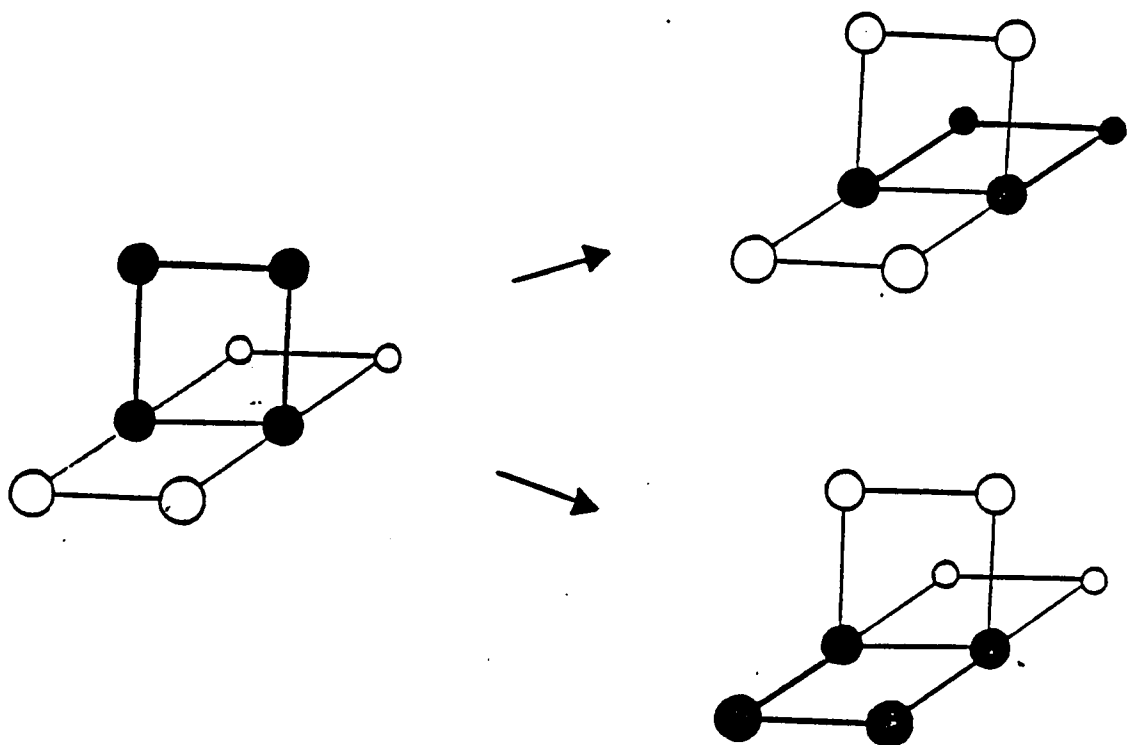


Figure 4. The 90° crankshaft motions.

results difficult to interpret.

In the latter paper of the two,²⁴ Verdier and Kranbuehl reported that the best fit for the data seemed to give a scaling law of

$$t = L^{2.6}. \quad (31)$$

More recently Verdier and Kranbuehl confirmed this scaling law for chains on body-centered cubic, face-centered cubic, and simple cubic lattices as well as for freely-jointed chains (i.e. chains not on a lattice where a two-bond segment can twist torsionally about a randomly selected angle).²⁵ All of these chains obeyed the excluded volume condition and possessed one- and two-bead motions.

The reason for the scaling exponent being unexpectedly larger than deGennes' prediction is that there were still unrealistic obstacles to the chain's relaxation due to the nature of the bead movement rules. The bead movements involved only motions which were the result of bond vector exchanges between the bonds connecting the bead or beads being moved to the rest of the chain. For example, in the simple cubic lattice, the crankshaft motion would thus be a 180° motion not the 90° recommended by Boots and Deutch. This meant that structures could not rotate out of the plane in which they lie. This was clearly not a reasonable restriction on an isolated chain's dynamics.

Other authors who modeled the dynamics of polymer chains using models involving one- and two-bead motions

found that the exponent relating the chain lengths and the relaxation times was greater than two but not as great as those observed by Verdier and co-workers. One of the more notable papers was written by Heilman and Rotne in 1982.²⁶ This paper was an extension of a rather obscure paper written by Heilman in 1968.²⁷ In his original paper, Heilman had used a combination of one and two bead moves long before it was suggested by Hillhorst and Deutch. In the latter paper, the authors found that in the presence of excluded volume the relaxation times scaled in a way which was consistent with the predictions of deGennes for chains possessing 90° crankshaft motion.

It is worth mentioning that some of the first dynamic simulations used a tetrahedral lattice. The Monte Carlo simulations using this lattice were pioneered by Monnerie and Geny.²⁸ They were interested in examining the motions of a chain at the atomic level as opposed to the longer range motions that most dynamic Monte Carlo studies were concerned with. The tetrahedral geometry of the lattice made it the obvious choice for such a study.

Assuming that bond lengths are fixed, the minimum length motion possible on a tetrahedral lattice would be a two-bead motion. It has become recognized that to get reasonable dynamics, it is necessary to include a three-bead motion.²⁹ This serves the same function that the crankshaft motion serves in the simple cubic lattice. Unfortunately,

there are no Monte Carlo simulations on this lattice which have examined the dynamic scaling properties of polymers so a comparison with this work is not possible.

This concludes the discussion of the previous models upon which the Monte Carlo simulations of polymer dynamics performed at the University of Tennessee are based. Before this work began a number of changes, tests, and modifications were made by previous workers within the University research group, and these efforts are reviewed in the next section.

E. Dynamic Monte Carlo Simulations for Single Chains

Performed at the University of Tennessee

In a paper published in 1982, Gurler and co-workers presented the results of Monte Carlo simulations which used a model with excluded volume along the lines of the one suggested by Boots and Deutch.³⁰ In this model, if an internal bead was selected for an attempted motion, then the angle formed by the bead and its bonded neighbors was examined. A linear conformation resulted in no attempted motion. However, if this was not the case, then a bond vector exchange was attempted between the bonds connecting the bead to the chain. If this move was not possible due to the excluded volume constraint then the local structure of the selected bead was analyzed. If the selected bead was found to be in a crankshaft structure then one of the two

90° crankshaft motions was randomly selected. The chain would then be moved to this position assuming the excluded volume condition was not violated. The motion of the end beads were the result of randomly selecting a bond vector from the next-to-end bead which was perpendicular to the bond vector connecting the end bead to the chain. The end bead would be moved to this location if the excluded volume condition was not violated. For programming simplicity, when a next-to-end bead was selected for an attempted motion, no crankshaft motion would be attempted.

The results of this simulation showed that the affect of excluded volume on dynamic scaling appeared to be fairly small. The times measured for the relaxation of the end-to-end distance scaled with the chain length in a manner similar to that predicted by deGennes. The scaling exponent measured was 2.13, close to deGennes' prediction of 2.2, but far from the value found in any of Verdier's results.

In a later paper, this model was used to examine the relaxation times for the normal modes of polymer chains.³¹ Unlike the studies of Verdier, these results showed that the autocorrelation functions of the normal modes decayed exponentially. The scaling exponent relating the relaxation times of a chain's normal modes and the mode number seemed to be around 2.15 for the longer chains ($L=35,47,59$) studied. This was slightly larger than the Rouse prediction of 2.0, and the reason for this was not known. When the

excluded volume constraint was removed this scaling exponent dropped to about 2.05.

While this model gave dynamical results which seemed fairly reasonable, it was still the object of some criticism. Romiszowski and Stockmayer³² objected to the use a bead cycle in which two different bead motions could be attempted during the same cycle, i.e. the crankshaft motion was attempted only after different motion was attempted and failed. Having two different motions during the same cycle could lead to an ill-defined and distorted time scale.

To examine this potential problem, a study was performed in which an internal bead was selected and a random choice was made as to whether its attempted motion was a two-bead crankshaft or a one-bead bond-vector exchange motion.³³ The relative probability of selecting a two-bead or one-bead motion was varied over a wide range. Except for the simulations with very high probabilities for two-bead motion, the scaling exponent relating the relaxation times of the end-to-end distance and the chain length was found to be about 2.14. This was not a significant difference from the earlier result.

The combined results did lend support to the idea that the model for the simulation gave reasonable dynamics and therefore could be used as a basis for more complicated simulations involving polymer dynamics. One area of great interest was (and is) highly dense systems. However, the

simple cubic lattice model appeared inappropriate for these systems. The reason for this is that at a high concentration, C , the probability of a successful one-bead motion would be proportional to $(1-C)$ while the probability of a successful two-bead motion would be proportional to $(1-C)^2$. Therefore, the crankshaft motion which was crucial to achieving reasonable dynamic motion would be preferentially frozen out at high concentrations. It seemed that developing simulations on lattices with higher coordination numbers would be necessary.

The face-centered cubic and body-centered cubic lattices both had the property that one-bead out-of-plane motions could be performed without changing the bond lengths between beads. The fact that this could not be done on the simple cubic lattice resulted in the necessity for two-bead crankshaft motions. These high coordination number lattices would also have the advantage of a well-defined time scale since only one-bead motions are performed. The development and testing of these models for single chains is one purpose of this thesis, and this effort will be discussed in later sections.

Aside from developing models appropriate for high concentrations, another item of interest is to develop simulations which involve interactions between chain segments over longer ranges. The previously discussed models had at most only two interactions. Firstly, the bond lengths

between beads were fixed. Secondly, the beads obeyed the excluded volume condition. For certain purposes it would be desirable to include interactions between beads which while spatially close together are far apart along the chain contour. These interactions could simulate the effects of the solvent and of temperature by causing chains with highly attractive interactions to contract and even collapse as temperature decreases.

Naghizadeh and Kovac have developed such a dynamical model using a simple cubic lattice.^{34,35} This model had a square-well potential between non-bonded beads. If two such beads occupied adjacent sites, an energy reduction occurred. The elementary motions were the same as the previously described model of Gurler et al.³⁰ This means that if a normal bead motion is not possible due to a violation of the excluded volume condition, then a 90° crankshaft motion will be attempted.

In this model each of the possible locations to which a bead or, in the case of the crankshaft motion, beads can move to, as well as the possibility of remaining at rest, will be assigned a Boltzmann factor. A random number is used to pick which of the possibilities will be accepted for the chain's new state. This procedure for selecting which elementary motions will be performed is different from the Metropolis method Gurler et al. used. Instead, it is an example of the generic Monte Carlo method discussed in

Chapter I, Section C (p 14). This method is also consistent with the Principles of Microscopic Reversibility and Detailed Balance.

This model showed that in good solvent conditions, the dynamics were in agreement with the bead-spring predictions of Equation 10 (p 11). The diffusion of the center-of-mass showed an expectedly sharp change at the theta point (defined as the point at which the attractive potential is great enough to cause the scaling exponent 2ν to decrease to its random walk value of 1.0). Below the theta point the collapsed chains diffused as if they were hard spheres. The dynamic properties of this model will be investigated further in this work.

Long range interactions such as those in the model described above have not often been included in dynamic Monte Carlo studies. However, interactions of this type have been included in a number of previous Monte Carlo simulations in which static properties of the chains were studied. Some of these simulations are discussed in the next section.

F. Previous Monte Carlo Simulations of Equilibrium Properties

A number of workers have been studied the properties of chains with non-bonded nearest-neighbor interactions on lattices or Lennard-Jones potentials for chains not

restricted to a lattice. These methods have included the use of different lattices and there is at least one notable off-lattice simulation. Different methods of generating chains have been used and different lengths of chains have been employed. Of all this data, what is most notable is that the only major difference in the observations is that resulting from simulations involving chains of greatly different length. Specifically, the effect of increasing the chain length seems to cause the chain to have a lower theta point, the temperature at which a chain's self-interactions offset the repulsive effects caused by the excluded volume condition. Thus, a chain at the theta point should resemble an ideal chain. Below is a brief summary of some of the more interesting articles and the observations of most importance to the present work.

Of the previous studies performed using Monte Carlo methods which allowed interactions between non-bonded beads, the first major studies were by Mazur and co-workers.^{11,36,37} These studies were also in greater depth than other studies and are of the most relevance to this work. The method used to generate chain conformations was a modification of the Rosenbluth walk.¹⁵ In this method a chain was grown from an initial bond vector. Each succeeding vector was added to the chain by examining the nearest-neighbors to the chain end and making a random choice between the unoccupied nearest-neighbor positions. If all

nearest-neighbor positions were occupied, the walk would be terminated and the process would start over. To obtain ensemble averages each walk had to be weighted according to how many unoccupied nearest neighbors there were to choose between at each step. Therefore the weighting, W , given a chain of length L would be

$$W = (q)^{-L}(n_1)(n_2) \dots (n_L), \quad (32)$$

where q is the coordination number of the lattice minus one and n_i is the number of unoccupied nearest neighbors for step i of the walk. Mazur and co-workers modified this method to include nearest-neighbor interactions. The method of doing so was exceedingly simple. The previously determined weighting of each chain was multiplied by the Boltzmann factor, B , which is given below.

$$B = \exp(ZE_p/k_B T) = \exp(ZE_r), \quad (33)$$

where E_p is the energy reduction resulting from the contact of non-bonded nearest neighbors and Z is the number of such contacts for the entire chain.

The studies of Mazur et al. examined a number of thermodynamic properties of chains and compared the simulation results with theoretical predictions for chains confined to a lattice. For this work the most important observations made involved examining the chain dimensions as a function of the coordination number of the lattice and as a function of the energy between pairs. In these simulations bonds were of fixed length and self-avoiding. The beads

interacted through a square-well, pair potential. This potential caused an energy reduction whenever two beads occupied adjacent positions. In their first paper,¹¹ Mazur and McCrackin reported that for a given value of the effective potential, $q \cdot E_r$, chains on the face-centered cubic and simple cubic lattices would have the same value for the static scaling exponent 2ν . For the chain lengths studied ($10 \leq L \leq 200$), the theta point occurred at $E_r = .14$ for the face-centered cubic lattice and at $E_r = .30$ for the simple cubic lattice. In a 1973 study^{35,36} for longer chains (L as great as 1000) these values decreased to .124 and .275 respectively. In these later reports, they also studied the mean-square radius of gyration, shown below.

$$\langle R_g^2 \rangle = N^{-1} \langle \sum_i (R_i - R_{CM})^2 \rangle \quad (34)$$

where R_i and R_{CM} are the coordinates of the bead i and the center-of-mass respectively. They found that the scaling exponent relating $\langle R_g^2 \rangle$ with L to be equal to 2ν in good solvent conditions. Guttman, their co-worker for these later papers extended these studies to include measurements of the hydrodynamic radius and cross-over behavior at the theta point.^{38,39}

Other authors have performed similar studies. In a Monte Carlo simulation aimed at investigating the second virial coefficient at the theta point, Janssens⁴⁰ reported a theta point for $E_r = .27$ as the asymptotic limit extrapolated for infinitely long chains. This was determined

from chains of length 10 to 40 beads lying on a simple cubic lattice. Unfortunately he was not very clear on how the simulation was performed.

Olaj and co-workers wrote a series of articles⁴¹⁻⁴⁴ dealing with the pair distribution function and the shapes of chains at the theta point as a function of concentration and/or distance between the centers of mass of isolated chains as they were brought together. In these simulations, both chains possessed a non-bonded nearest-neighbor interaction between the beads irregardless of what chain the neighbors belonged to. The simple cubic lattice was used. Individual chain contours were generated by a Metropolis method in which the smaller end of the chain was rotated about a randomly selected bond. This was done for four-way chains (i.e. chains in which the bond angles are always 90° and hence four possible directions at each step of the walk) and five-way chains (in which a 180° angle is allowed). Olaj found for four-way chains that the theta point occurred at about $E_r=.27$ although he did not state the length of the chains used to determine this. For five-way chains of length as large as 400 beads, he also found the theta point at $E_r=.27$. In his later studies, he assumed the theta value to be $E_r=.265$ for four- and five-way chains. It is possible that this assumption introduced an error into his results.

Curro and Schaefer⁴⁵ also studied chains with non-bonded nearest neighbor interactions. The chains were

generated using a slithering snake method.¹⁴ This method involves selecting a bead at the end of the chain. A random bond vector is added to this end of the chain and the last bond on the opposite end of the chain is eliminated. Whether this new conformation is accepted is determined by its energy difference with the original conformation in the manner of a Metropolis processes. Using a simple cubic lattice and chains of length as great as $L=299$, Curro and Schaefer found the theta point at $E_r=.28$. Their most important observation involved the observation of internal expansion within chains. They found that above the theta point, the length per monomer of a short chain segment was greater than that of the chain as a whole. This the opposite of what deGennes predicted in his blob model,⁷ but is in agreement with the predictions Fixman obtained using perturbation theory applied to the interior segments of a polymer chain.⁴⁶ In the arguments of Fixman, repulsion between the chain ends caused a repulsive perturbation which caused interior segments to expand beyond the size the segment would have if it were isolated and was not connected to other segments.

Kremer and co-workers⁴⁷ performed a simulation with nearest-neighbor interactions on a tetrahedral lattice and compared their results to those of Curro and Schaefer. To generate chains they used three different methods; a random walk which aborted whenever the excluded volume condition

was violated, a slithering snake method, and a dynamical technique involving crankshaft-like twists of randomly selected three- and four-bond internal sequences of beads. The weight of each chain in the ensemble was then determined by its Boltzmann factor. The theta point was extrapolated to occur at $E_T = .444$ for an infinitely long chain. They found cross-over behavior consistent with the blob model.^{7,9} The width of the theta region decreased as $L^{-1/2}$, which is in agreement with renormalization predictions. What differences they observed from the blob model they felt could be explained by the fact that the blob model assumes infinitely long chains. Kremer and his co-workers wrote that, in their opinion, the internal chain expansion which Curro and Schaefer observed was probably the result of local chain stiffness and the finite length of the chains used. These features would disappear for extremely long chains.

Another Monte Carlo simulation of this sort was performed by Webman, Lebowitz, and Kalos.⁴⁸ Their method used chains made of vectors which were not constrained to a lattice. These chains were constructed by a slithering snake method where a randomly selected vector was added to the end of the chain while a segment was removed from the other end. The vectors were added to a randomly selected chain end. This vector could be of fixed length to give a chain made of rods, or the length could be variable. For the chains with variable lengths, each segment was given an energy

corresponding to the extension of a spring. For both types of chains, non-bonded beads interacted via a Lennard-Jones potential. New chain conformations were accepted to replace the old according to the Metropolis scheme. The authors found that at the theta point the collapse of chains behaved in a similar manner for the different types of chains. As the temperature was decreased the collapse was more rapid for larger chains. In fact, their plot of the collapse appeared very similar to one given by Mazur and McCrackin obtained from lattice simulations.¹¹ These results seem to confirm that the static behavior of polymers is not distorted by lattice models.

A recent study of this type was performed by Kolinski, Skolnick, and Yaris.^{49,50} The study was conducted using chains of lengths from 100 to 800 units lying on a tetrahedral lattice. Chain conformations were generated by taking an existing chain and attempting either a snake-like motion from one of the ends, a rotation of the last two beads of the chain, or a crankshaft-like motion of a randomly selected internal segment. Whether this new conformation was accepted as the new chain conformation was determined by the Metropolis procedure. In Reference 47, an energy difference between gauche and trans states was included in addition to a non-bonded nearest-neighbor interaction. It was found that the collapsed chains had very different forms depending on how strong the preference for

the trans state was. If the preference was strong, the collapsed chain consisted of long linear segments with occasional sharp folds. When the preference was weak, the chain appeared to be a disordered collapsed Gaussian coil. In the second article, Reference 48, no preference was given to trans states. By extrapolation the authors found the theta point to be approximately $E_p = .47k_B T$ for infinitely long chains. They also found that the theta point of a given chain fit the equation,

$$k_B T_L / E_p = c_1 L^{-1/2} + c_2, \quad (35)$$

where T_L is the theta point as determined for a chain of length L and c_1 and c_2 are constants. This is in agreement with the theoretical predictions of Duplantier, Jannick, and desCloizeaux.⁵¹

All of the above works give somewhat similar results when allowance is made for the fact that different chain lengths and lattices are used. The data appears quite consistent if one remembers two observations: one, the observation of Mazur and McCrackin that the scaling exponents obtained on different lattices are equal for a given value of $q^* E_r$, two, that the theta point is not independent of chain length.

This concludes the review of Monte Carlo studies of static properties of polymers. The next section is devoted to Monte Carlo studies of the dynamic properties of concentrated systems. Although this work involves

simulations of isolated chains, which have already been reviewed, the literature concerning the dynamics of more concentrated solutions is worth mentioning since the models developed here may be useful in simulating dense systems. Such systems have little if any solvent interaction. Therefore, simulations such as these in which the solvent is ignored may be appropriate.

G. Monte Carlo Simulations of the Dynamics of Concentrated Systems

The dynamics of polymers in concentrated solutions are quite different from the dynamics of dilute solutions. In the melt, the viscosity (and presumably the relaxation times) are proportional to the length of the chains raised to the 3.4 power for chains above a critical molecular weight. The best theoretical description for this property has been developed by deGennes.⁵² deGennes assumes that the motion of a polymer chain in a melt is similar to that of a single, mobile chain in a network of closely spaced, fixed obstacles. This confines the chain's net movement to be along its contour. This means that local structures within the chain can only be removed by the diffusion of these structures to the ends of the chain. This is essentially the same one-dimensional diffusion which was observed by Verdier and Kranbuehl in their simple cubic lattice model. Such diffusion takes place on a time scale proportional to the

chain length cubed.

Doi and Edwards have attempted to modify deGennes' original theory to take into account small motions perpendicular to the chain's path and the fact that the ends of the chain are more mobile than the central monomers.⁵³ The proposed modifications also attempt to take into account the mobility of the chains which form the cage that confines the chain to motions along its contour. These modifications attempt to make the model more self-consistent and explain the larger chain length dependence of viscosity than that given by deGennes' original model.

The model of deGennes and its subsequent modifications is referred to as the reptation model since the motion of the chain resembles that of a snake sliding through a tube of fixed obstacles. One of the major successes of the model is its correct prediction of the relation between chain length and the center-of-mass diffusion coefficient. The diffusion coefficient is defined by

$$D_{CM} = \langle (C_m(t) - C_m(0))^2 \rangle / 6t \quad (36)$$

where C_m is the position of the center-of-mass. In concentrated systems it is found that D_{CM} is inversely proportional to chain length squared, which is what deGennes' theory predicts. One signature feature of the reptation model is the prediction for the behavior for the mean-square displacement of a central monomer within the

chain. For the i 'th monomer this is defined as

$$g_i(t) = \langle (R_i(t) - R_i(0))^2 \rangle. \quad (37)$$

For an isolated chain obeying Rouse dynamics,

$$g_i(t) \sim t^y \quad (38)$$

where $y=1$, $1/2$, and 1 respectively for increasingly long times. The reptation model predicts that at high concentrations the intermediate region will be broken into three regions in which $y=1/2$, $1/4$, and $1/2$ for increasingly long times respectively. Observing a region in which $y=1/4$ would be important evidence for reptation dynamics.

Unfortunately, making such an observation experimentally would be quite difficult, although deGennes claims to have seen some experimental evidence for it.⁵⁴ Several computer studies have been conducted trying to find evidence of reptation in the dynamics of the simulation. Only a few proved to have relevant information. Most had movement rules that in one manner or another cast doubt on their validity. Typical problems with such simulations were movements rules which biased the chain towards reptating motions or rules in which the excluded volume condition was not always enforced. However, there are a few studies worth mentioning.

The first of these studies was conducted by Baumgartner and Binder⁵⁵. Their simulation involved ten chains of 16 beads packed tightly in a periodic box. The chains interacted through a Lennard-Jones potential and were

self-avoiding. The temperature and concentration were varied. The data did not show evidence of reptation for the mobile chains, even when the chains' mobility dropped to zero and a glassy state was formed. One possible problem with this study was that the chains were very short and possibly not very entangled. Within this study, they also examined the dynamics of a single mobile chain moving among fixed immobile chains. In this simulation, they observed a region in which $y=1/4$.

Kremer⁵⁶ conducted a simulation on a diamond lattice using self-avoiding chains of 200 beads with a concentration of 34.4% of the lattice sites filled. Although he showed that the chains were quite entangled he found no evidence for reptation. When he studied the movement of one chain in the presence of fixed chains he obtained data for $g_1(t)$ consistent with reptation.

Crabb and Kovac have performed dynamic Monte Carlo simulations of dense systems.⁵⁷ Originally, they used a simple cubic lattice with the same movement rules as Gurler, et. al.³⁰ They varied chain length between 12 and 48 beads. The concentration was varied up to 90% occupancy. Two scaling exponents were obtained. One was the scaling exponent relating chain length and the relaxation time of the end-to-end vector, t_R , where

$$t_R = \langle R(t)R(0) \rangle / \langle R^2 \rangle. \quad (39)$$

The scaling law is

$$t_R \sim L^w. \quad (40)$$

t_R should be approximately equal to the relaxation time of the first normal mode at long times since at these times only the slowest relaxation process is contributing to the motion of the chain ends. The other scaling law related the center-of-mass diffusion coefficient with the chain length according to

$$D_{CM} \sim L^h. \quad (41)$$

Crabb and Kovac found that at a concentration of 90%, $w=2.7$ and $h=1.68$. Both the values are quite different from those found for dilute solutions, but are still not very close to that predicted by the reptation model. The data obtained for $g_i(t)$ indicates deviations from dilute solution behavior, but a range in which $y=1/4$ was not observed. One possible problem with this study is the use of relatively short chains.

In a later study Crabb, Kovac, and co-workers⁵⁸ found the relaxation times for the normal modes for chains at high concentrations on both the simple cubic and the face-centered cubic lattice. At 90% concentration, the $a(k)$ values for the face-centered cubic lattice were only about 2.5. This low value indicated that reptation was not taking place and that the higher values of $a(k)$ obtained for the simple cubic lattice in this study were probably due to the low probability of successfully performing a two bead motion at high concentration.

In another study performed at the University of Tennessee, Naghizadeh and Kovac studied an entangled system.⁵⁹ Mobile chains of up to 48 beads were placed in an array with obstacles which consisted of lines lying along the x, y, and z axes. For self-avoiding chains in an array of fixed, regularly spaced obstacles separated by three bond lengths, they found $h=3.34$ and $w=2.12$. This is in good agreement with the reptation model. When the obstacles were allowed to move the dynamics were similar to those of a dilute solution.

The most thorough dynamic Monte Carlo study of dense systems performed to date is the work of Skolnick, Kolinski, and Yaris.⁶⁰ The first of their studies involved chains of 49, 98, and 147 beads lying on a tetrahedral lattice.⁶¹ As concentration was increased, they found a region in which $y < 1/2$. As the concentration was increased, y decreased in this region until at 92% concentration $y=0$. This indicated that a glassy state had been formed. In a later study using the tetrahedral lattice,⁶² they reported that $h=2.06$ and $w=3.36$ at 75% concentration and for chains up to 96 beads long. These values are in good agreement with experimental work, but they found that chains' motion in dense systems showed no preference for motion along its contour. Instead the chain moved in an isotropic manner. They later confirmed this observation for longer chains (up to 800 beads) lying on a simple cubic lattice at 50% concentration.⁶³ In this

study they also found $h=1.52$ and $w=2.63$ for chains of up to 216 beads. They also studied the effect of increasing the length of mobile, solvent chains in which a solute chain was allowed to move.⁶⁴ They found the probe chain's diffusion rate was slowed in a manner consistent with experimental data.

In another study of dense systems, they investigated the static properties of densely packed chains on a tetrahedral lattice in which varying degrees of preference were given for trans vs. gauche conformations.⁶⁵ Local ordering was observed to increase with increasing chain stiffness. A study of static properties involved tetrahedral chains of 12 or 24 beads at concentrations of 50% and 75%.⁶⁶ It was found that increasingly attractive nearest-neighbor interactions between non-bonded beads lead to a transition from an isotropic to anisotropic state. This agreed with previous work by Baumgartner⁶⁷, but Baumgartner's study only allowed favorable interactions between parallel bonds and so was not as general as the study of Skolnick and his co-workers.

The only study involving a tightly coiled chain also deserves mention here. Baumgartner studied freely-jointed, self-avoiding chains of up to 64 beads which interacted through a Lennard-Jones potential.^{68,69} Two bond segments were moved by rotation about a randomly selected angle according to a Metropolis procedure. Although he was mainly

interested in static properties, he did report that the density fluctuations of the chains were consistent with Bead-Spring models above the theta temperature but not below. At very low temperature he found an apparent glass transition. In the glassy state, he reported observing $\gamma=1/4$ at intermediate times. Baumgartner's study is particularly notable for two reasons. First, it is the only Monte Carlo simulation in which reptation-like dynamics has been observed where all occupied lattice points are filled by mobile beads. Second, it is the first dynamic study in which longer range interactions are considered. In fact prior to this work reported in this thesis, the only other dynamic Monte Carlo simulation employing interactions with a longer range than the excluded volume interaction was that of Naghizadeh and Kovac.^{34,35} By the use of such interactions, temperature effects could be studied.

Pakula⁷⁰ and Pakula and Geyler^{71,72} have studied dynamic properties of dense systems by a unique Monte Carlo technique known as cooperative relaxations. In this method, all lattice sites are filled and the only possible motions are from the simultaneous, cooperative motions of beads. For long chains of 512 beads, Pakula and Geyler⁷¹ found that the scaling exponent, γ , had a minimum value at intermediate times of .43. This was significantly less than $1/2$, the value expected for Rouse chains, but was still not very close to $1/4$, the value predicted for reptating chains. The

data did show that the values of the center-of-mass diffusion constant for long chains did show good agreement with the scaling predictions of the reptation model. They also found that cyclic chains had essentially the same self-diffusion properties as linear chains.⁷².

This concludes the discussion of dynamic Monte Carlo simulations of dense systems. The following section briefly reviews experimental methods of observing polymer dynamics in dilute solutions. Before proceeding there are a couple of computer simulations of dense systems which deserve mention at this time.

Kremer and co-workers^{73,74} have performed a Brownian Dynamics simulation on densely packed polymers. The chains interacted through a Lennard-Jones potential and were also subjected to white noise. For 20 chains of 150 monomers and 85% concentration, the authors found $\alpha(1)=3$ and a region for which $\gamma=1/4$. Both of these observations are in good agreement with the reptation model.

This same method was used to study the scaling law which relates relaxation times of the end-to-end vector of the arm of a star polymer (a polymer with a number of linear strands connected at approximately the same point) with the number of arms.⁷⁵ The authors found good agreement with the Daoud-Cotton blob model,⁷⁶ which predicted little change in the relaxation times as the number of arms increased. Despite the apparent success of this Brownian Dynamics

method, it is doubtful that Brownian Dynamics will replace Monte Carlo studies in this field as this study took a huge amount of super computer time.

H. Comparison with Experiment

Before proceeding, it is appropriate to note that experimental results have shown good agreement with bead-spring models. It is well known that polymers in a good solvent obey the static scaling law, Equation 14 (p 11). This has been confirmed by light scattering, measurements of the viscosities of dilute solutions, and photon beat methods.⁷ These methods give slightly different values for the scaling exponent 2ν , but all are very close to the bead-spring prediction for three dimensions of $2\nu=6/5$.

The dynamics of a chain are harder to observe, but there have been studies confirming the usefulness of the bead-spring description. To describe the dynamics of a polymer in a dilute solution, it is necessary to include hydrodynamic interactions. This requires the use of Zimm's methods. Ferry's monograph, Viscoelastic Properties of Polymers,⁷⁷ gives a number of light scattering studies of viscoelastic dynamics which show, at least indirectly, good agreement with Zimm's theoretical approach for dilute solutions.

Recently new methods of investigating polymer dynamics have appeared which show some promise in solving

problems associated with older methods. These methods involve attaching chromophores to a polymer, exciting these chromophores, and then observing the emissions or absorptions of the chromophores. These methods can precisely probe the motions of small chain segments. Previous methods have been unable to do this.

Austin and co-workers have attached chromophores to DNA strands and then excited these strands with polarized light.^{78,79} The changes in the chromophores' anisotropic absorption with time is then used to determine the motions of the strand. Over long ranges and short time frames, the resulting dynamics showed good agreement with Barkely and Zimm's treatment⁸⁰ of a stiff chain. The Barkely-Zimm theory is essentially Zimm's bead-spring model with the inclusion of terms which account for a chain's stiffness to bending.

Winnik and co-workers have used a similar method to study the rates of end-to-end cyclization for polystyrenes of various lengths.^{81,85} To determine the rate of cyclization, Winnik attaches pyrene chromophores to the chain ends. The chromophores are then excited. If the chromophores make contact, an excimer is formed. Assuming the reaction mechanism is correctly determined, the rate at which the excimer is formed can be used to determine the rate at which cyclization occurs.

The cyclization reaction takes place at long ranges and over long time frames. Therefore, only the lowest mode

should be contributing to the motions resulting in cyclization. In the presence of strong hydrodynamic forces, Zimm's theory predicts

$$t_1 \sim L^{3/2} \quad (42)$$

and

$$D_{CM} \sim L^{-1/2} \quad (43)$$

The presence of strong hydrodynamic forces cause the scaling exponent $a(k)$ to drop by $-1/2$ from the values predicted by the original Rouse model in which hydrodynamic forces are ignored, i.e. $a(k)=2$. Likewise, the scaling exponent e increases by $1/2$ from -1 to $-1/2$. It seems logical to describe the decrease in t_1 due to solvent effects in terms of D_{CM} , especially since D_{CM} is a measurable quantity. Therefore, we rewrite Equation 10 (p 11) as

$$t_1 \sim L^{2v}/D_{CM} \sim \langle R^2 \rangle / D_{CM} \quad (44)$$

Using values of $\langle R^2 \rangle$ and D_{CM} obtained from literature, Cuniberti and Perico⁸⁶ find that Winnik's cyclization results of Reference 76 for different chain lengths show scaling in good agreement with the Zimm's theory.

In two more recent papers, Winnik and co-workers have studied the effect of excluded volume on the rate of cyclization.^{89,90} The results were consistent with the assumption that chains at the theta point had a distribution for R which was much closer to being Gaussian than chains which were in a good solvent. Overall, the work of Winnik and his co-workers seem to give results consistent with

bead-spring theories.

However, the scaling results for cyclization kinetics obtained by Horie and co-workers for the same polymers gave very different results.^{81,82} Much of their data could not even be fit by a simple scaling law. To obtain their data, Horie's group used a chromophore which when excited formed a triplet. When triplets met annihilation occurred. By following annihilations, the cyclization rate could be determined, but to do so the assumed mechanism had to be correctly assigned. It was the judgment of Cuniberti and Perico that this was the potential problem in the data of Horie and his co-workers.⁸⁶

These new methods involving the use of chromophores to study polymer dynamics promise to be a great improvement over older methods to examine short range polymer dynamics. This is not to say that there are not potential difficulties. We have already seen that the mechanism of the excitations must be correctly assigned to get the proper results. It is also necessary to use very dilute solutions so that intermolecular interactions do not effect the results. Winnik has pointed out other potential problems.⁸³ The molecular weight distribution must be small. The chains' ends must be close to 100% substituted with the chromophore, and fluorescent impurities must be eliminated. Some of these problems invalidated Winnik's earliest reported results.⁸¹ Despite these problems this type of method is a great leap

forward in experimental methods of examining polymer motions. Still it is unlikely that these methods will make Monte Carlo studies of dynamics obsolete in the immediate future.

This concludes the review of literature of particular interest to this thesis. For readers interested in a broader overview of Monte Carlo studies of polymer properties there is a recent review by Kremer and Binder which discusses most of the more common Monte Carlo techniques and some of the more interesting results.⁹¹ In the following chapter, the Monte Carlo lattice models to be used in this work will be discussed in detail. The methods of obtaining relaxation times is also discussed.

CHAPTER II

MODELS AND CALCULATIONS

A. Introduction

In this chapter the simulation models used in this work will be discussed in detail. The first two models are a face-centered cubic and a body-centered cubic lattice models designed to closely resemble the previously developed simple cubic lattice model.³⁰ These models simulate polymer dynamics under athermal solvent conditions only, i.e. conditions where all allowed conformations of the chain have equal energy (probability) and therefore the properties are not temperature dependent. The models with this property will be referred to as athermal models.

The models will be tested to see if they can reproduce the scaling behavior of the SC lattice model for simulations with and without the excluded volume restriction. If they can, this will help confirm the appropriateness of using these lattice models to simulate polymer dynamics. One advantage of these two models is that they require only one-bead elementary motions to achieve the out-of-plane motions that were necessary for reasonable dynamics in the simple cubic lattice. It is especially important to develop such models for studies of dense systems since at a high concentration, C , two-bead motions would be successfully performed at a rate proportional to

$(1-C)^2$ while the one-bead motions would be performed at a rate of $(1-C)$. The effect of this on the dynamics may invalidate the data obtained.

After the two new models are developed, more complex models will be developed to include more complicated self-interactions. Most previous studies of polymer dynamics have studied polymers under athermal conditions. Under these conditions the only self-interaction is the excluded volume requirement which prohibits the double occupancy of a site. Polymer behavior under other conditions such as in the region of the theta point is of extreme interest, but with the exception of the studies by Naghizadeh and Kovac^{34,35} and Baumgartner^{68,69} thermal solvent effects on dynamics have not been examined by simulations.

In order to simulate thermal conditions, it is necessary to include longer range self-interactions. Studies of static properties have used both square-well and Lennard-Jones potentials to do this. The similarity of the results obtained for these two potentials means that the simpler square-well potential should be sufficient to provide the longer range self-interactions. The models used in this work have square-well, pair interactions which are capable of simulating thermal solvent effects, by creating a net attraction (or repulsion) between non-bonded beads of the chain. This potential will cause the polymer chain to contract as the attractive interaction increases (or

temperature decreases), thus simulating the effect of an increasingly poor solvent. Therefore, these models will be referred to as the thermal models. The details of the individual models will be given in the following sections.

B. The Athermal Face-Centered Cubic Lattice Model

Preliminary work on the athermal face-centered cubic model was performed by Crabb.² A number of modifications of the Crabb's computer algorithm were made in this work to simplify the code of the simulation. The model is constructed as follows. The beads of the chain are placed on the vertices of a FCC lattice. A typical chain contour is shown in Figure 5 (p 62). The lattice points are located in a periodic box described by a large array of memory. In the FCC lattice model, the vectors from one lattice point to its twelve nearest neighbors are $(\pm 1, \pm 1, 0)$, $(\pm 1, 0, \pm 1)$, or $(0, \pm 1, \pm 1)$. Choosing vectors between neighboring lattice points in this manner ensures that position vectors of the beads of the chain can be determined by integer arithmetic.

The elementary motions are performed as follows. First, a bead is chosen at random. If it is a bead on the end of the chain, then one of the other eleven lattice sites which are nearest neighbors of the next-to-end bead is chosen at random. In the presence of excluded volume, this location is analyzed to see if it is already occupied, if not then the end-bead is moved to this new location.

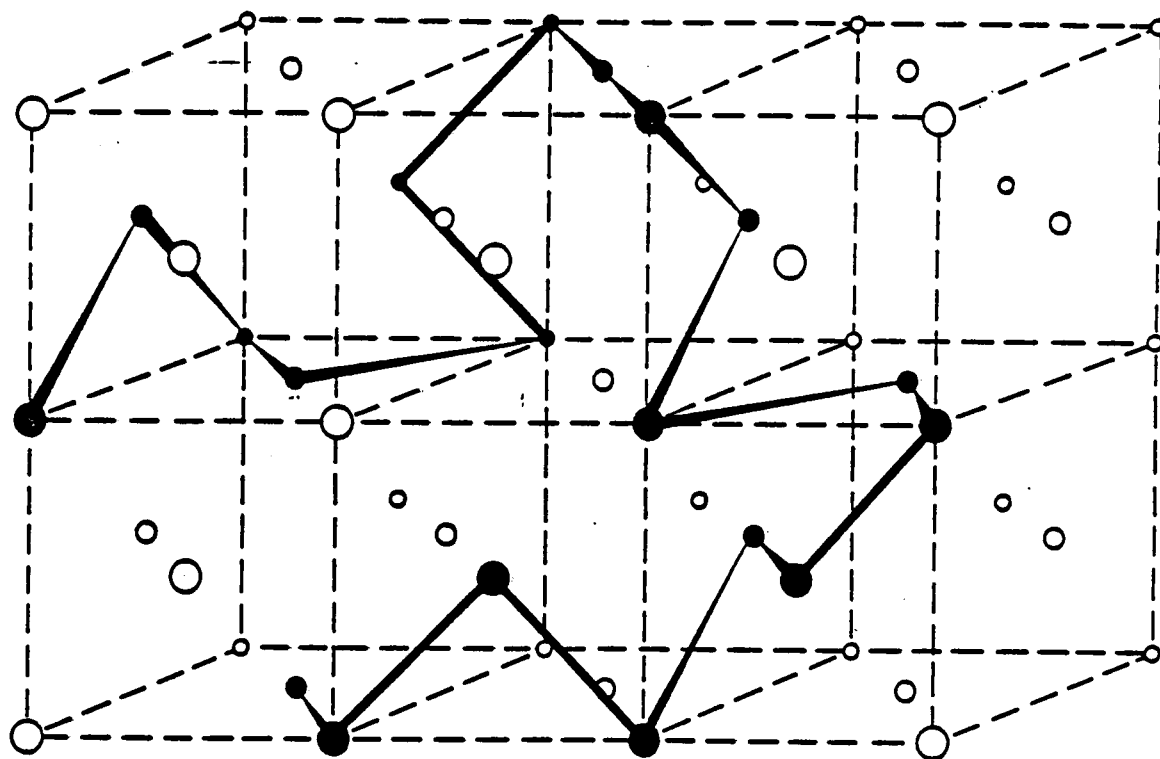


Figure 5. The contour of a typical chain placed on a FCC lattice.

If an interior bead is chosen, its conformation in relation to the two beads with which it is bonded is determined. In the presence of excluded volume the two bonds can form four different angles: 60° , 90° , 120° , and 180° . The elementary motions possible depend on the bond angle. If the angle is 180° the bonds are collinear and no motion is possible since all the models used in this work have fixed bond lengths. If the angle is found to be 180° , the attempted motion of the bead is abandoned. If the bond angle found is 120° then the only allowed motion which will maintain the fixed length of the bonds is a bond vector exchange between the bead's bonded neighbors as is shown in Figure 6 (p 64). This is analogous to the normal bead motion of the SC lattice model discussed in the previous chapter. If this position is unoccupied the bead is moved to the new location. If it is not, the attempted motion is abandoned.

Both the 60° and 90° angles have a greater number of possible moves. In both cases, the bead may undergo a bond-vector exchange type motion in the manner of the 120° bond. Both conformations also allow out-of-plane motions that are roughly analogous to the crankshaft-like motions of the simple cubic lattice model. When a 60° or 90° angle is found a random choice is made between one of the three possible sites to which the bead could move. The site selected is then checked for the excluded volume condition and if the site is unoccupied the bead is moved. Otherwise the



Figure 6. The motion of a bead in a 120° angle conformation for a chain on a FCC lattice.

attempted motion is abandoned. The possible motions of the 60° and 90° degree conformations are shown in Figure 7 (p 66).

If excluded volume is not considered, then the only change in the above rules is that the occupancy of the site chosen for the bead's new location is not considered. Therefore, the bead is moved to the selected location irregardless of the occupancy of the site. Without excluded volume, there is also the possibility of a spike conformation in which the bonds to a bead form a 0° angle. The attempted motion of a bead in a spike conformation is treated in the same manner as an end bead.

From the above movement rules it can be seen that this simulation can be thought of as a Metropolis method in which there are only two energy levels. One energy level is infinite. This level occurs for states in which the excluded volume condition is violated. All other states have the same energy. In this simulation, when there is a choice between two states with the same energy (the original and the selected state), the new state is always preferred and the transition to the selected state takes place.

This concludes the discussion of this model. The data and dynamic properties obtained for this model will be discussed in the next chapter. In the next section the athermal body-centered cubic model will be discussed.

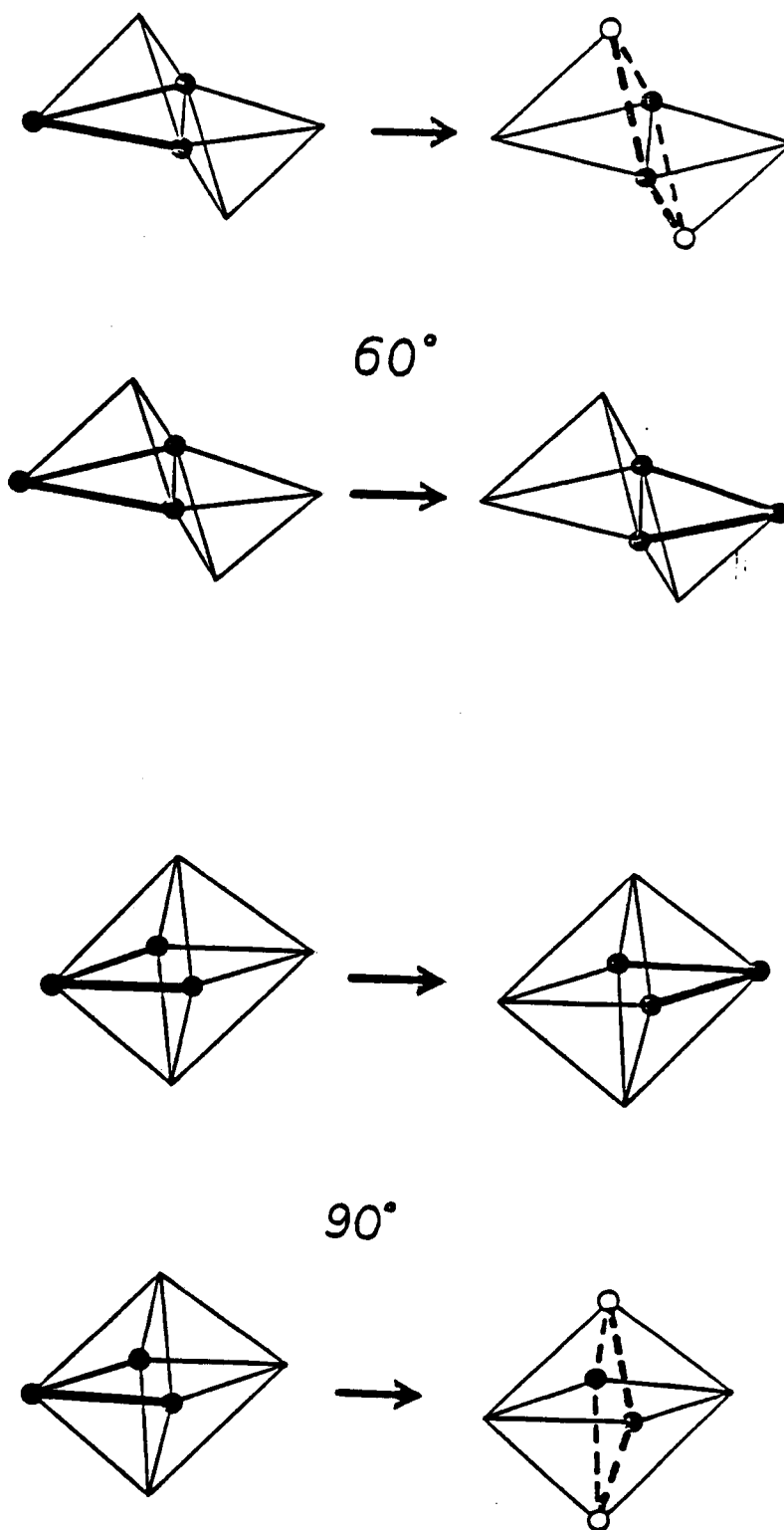


Figure 7. The possible motions of a bead in a 60° or a 90° angle conformation for a chain on a FCC lattice.

C. The Athermal Body-Centered Cubic Lattice Model

This model closely resembles the FCC lattice model. The beads of the chain are placed at the vertices of a body-centered cubic lattice. The vectors between a lattice point and its eight nearest neighbors are $(\pm 1, \pm 1, \pm 1)$. This choice ensures that the components of a vector between any two lattice points will be integers. A contour for a typical chain, placed on a BCC lattice and obeying the excluded volume constraint is shown in Figure 8 (p 68).

The elementary motions occur as follows. First a bead is chosen at random. If it is an end bead then one of the other seven locations which are nearest-neighbors of the next-to-end bead is chosen at random. In the presence of excluded volume, the position is checked to see if it is occupied. If it is, the attempted motion is abandoned. If not, the bead is moved to the new location.

If the selected bead is an internal bead then the angle formed by the bonds with its neighbors is either 60° , 120° , or 180° . If the angle is 180° , then no motion is possible. If the angle is 120° , then the only motion possible is a bond vector exchange. This is identical to the 120° motion of the FCC lattice shown in Figure 6 (p 64). When the bond angle is 60° , there are three possibilities. These possibilities are shown in Figure 9 (p 69). One is a bond vector exchange and the other two are out-of-plane motions. This out-of-plane motion allows new bond vectors to

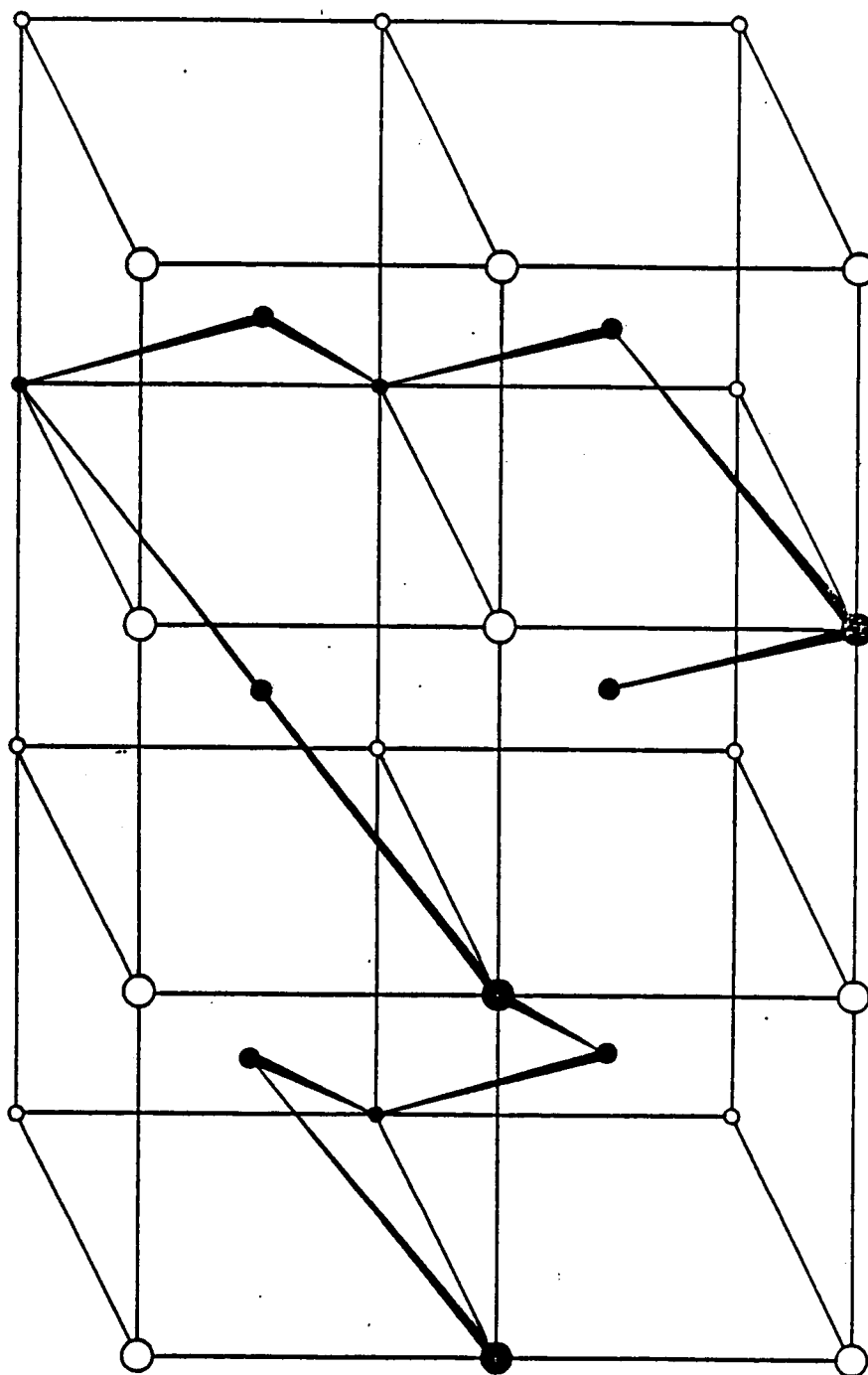


Figure 8. A typical contour for a chain placed on a BCC lattice.

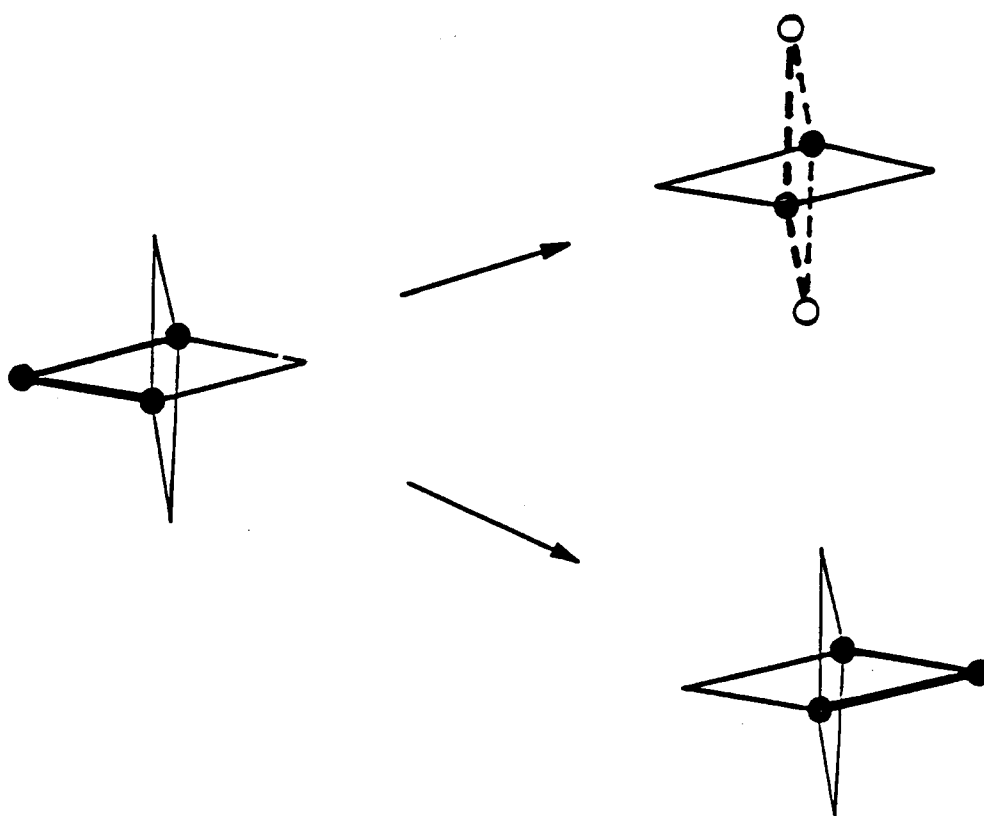


Figure 9. The possible motions of a bead in a 60° angle conformation for a chain placed on a BCC lattice.

be created in the chain's interior. This serves the same purpose as the crankshaft motion in the simple cubic lattice model. When a 60° angle is found, a random choice is made between one of the three possible locations to which the chain may be moved. Next, the occupancy of the selected site is analyzed. If the site is vacant, the bead is moved. If not the attempted motion is abandoned.

If excluded volume is absent, the occupancy of a selected site is not examined and the bead is moved to the selected location. Without excluded volume, there is the possibility of a 0° angle. If a bead selected for an attempted move is found to be in this conformation, the attempted motion will be treated in the same manner as an end bead. As was the case of the previously discussed FCC lattice model, the attempted motions of this model can be thought of as a Metropolis process in which all attempted motions between states of equal energy are accepted. Without excluded volume, every possible motion leads to a state of equal internal energy. In the presence of excluded volume, the possible motions may lead to one of two energy levels. Any state in which the excluded volume condition is violated has an infinite energy, and therefore motions that create such a state are rejected.

This concludes the discussion of this model. The calculations and dynamics for this model can be found in the next chapter. The following sections describe the thermal

models.

D. The Thermal Lattice Models

The thermal models used in this work are all modifications of athermal models. These models use the same elementary motions as the athermal models. The elementary motions of the athermal FCC and BCC models have been described in Sections B and C above. The elementary motions of the thermal SC model are based on the athermal model of Gurler et al.³⁰ which was discussed in Chapter I, Section 5. The thermal SC model used in this work was recently developed by Naghizadeh and Kovac.^{34,35} The thermal FCC and BCC models developed for this work were patterned closely after the Naghizadeh and Kovac model.

There are two major modifications made to the athermal models. One is the inclusion of a square-well potential between non-bonded bead pairs. The potential, $V(r)$, has the property

$$\begin{aligned} V(r) &= 0 & , & & r > l_0 \\ V(r) &= -E_p & , & & r = l_0 \\ V(r) &= \infty & , & & r < l_0 \end{aligned} \tag{45}$$

where l_0 is the bond length. The last condition indicates that the excluded volume condition is in effect. E_p is the reduction in the chain's energy resulting from each bead pair contact. When a bead is selected for an attempted motion, its conformation is examined as was the case with

the athermal models. Next, the possible motions allowed by the chain's conformation are identified. The energy which would result for each of the possible motions is calculated by finding the number of bead pair contacts. Each of the positions to which the bead (or in the case of the crankshaft structure beads) may move as well as that of the original position is given an unnormalized probability corresponding to a Boltzmann factor, P_i . P_i is set to be zero if the excluded volume condition is violated. Otherwise,

$$P_i = \exp(z_i E / k_B T) \quad (46)$$

where z_i is the number of bead pair contacts which would be made by the bead(s) involved in the attempted motion assuming the bead(s) in question is(are) placed in position i . In the athermal models one of the possible positions would be chosen randomly and the choice of whether to move the bead to this location would be determined in a Metropolis procedure (the motion would be made unless the excluded volume condition was violated). For the thermal models, the choice of which position will be selected follows the generic Monte Carlo procedure outlined in Chapter I, Section C (p 14). The choice between the allowed positions (including the original position) is determined by the use of a random number X chosen such that

$$0 < X < \sum_i P_i \quad (47)$$

If

$$P_1 + \dots + P_{j-1} < Z < P_1 + \dots + P_j \quad (48)$$

then the chain is moved to position j . This selection method is consistent with the Principle of Detailed Balance. This concludes the section on the elementary motions of the thermal models. In the next section, the methods of studying the dynamics are described.

E. Calculations

The properties of the chains are studied by the use of samples of the chain coordinates taken at regular intervals. Between 20,000 and 30,000 samples will be collected for each computer run. For most of this work the sampling interval is chosen to correspond to a decay of about 0.7% in the autocorrelation function of the first mode. For the work involving highly collapsed chains the interval will be increased to $(N/12)^2$ bead cycles. The autocorrelation functions of the modes are calculated from the chain coordinates by the equation below.

$$F_k(t) = \langle U_k(t)U_k(0) \rangle / \langle U_k(t)^2 \rangle \quad (49)$$

where U_k is the k 'th normal coordinate defined by Equation 30. The autocorrelation function of the mean end-to-end vector is calculated in a similar manner as is shown below.

$$F_R(t) = \langle R(t)R(0) \rangle / \langle R(t)^2 \rangle \quad (50)$$

From the autocorrelation functions, the relaxation times of the normal modes and the mean end-to-end vector are found by a least-squares plot of $\ln(F)$ vs. t . The negative of the

slope of this line is the relaxation time. For the normal modes, the slope is calculated from data within the range

$$0.0 < \ln[F_k(t)] < -1.2. \quad (51)$$

For the mean end-to-end vector, the range is

$$-0.4 < \ln[F_R(t)] < -1.2 \quad (52)$$

The relaxation times of the normal modes obtained are fit to the scaling laws

$$t(L,k) \sim L^a(k) \quad (53)$$

and

$$t(L,k) \sim k^b(L). \quad (54)$$

by means of an unweighted least-squares fit of $\ln\{t(L,k)\}$ vs. $\ln(L)$ and $\ln(k)$ respectively. The relaxation times of the mean square end-to-end vector are fit to the scaling law, Equation 40 (p 49). The values for the mean square end-to-end distance will also be obtained and fit to the equation

$$\langle R^2 \rangle \sim L^{2\nu} \quad (55)$$

by an unweighted least squares plot of $\ln\langle R^2 \rangle$ vs. $\ln(L)$.

The scaling exponents obtained should give insight into the dynamic properties of polymers. Special attention will be paid to how well the results of the simulations agreed with bead spring models and the relationship between static and dynamic properties of the chains. Also of great interest is whether the models give results consistent with one another. This is necessary if the generality of the results is to be accepted.

CHAPTER III

RESULTS AND DISCUSSION

A. The Athermal Models

Simulation runs were performed on chains of 12, 24, 36, 48, and 60 beads for both the face-centered cubic (FCC) and body-centered cubic (BCC) lattices. Simulations with and without the excluded volume constraint were performed for both lattices and compared to the results obtained earlier for the simple cubic (SC) lattice.^{30,31} At least three computer runs were performed to obtain each item of data. 30,000 coordinate samples were recorded for each run. From these samples, the relaxation times of the end-to-end vector autocorrelation functions and the autocorrelation functions of the first three normal modes were calculated.

The average values of the relaxation times of the autocorrelation functions of the end-to-end vector and the first three normal modes for the three lattices are shown in Tables 1-4 (pp 76-79). Typical autocorrelation functions are plotted in Figures 10-15 (pp 80-85). From the figures it can be seen that the normal coordinates obtained from the Rouse equation do relax exponentially both in the presence and absence of excluded volume. Verdier had reported that this was not the case for his model when the excluded volume constraint was included.¹⁸ From the data it can be seen, that within the limits of the study, the relaxation times

Table 1. Values of the Relaxation Time of the End-to-End Vector, $t_R(L)$, for Chains With [and Without] the Excluded Volume Constraint as a Function of Chain Length, L , and Lattice Type.^{a,b,c}

Chain Length	Lattice Type		
	SC	FCC	BCC
11	38.5 (.9) [20.2 (.5)]	46.2 (3.6) [18.3 (2.2)]	52.2 (2.6) [18.3 (.8)]
23	179 (8) [78.0 (3.2)]	249 (84.1) [84.1 (7.8)]	289 (45) [76.5 (1.7)]
35	441 (30) [168 (8)]	643 (23) [187 (24)]	776 (72) [176 (18)]
47	870 (120) [320 (40)]	1190 (120) [316 (7)]	1460 (165) [309 (11)]
59	1330 (150) [465 (51)]	2030 (120) [533 (34)]	2330 (130) [490 (40)]

^a Values of $t_R(L)$ for chains without the excluded volume constraint are in parentheses.

^b SC lattice values are from Reference 30.

^c Standard deviations of the runs are in parentheses.

Table 2. Values of the Relaxation Time of the First Normal Mode, $t(L,1)$, for Chains With [and Without] the Excluded Volume Constraint as a Function of Chain Length, L , and Lattice Type.^{a,b,c}

Chain Length	Lattice Type		
	SC	FCC	BCC
11	36.49 [18.67]	46.4 (18.7) [18.7 (1.3)]	51.9 (2.5) [18.6 (.9)]
23	180.97 [78.10]	252 (80.0) [80.0 (4.0)]	293 (44) [76.5 (1.6)]
35	425.0 [175.3]	649 (14) [194 (21)]	781 (70) [177 (19)]
47	809.3 [310.5]	1220 (120) [314 (4)]	1460 (310) [310 (16)]
59	1315.1 [501.1]	2050 (90) [552 (39)]	2350 (100) [495 (51)]

^a Values of $t(L,1)$ for chains without the excluded volume constraint are in brackets.

^b Standard deviations of the runs are in parentheses.

^c SC lattice values are from Reference 31.

Table 3. Values of the Relaxation Time of the Second Normal Mode, $t(L,2)$, for Chains With [and Without] the Excluded Volume Constraint as a Function of Chain Length, L , and Lattice Type.^{a,b,c}

Chain Length	Lattice Type		
	SC	FCC	BCC
11	6.574 [3.289]	9.78 (.26) [4.66 (.28)]	10.7 (4.7) [4.74 (.13)]
23	38.14 [18.31]	57.0 (5.0) [18.7 (.4)]	66.8 (3.3) [20.1 (.4)]
35	101.2 [42.64]	150 (2.2) [44.4 (2.1)]	167 (45.0) [45.0 (2.8)]
47	187.0 [77.38]	298 (19) [81.1 (4.7)]	316 (7.0) [78.8 (2.1)]
59	310.8 [120.9]	476 (39) [125 (3)]	523 (27) [126 (1)]

^a Values of $t(L,2)$ for chains without the excluded volume constraint are in brackets.

^b Standard deviations of the runs are in parentheses.

^c SC lattice values are from Reference 31.

Table 4. Values of the Relaxation Time of the Third Normal Mode, $t(L,3)$, for Chains With [and Without] the Excluded Volume Constraint as a Function of Chain Length, L , and Lattice Type.^{a,b,c}

Chain Length	Lattice Type		
	SC	FCC	BCC
11	1.264 [.904]	3.81 (.14) [2.20 (.05)]	4.21 (2.1) [2.12 (.10)]
23	13.04 [7.408]	22.7 (1.2) [9.23 (.17)]	27.2 (8.5) [8.52 (.25)]
35	38.00 [17.86]	60.7 (20.7) [20.7 (1.2)]	68.3 (3.3) [20.1 (1.0)]
47	78.48 [33.68]	125 (4) [36.4 (1.8)]	139 (10) [37.5 (2.2)]
59	124.0 [51.59]	200 (9) [58.6 (1.7)]	228 (13) [55.6 (2.2)]

^a Values of $t(L,3)$ for chains without the excluded volume constraint are in brackets.

^b Standard deviations of the runs are in parentheses.

^c SC lattice values are from Reference 31.

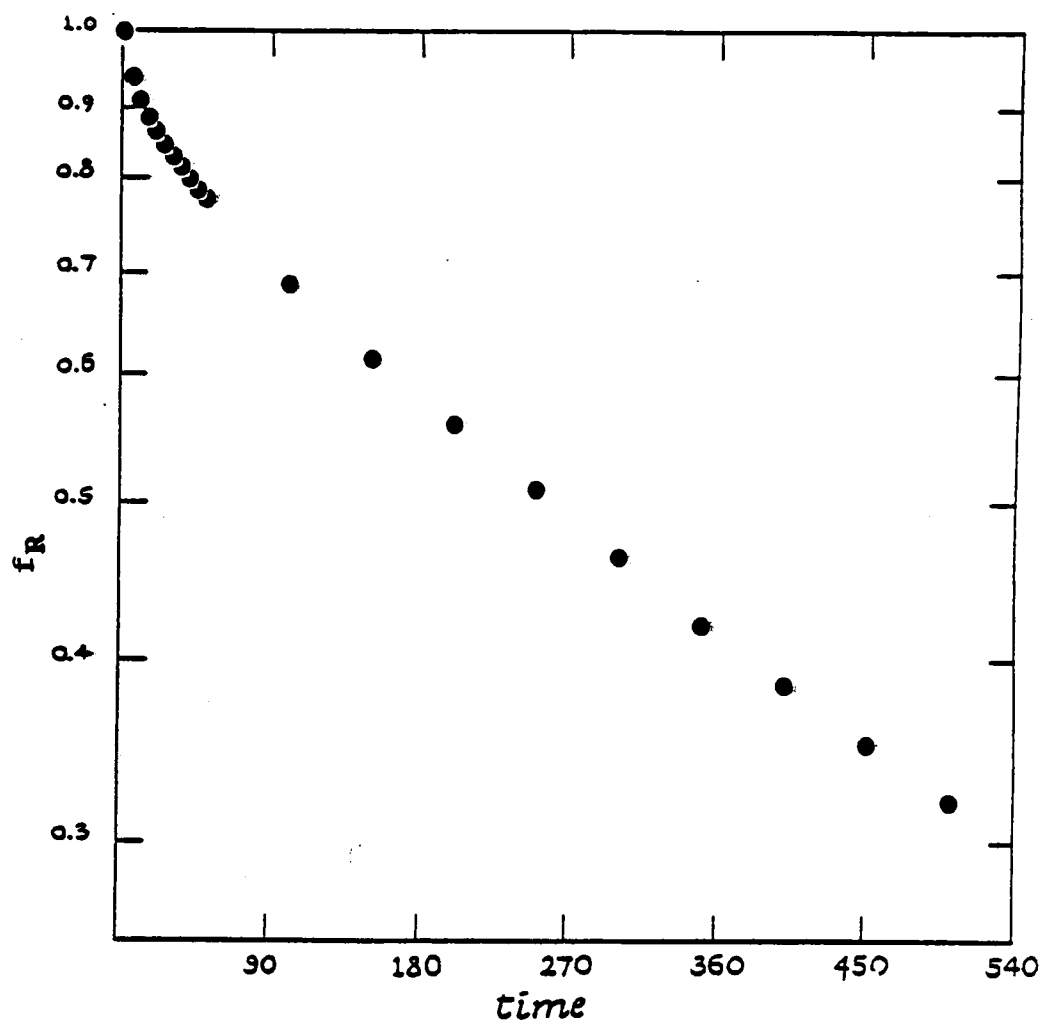


Figure 10. Semi-log plot of the autocorrelation function of the end-to-end vector vs. time for a chain of length $L=59$ placed on a FCC lattice without the excluded volume constraint.

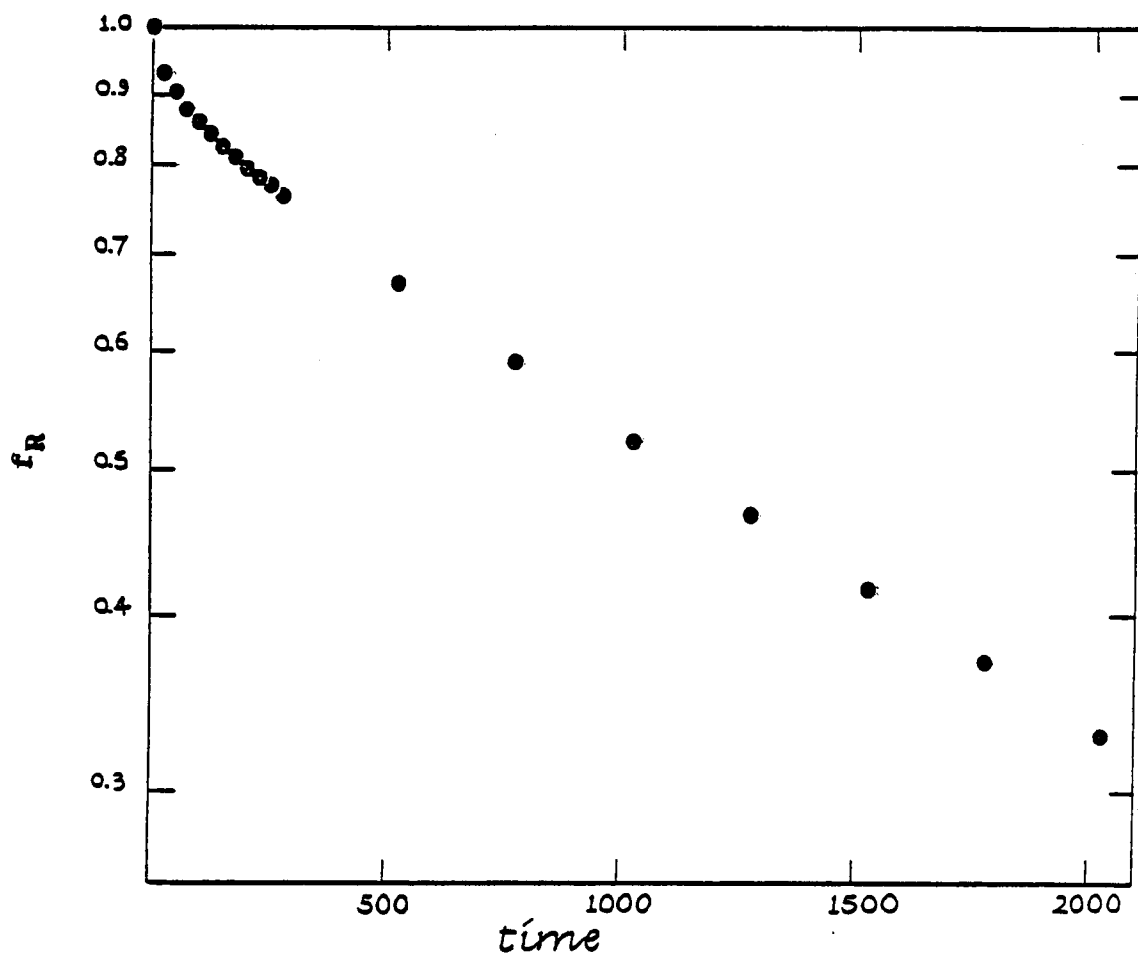


Figure 11. Semi-log plot of the autocorrelation function of the end-to-end vector of a chain of length $L=59$ for a chain placed on a FCC lattice with the excluded volume constraint.

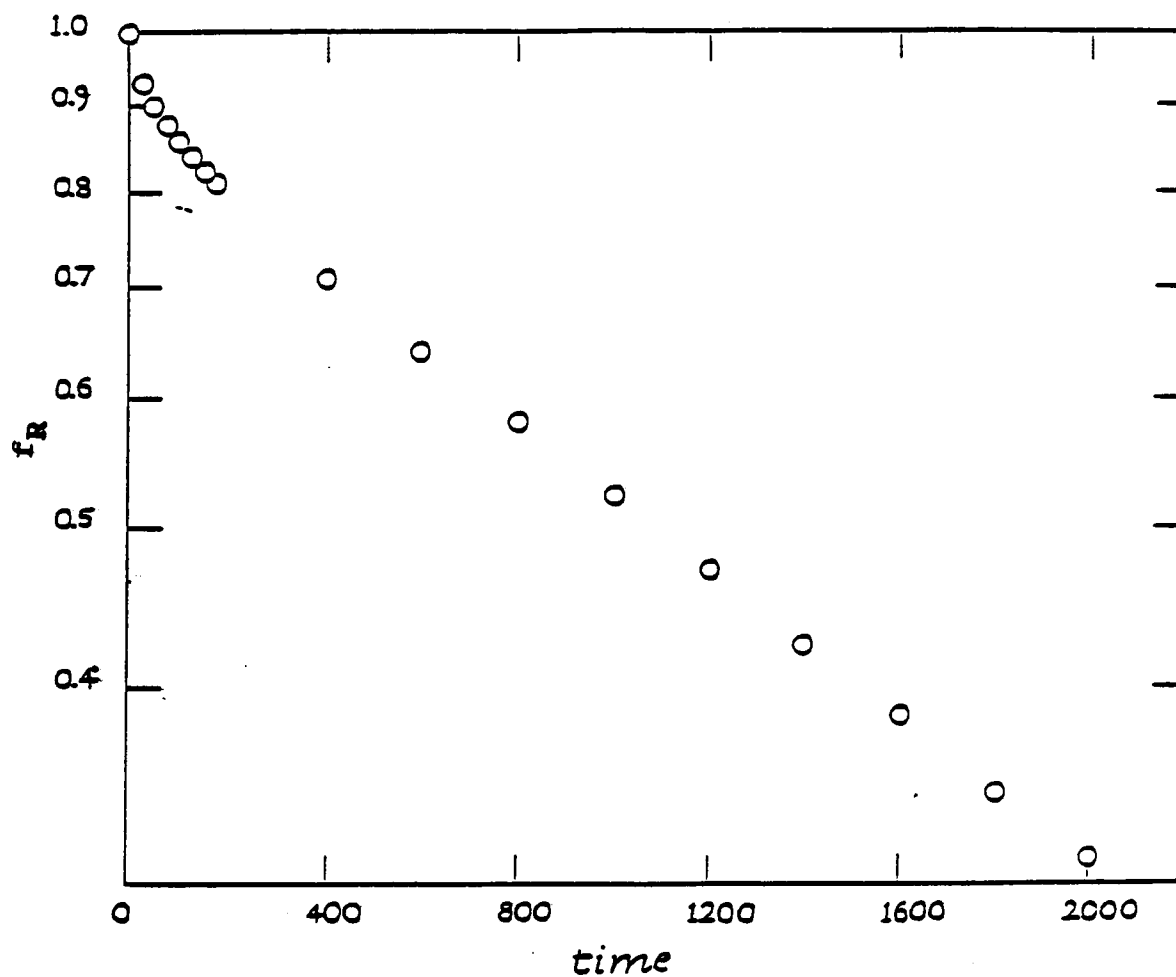


Figure 12. Semi-log plot of the autocorrelation function of the end-to-end vector of a chain of length $L=59$ placed on a BCC lattice with the excluded volume constraint.

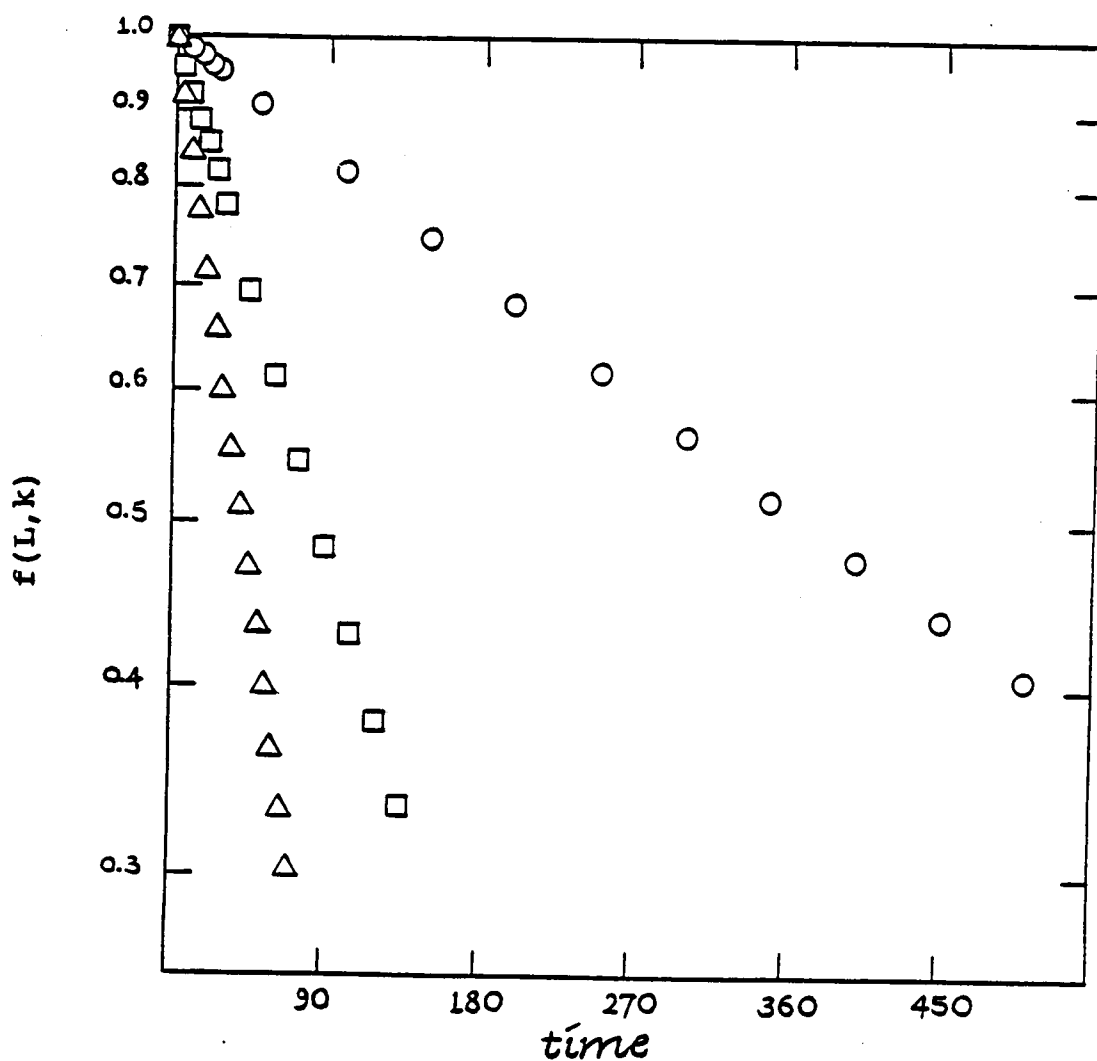


Figure 13. Semi-log plot of the autocorrelation functions of the first three normal modes for a chain of length $L=59$ for a chain placed on a FCC lattice without the excluded volume constraint.

$k = 1(\bigcirc)$, $2(\square)$, and $3(\triangle)$.

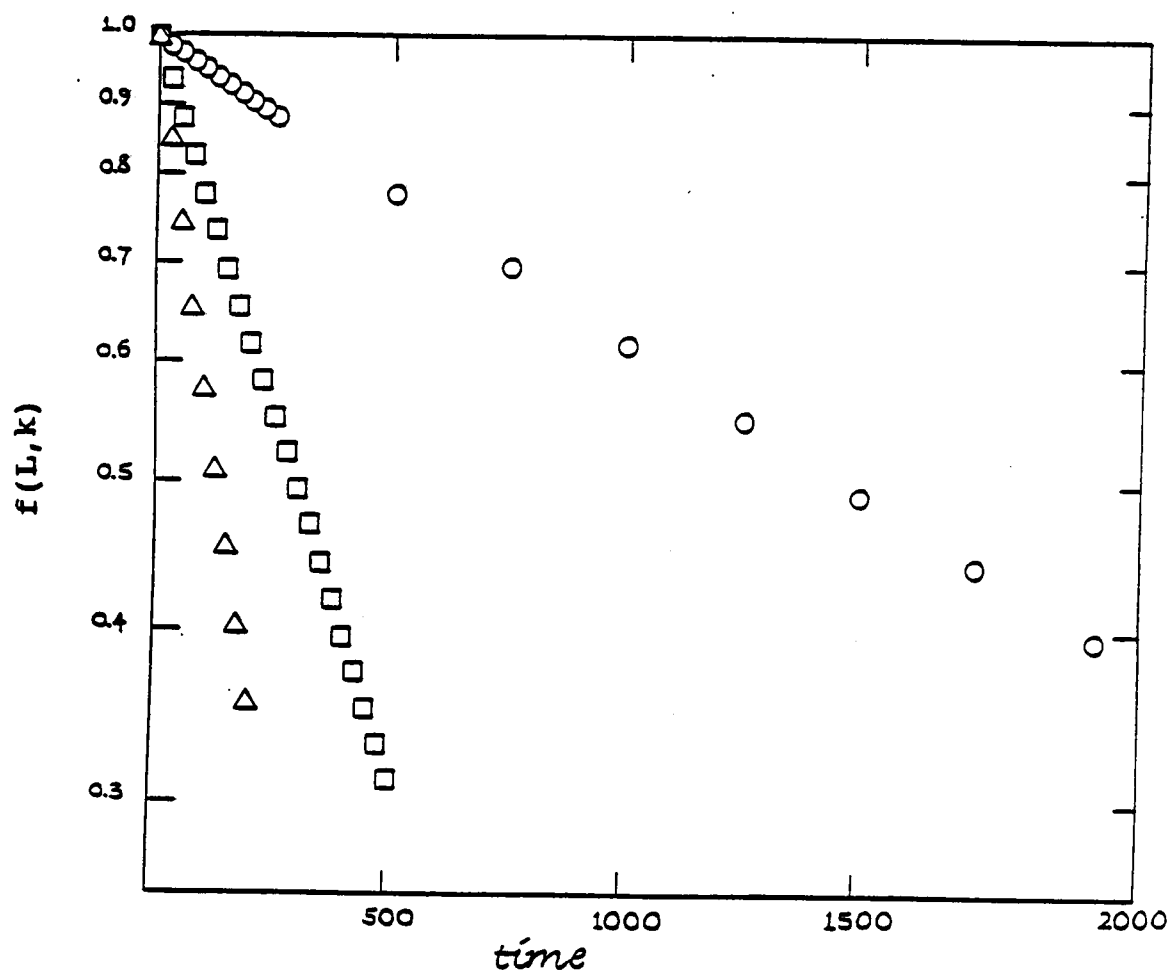


Figure 14. Semi-log plot of the autocorrelation functions of the first three normal modes for a chain of length $L=59$ placed on a FCC lattice with the excluded volume constraint.

$k = 1(\bigcirc)$, $2(\square)$, and $3(\triangle)$.

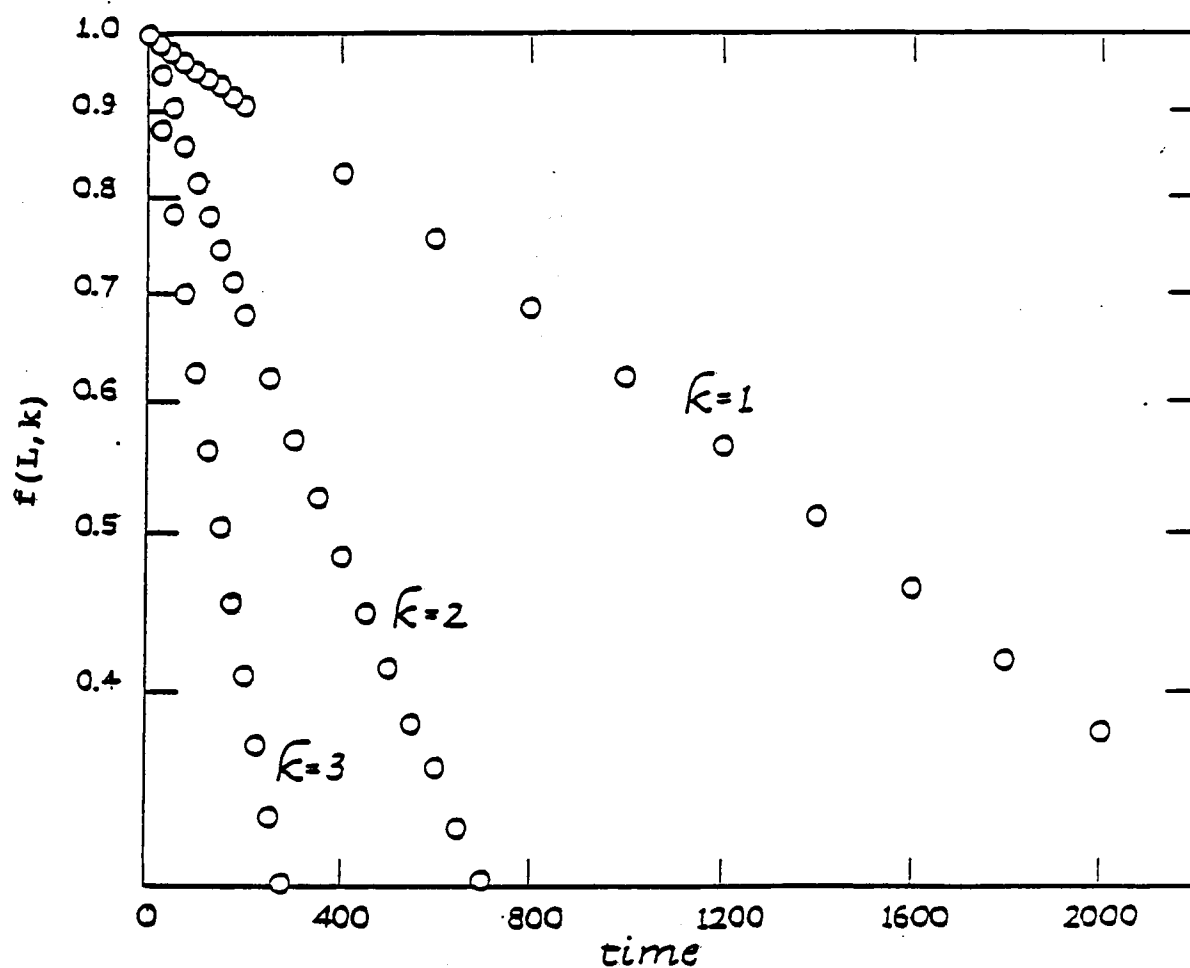


Figure 15. Semi-log plot of the autocorrelation functions of the first three normal modes of a chain of length $L=59$ placed on a BCC lattice with the excluded volume constraint.

are about same the for all three lattice models when excluded volume is absent. In the presence of excluded volume, the chains of the SC model relax the most quickly, while the BCC model gives the longest relaxation times.

In order to test the dynamic scaling hypothesis, the mean-square end-to-end distance, $\langle R^2 \rangle$, was also found for chains of various lengths. The values obtained for $\langle R^2 \rangle$ are listed in Table 5 (p 87). Using these values, the static scaling exponent, 2ν , was found for each model, and the results are listed in Table 6 (p 88). The values found for 2ν are about 1.0 in the absence of excluded volume. This is in good agreement with the Rouse model. In the presence of excluded volume, 2ν is approximately 1.2, the value predicted by the scaling arguments given in Chapter I, Section B. Note: For chains obeying the excluded volume restriction, the relaxation times for chains of length $L=11$ were not used to calculate the scaling exponents, 2ν , w , and $a(k)$ because this chain was apparently too short to give good asymptotic scaling. The evidence for this will be presented later.

From the data for the relaxation times of the end-to-end vector, the values for the scaling exponent, w , defined by Equation 40 (p 48) have been found for each lattice both in the absence and presence of excluded volume. These values are listed in Table 6 (p 88). In the absence of excluded volume, the resulting values are, within the limits of the

Table 5. Values of the Mean-Squared End-to-End Distance, $\langle R^2 \rangle$, for Chains With [and Without] the Excluded Volume Constraint as a Function of Chain Length and Lattice Type.^{a,b,c}

Chain Length	Lattice Type		
	SC	FCC	BCC
11	18.9 (.1) [11.1 (.5)]	16.4 (.3) [10.9 (.3)]	17.4 (.4) [11.1 (.5)]
23	46.2 (23.4) [23.4 (.4)]	39.8 (22.4) [22.4 (.6)]	41.8 (23.2) [23.2 (1.4)]
35	76.2 (2.2) [36.1 (.1)]	65.9 (1.6) [34.9 (1.5)]	66.8 (1.5) [33.4 (.7)]
47	108 (3.2) [48.8 (1.9)]	91.7 (1.3) [46.9 (.8)]	96.1 (3.3) [47.1 (2.0)]
59	140 (6) [60.1 (3.3)]	121 (4.7) [57.5 (.5)]	122 (4) [57.2 (.7)]

^a Values of $\langle R^2 \rangle$ for chains without the excluded volume constraint are in brackets below the respective entry for chains with excluded volume.

^b Standard deviations of the runs are in parentheses.

^c SC lattice values are from Reference 30.

Table 6. Values of the Scaling Exponents for Chains With
(and Without) the Excluded Volume Constraint as a
Function of Lattice Type.^{a,b,c}

Lattice Type	Scaling Exponent						
	2v	w	a(1)	a(2)	a(3)	w-2v	a(1)-2v
SC	1.18 (1.01)	2.13 (1.88)	2.13 (1.95)	2.30 (2.14)	2.41 (2.07)	.95 (.87)	.95 (.94)
FCC	1.17 (1.00)	2.25 (1.98)	2.21 (1.99)	2.27 (1.97)	2.33 (1.95)	1.08 (.98)	1.04 (.99)
BCC	1.14 (.98)	2.27 (1.98)	2.21 (1.95)	2.18 (1.95)	2.27 (1.97)	1.13 (1.00)	1.07 (.97)

^a Values of the scaling exponents for chains without the excluded volume constraint are in parentheses below the values for the chains with excluded volume.

^b Values of 2v and w for the SC lattice are from Reference 30.

^c Values of a(1), a(2), and a(3) for the SC lattice are from Reference 31.

study, equal to the Rouse prediction of $w=2.0$. This is not surprising since Iwata and Kurata have analytically proven that a continuum model with Rouse-like, elementary motions gives the Rouse result in the absence of excluded volume.⁹² Therefore, the results here merely show that no exotic dynamic features were accidentally included in the models. In the presence of excluded volume, the values of w are quite close to the value of 2.2 predicted by the scaling arguments of deGennes which were discussed earlier.⁹

The scaling exponents, $a(k)$ defined by Equation 53 (p 74) were obtained from the relaxation times of the normal modes and are also listed in Table 6 (p 88). In the absence of excluded volume, the values of $a(k)$ are, within the limits of this study, equal to the Rouse theory's prediction of 2.0. In the presence of excluded volume the values of $a(1)$ are quite close to the deGennes' scaling predictions of 2.2. The values obtained for dynamic scaling exponents, w and $a(1)$, and the static scaling exponent, $2v$, showed good agreement with the dynamic scaling hypothesis, Equation 10 (p 11). For each lattice, it is found that $a(1)-2v$ and $w-2v$ are close to 1.0, the value predicted by the dynamic scaling hypothesis. This can be seen in the last two columns of Table 6. This is true for chains with and without the excluded volume constraint.

The values for the higher modes show $a(k)$ increases with k . This was observed previously for the SC lattice.³¹

Increasing values of $a(k)$ indicate that short range motions are relaxing more slowly relative to long range motions as chain length increases. If the dynamic scaling hypothesis correctly describes the motions of the internal segments, then as the chain length is increased, the short range segments of the chain must be increasing in length at a faster rate than the longer segments. This obviously cannot be the case for asymptotically long segments, but it may be possible for the short chains used here. It is worth noting that Curro and Schaefer⁴⁵ have observed that short range segments are more expanded than long range segments. This observation is in agreement with the predictions Fixman obtained using perturbation treatments,⁴⁶ but is contrary to the predictions of the blob model that predict short segments to be contracted in the manner of a random walk.⁷ Unfortunately, it is not known how the expansion changes with chain length for the models studied in this work. This is a matter which deserves further study.

There appears to be some difference between the values of $a(k)$ obtained for the SC lattice and those obtained for the others, particularly for the higher modes. There may be larger sources of statistical errors in the earlier study, but it is more likely that this is due to the short chain lengths used and the fact that the two-bead crankshaft motions may be too close in size to the range of motion being probed by the higher modes.

The reason for this is that the k 'th mode probes motions with a range of approximately L/k bonds. For the third mode in a chain of $L=11$, we have $L/k < 4$. The crankshaft motion involves the movement of three bonds, and therefore the third mode in a chain of 11 would be examining motions on the same length scale as the elementary motions. It is for this reason that the relaxation time of the third mode was not used to calculate the scaling exponent, $b(11)$, in the simple cubic lattice.³¹

The scaling exponents, $b(L)$, defined by Equation 54 (p 74), are listed in Table 7 (p 92). From the data it can be seen that there is no obvious lattice dependence for these values with the possible exception of the shortest chain lengths. For the short chains the $b(L)$ values obtained for the SC model are higher than those of FCC and BCC models. Again this is likely to be due to the crankshaft motion being too close in size to the range of motion being probed by the normal modes. In the shorter chains, the values of $b(L)$ decrease with increasing L . If short-range segments are expanding faster than long range segments with increasing chain length, then this observation would be consistent with the dynamic scaling hypothesis. The decrease in $b(L)$ with increasing chain length seems to disappear for the longer chains.

To determine how well the data for the simulations with the excluded volume constraint fit the scaling

Table 7. Values of the Scaling Exponent, $b(L)$, for Chains With (and Without) the Excluded Volume Constraint as a Function of Chain Length, L , and Lattice Type.^{a,b}

Chain Length	Lattice Type		
	SC	FCC	BCC
11	2.47 (2.50)	2.27 (1.96)	2.29 (2.21)
23	2.38 (2.13)	2.19 (1.98)	2.16 (1.99)
35	2.18 (2.07)	2.15 (2.05)	2.22 (1.98)
47	2.12 (2.02)	2.07 (1.96)	2.15 (1.93)
59	2.14 (2.07)	2.12 (2.05)	2.13 (1.99)

^a Values of $b(L)$ for chains without the excluded volume constraint are in parentheses.

^b SC lattice values for $b(L)$ are from Reference 31.

relation given by Equation 25 (p 13) we define the constant which satisfies the equality suggested by the equation as

$$A(L,k) = k^{b(L)} / \{t(L,k)L^{a(k)}\} \quad (56)$$

$A(L,k)$ is plotted verses L and k for both the FCC and BCC lattices in Figures 16-19 (pp 94-97). $a(k)$ was set to the value predicted by deGennes of 2.2. $b(L)$ was set to the value which best seemed to fit the data for long chains. For the FCC lattice this was 2.11, and for the BCC lattice this was 2.14. From the figures, it can be seen that the scaling exponents fit the data quite well. The values of $A(k,L)$ show relatively little dependence on k or L . The one exception to this is the data obtained for chains of length, $L=11$, obeying the excluded volume restriction. Since these chains appear to be too short to give good asymptotic scaling, the chains of length, $L=11$, were not used to fit the scaling exponents, $2v$, w , and $a(k)$, for either the FCC or BCC model. The near constant values of $A(L,k)$ obtained indicate that the chains are long enough to give a fair estimate of the asymptotic values of the scaling exponents. Similar results were found for the SC model. For a comparison of these figures with the figures obtained for the SC lattice see Reference 30.

The results above indicate the lattice models give data in agreement with bead-spring predictions, that are consistent with one another, and can give values close to that of an asymptotically long chain. The simulations

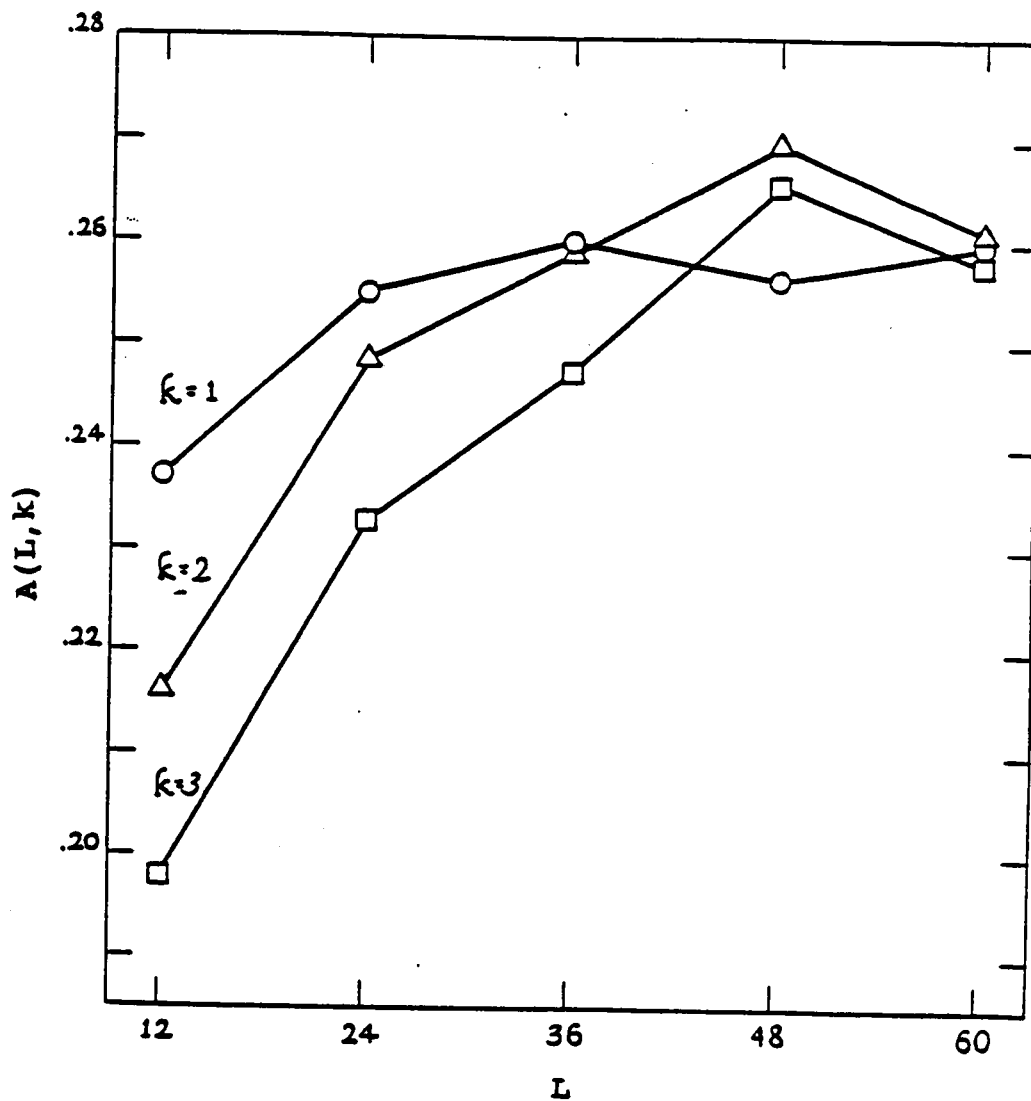


Figure 16. $A(L, k)$ as a function of chain length, L , for the data obtained from the athermal FCC model.

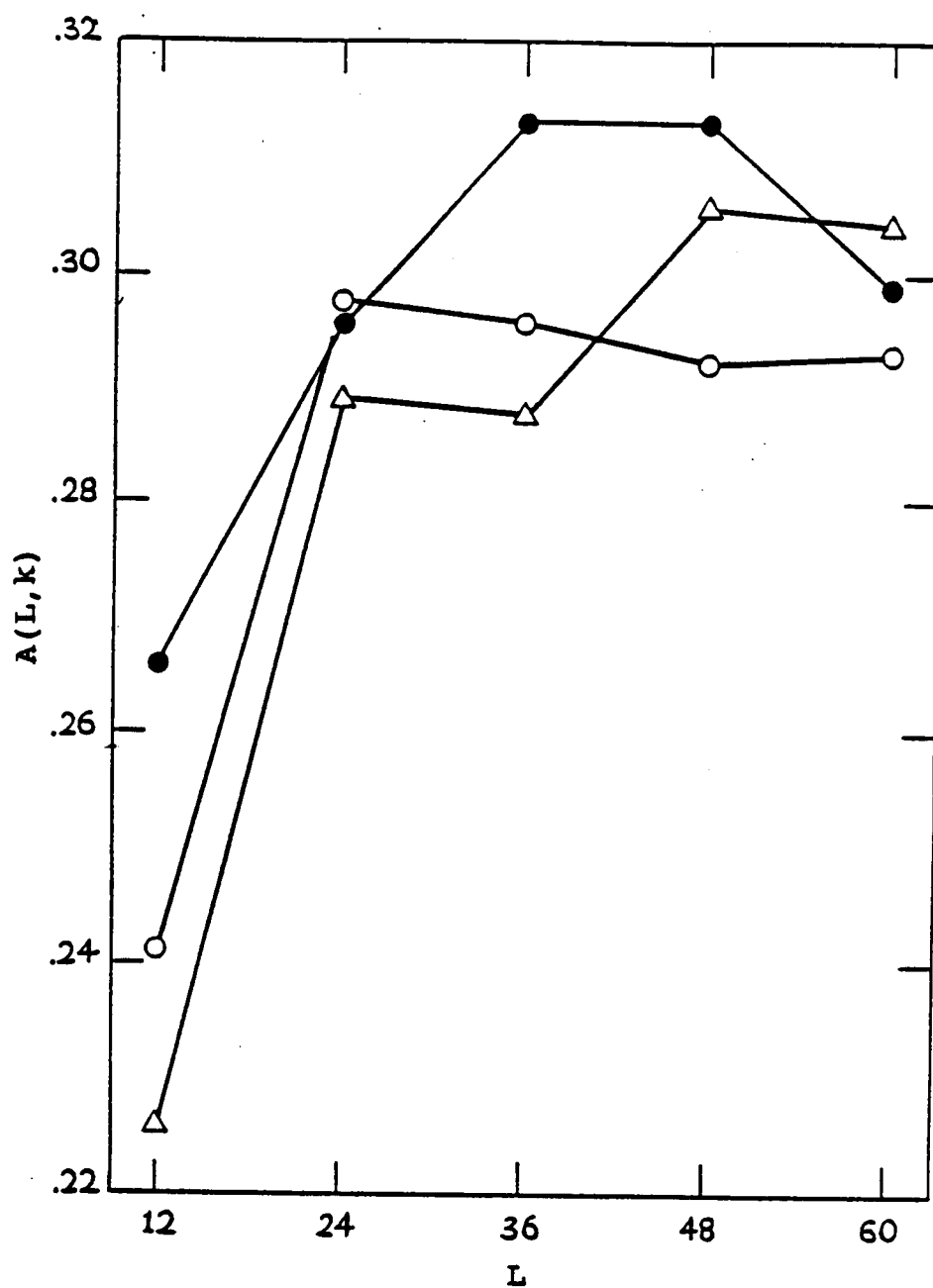


Figure 17. $A(L, k)$ as a function of chain length, L , for the data obtained from the athermal BCC model.

$k = 1(\bullet)$, $2(\circ)$, and $3(\triangle)$.

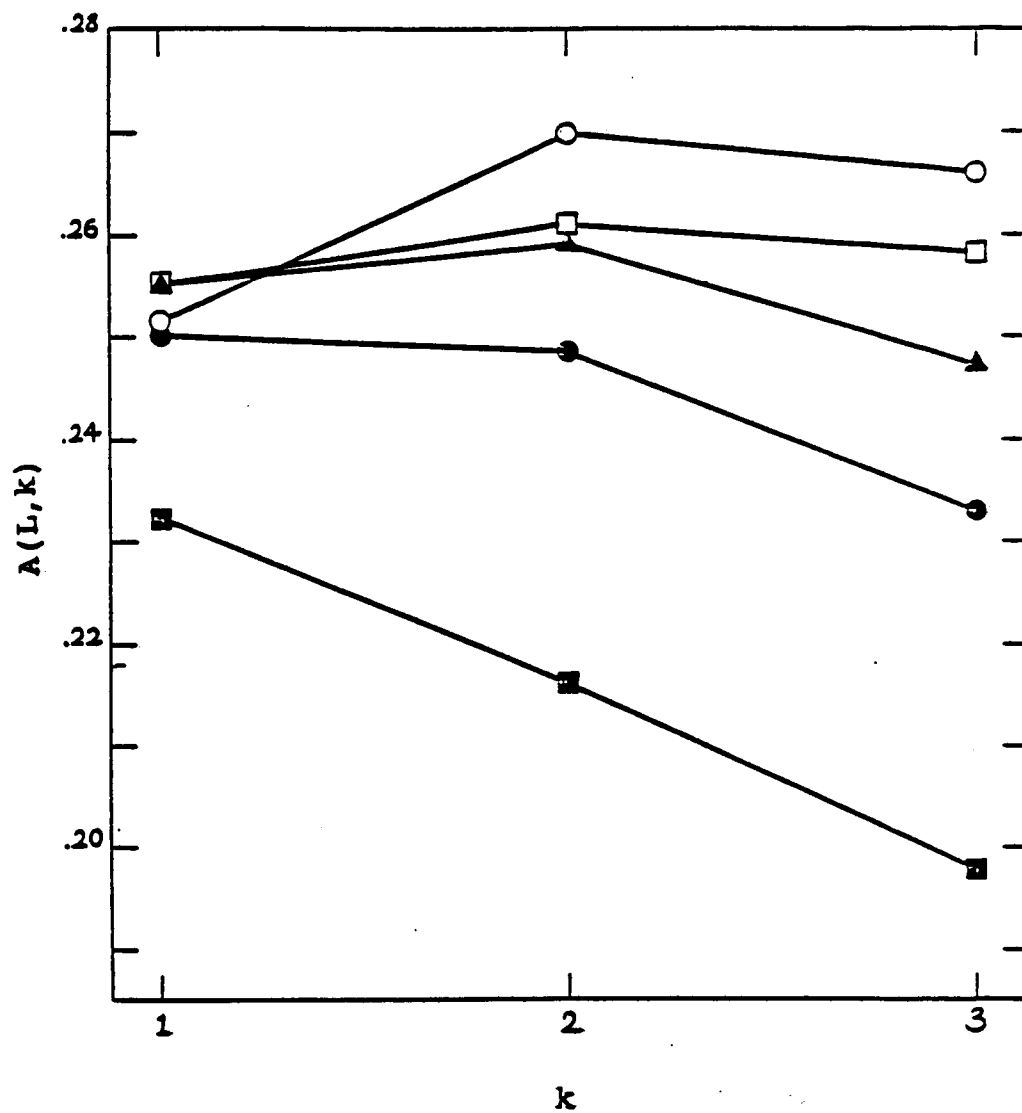


Figure 18. $A(L, k)$ as a function of the mode number, k , for the data obtained from the athermal FCC model.

$L = 11(\blacksquare)$, $23(\bullet)$, $35(\blacktriangle)$, $47(\circ)$, and $59(\square)$.

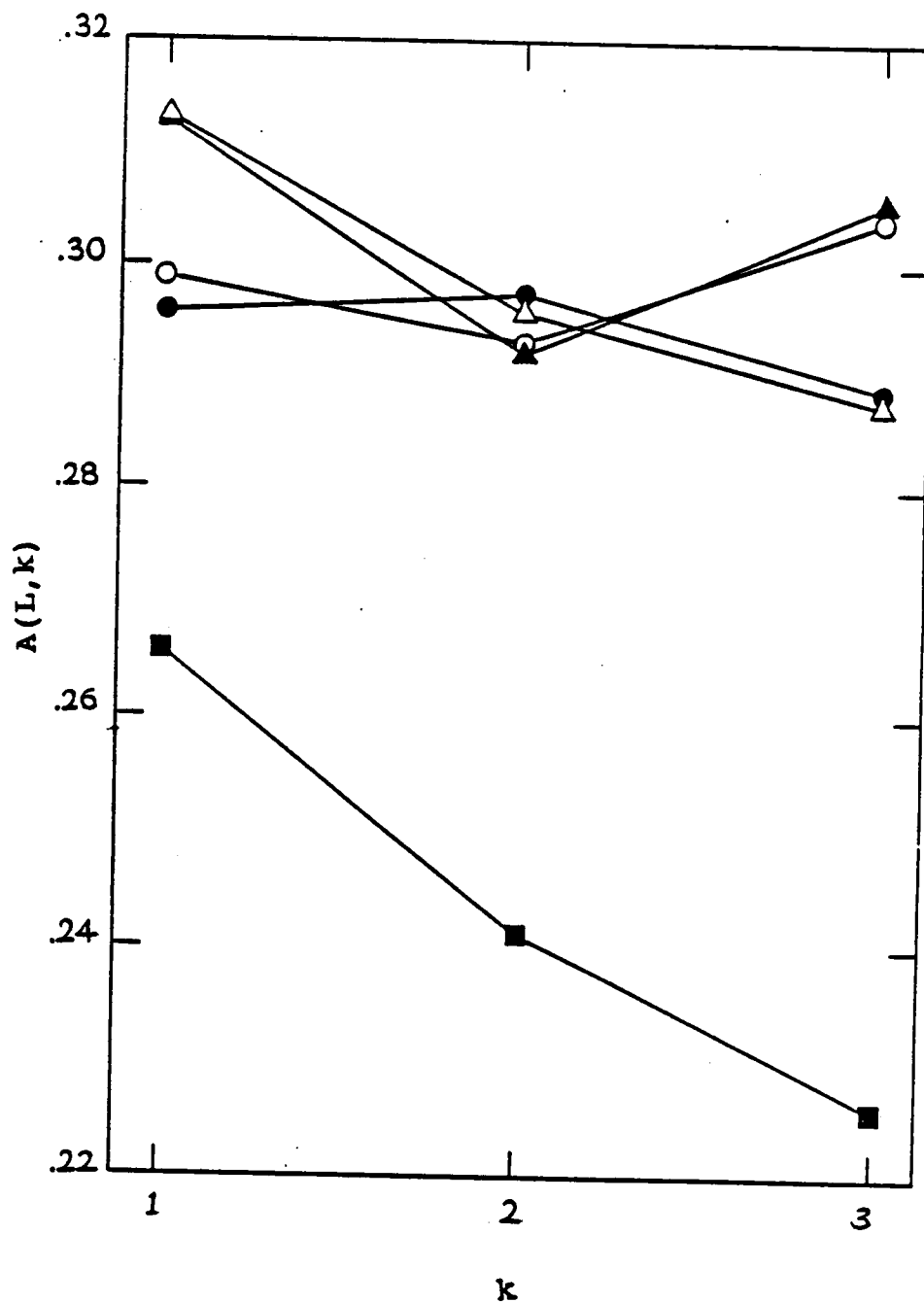


Figure 19. $A(L, k)$ as a function of the mode number, k , for the data obtained from the athermal BCC model.

$L = 11$ (■), 23 (●), 35 (△), 47 (▲), and 59 (○).

required only small amounts of computer time and therefore there appear to be no obvious problems with extending these simulations to include temperature (solvent) effects. The next step is to include a square-well potential between non-bonded beads of the FCC and BCC models. Data generated using these two lattice models and the previously developed SC model of Naghizadeh and Kovac^{34,35} will be used to investigate polymer dynamics in good, theta, and poor solvent conditions. Of particular interest is testing the usefulness of bead-spring models in describing the dynamics of chains under these solvent conditions, and whether the models will give results that are consistent with one another.

B. The Good and Theta Solvent Regime

Simulations were conducted for chains of 24, 36, 48, 60, and 72 beads for the thermal SC and FCC models. 25,000 and 20,000 samples were recorded for the SC and FCC models respectively in each computer run. At least three runs were performed to obtain an average for each item of data. The nearest-neighbor potential, E_p , was varied over a wide range of values, including repulsive potentials. The relaxation times were obtained from the autocorrelation functions of the mean end-to-end vector and the first three normal modes. Some typical autocorrelation functions are shown for chains of length $L=59$ in Figures 20-27 (pp 99-106) for both models.

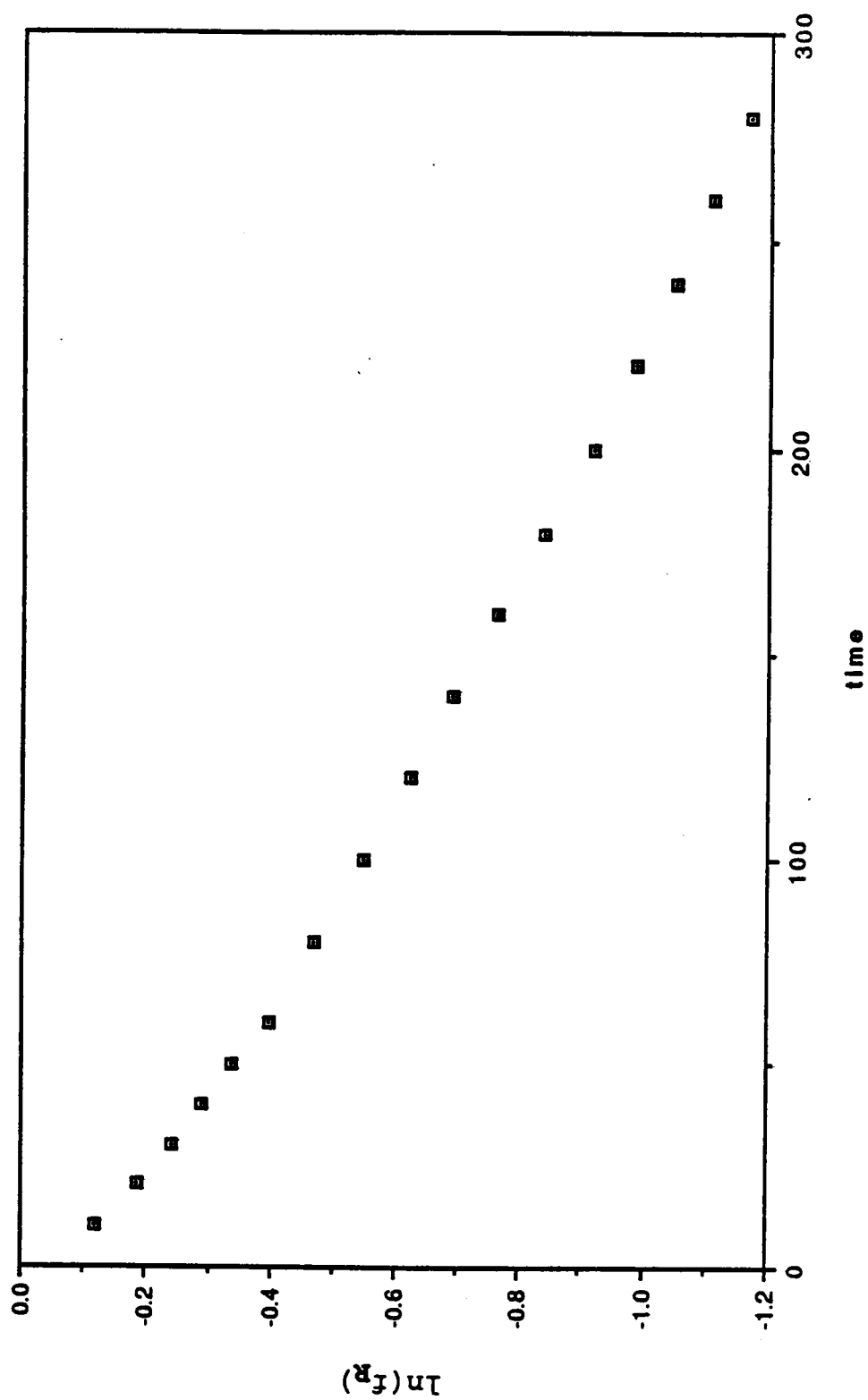


Figure 20. Semi-log plot of the autocorrelation function of the end-to-end vector for $E_r = .10$. SC model.

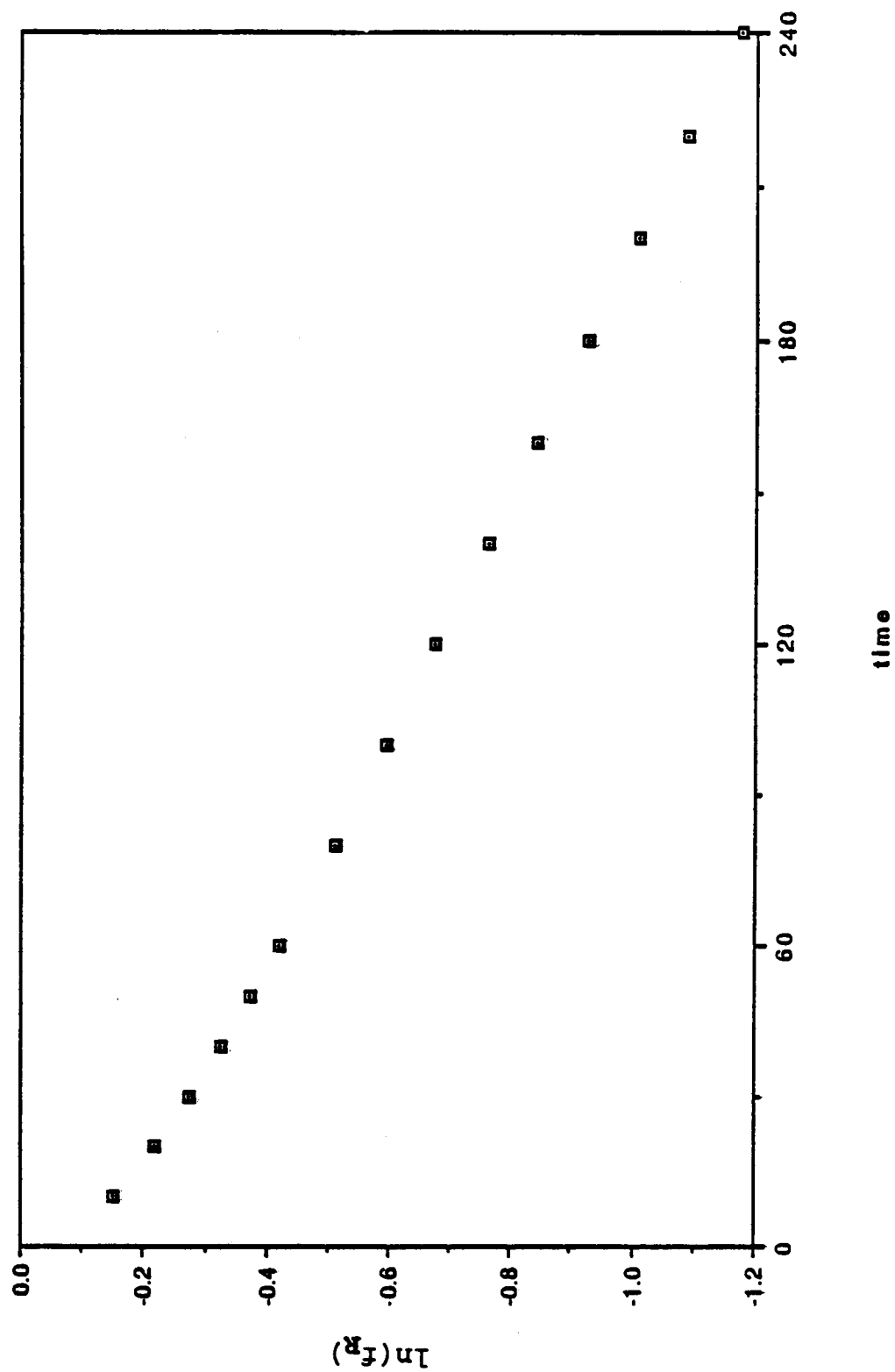


Figure 21. Semi-log plot of the autocorrelation function of the end-to-end vector for $E_r = .10$. FCC model

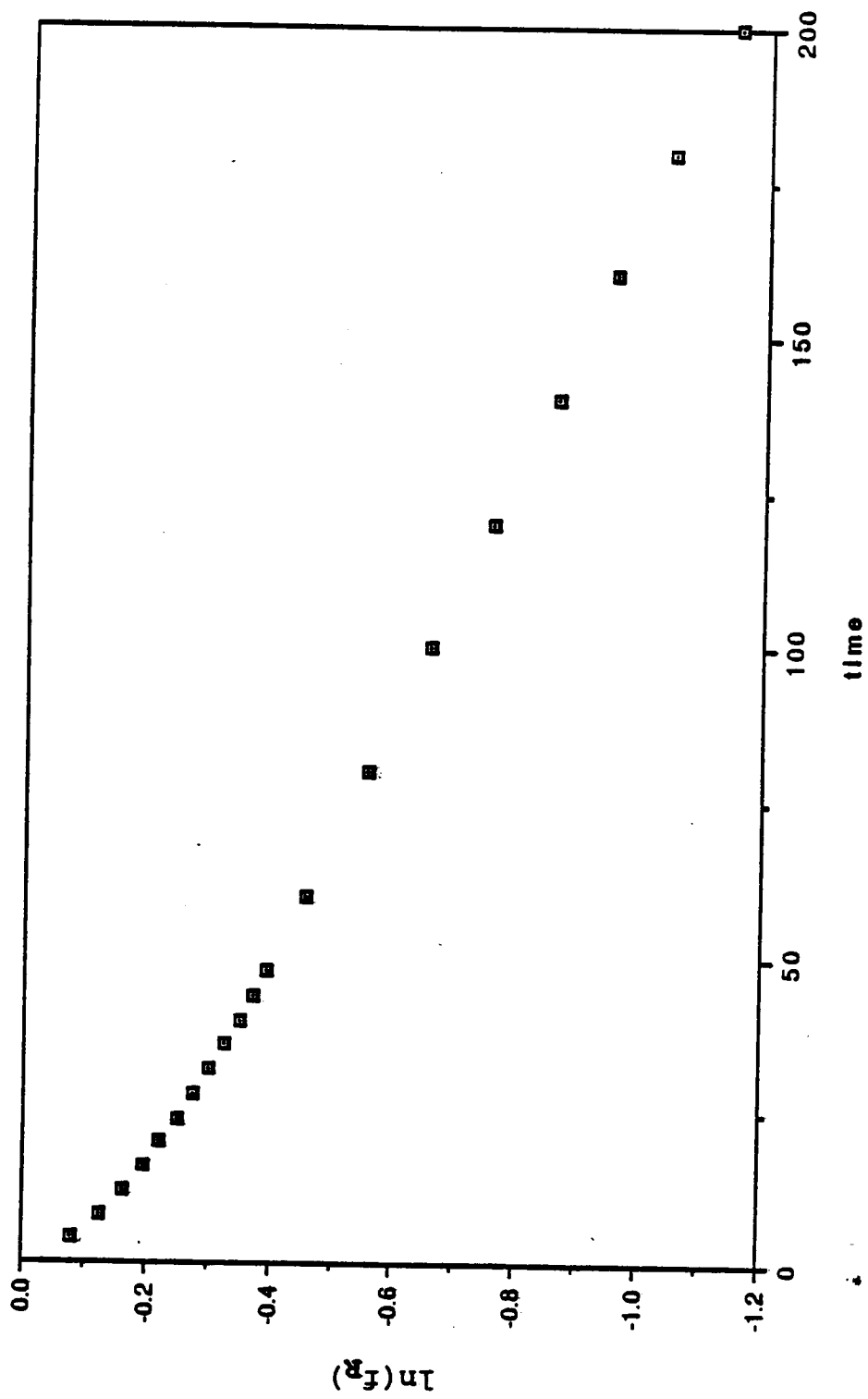


Figure 22. Semi-log plot of the autocorrelation function of the end-to-end vector for $E_r = .34$. SC model

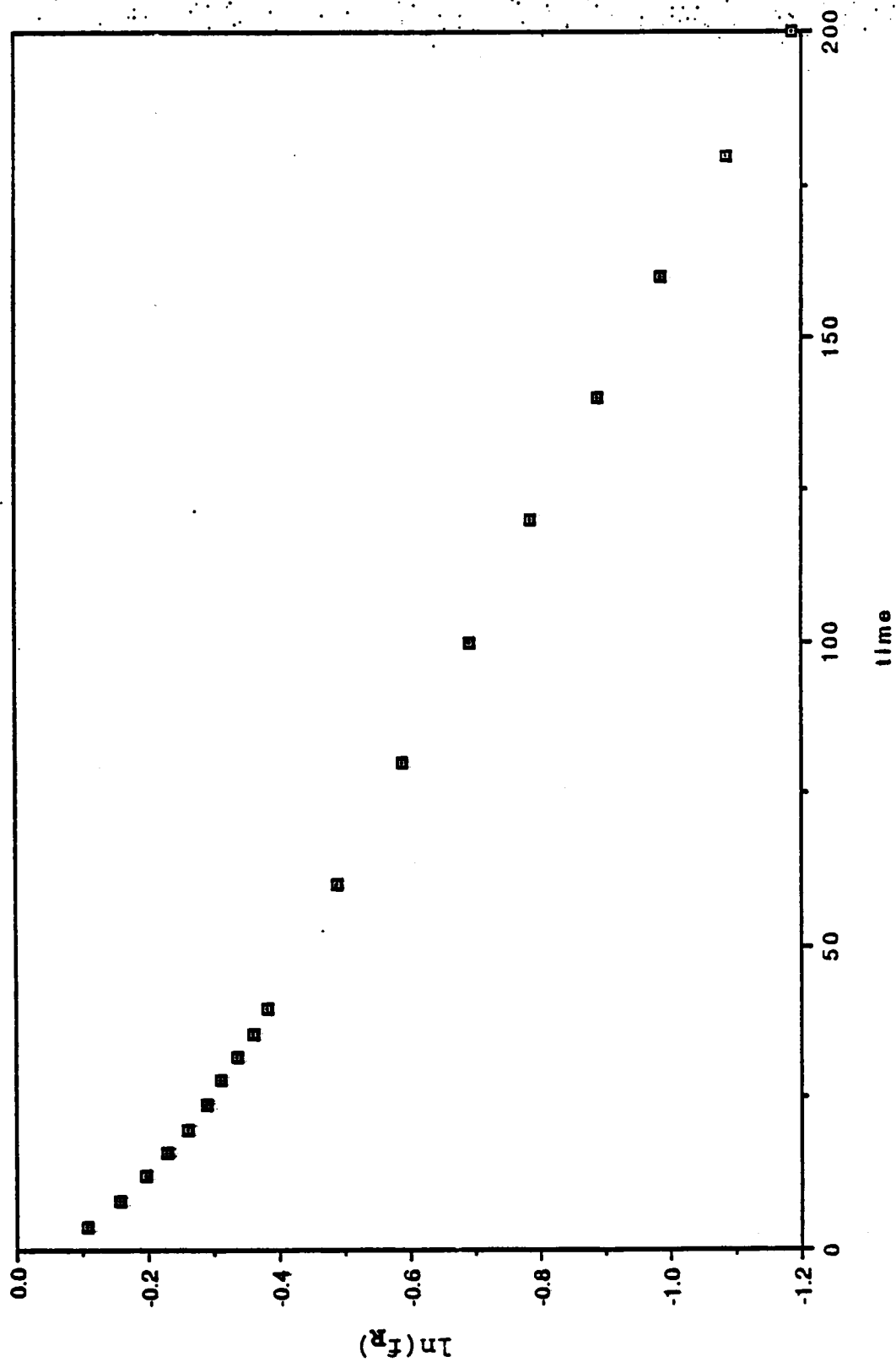


Figure 23. Semi-log plot of the autocorrelation function of the end-to-end vector for $E_r = .16$. FCC model

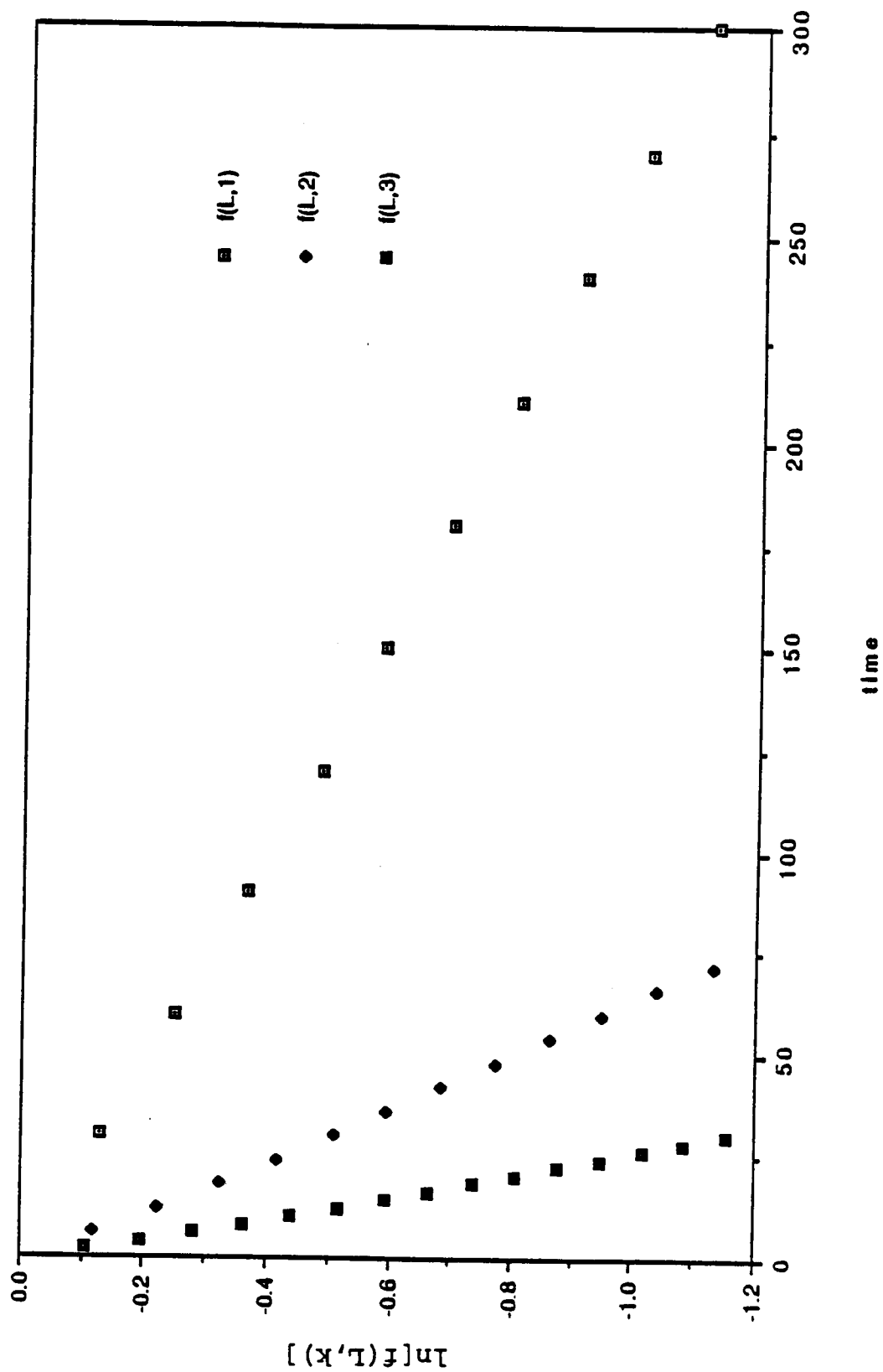


Figure 24. Semi-log plot of the autocorrelation functions of the first three normal modes for $E_F = .10$. SC model

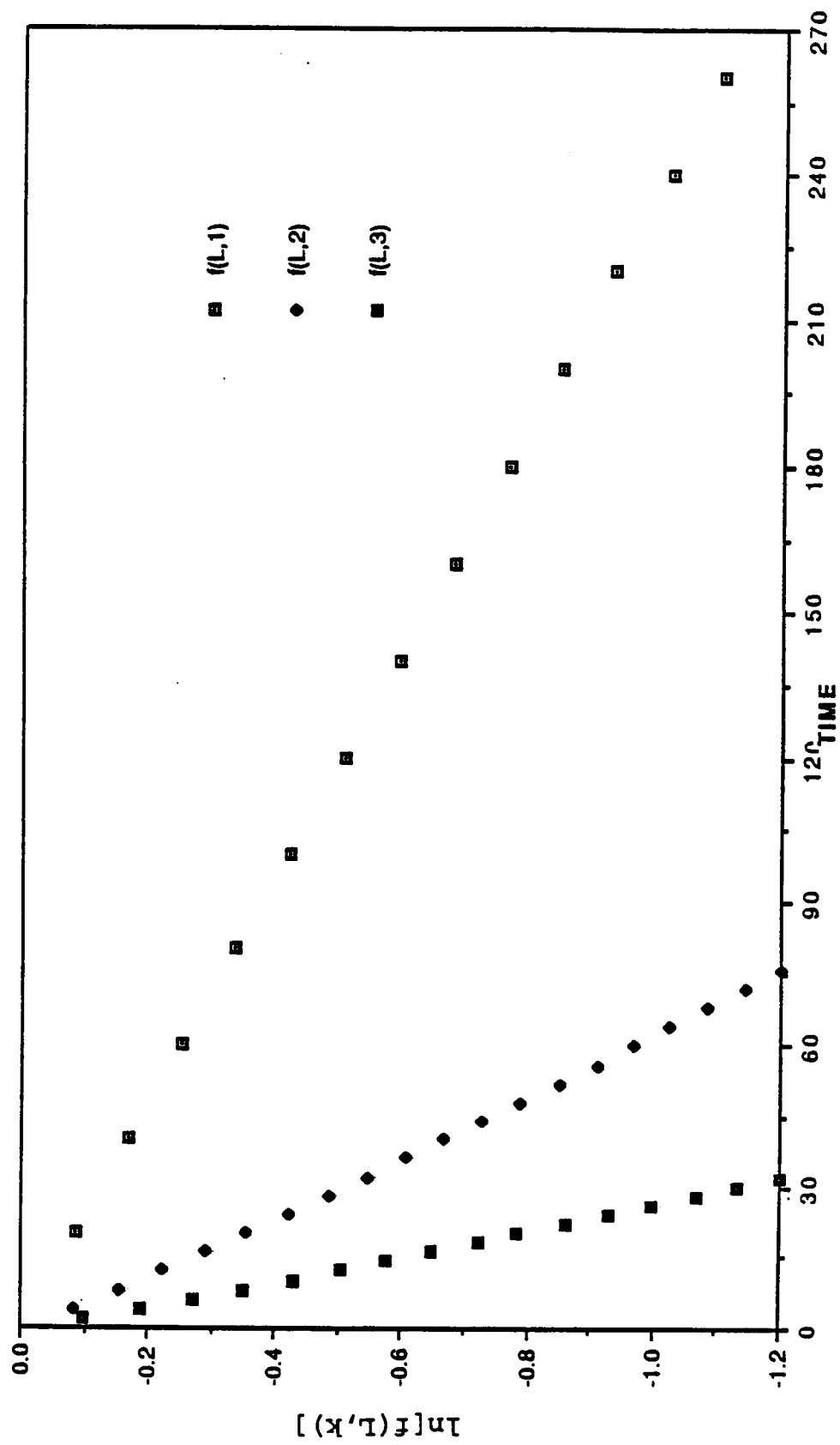


Figure 25. Semi-log plot of the autocorrelation functions of the first three normal modes for $E_r = .10$. FCC model

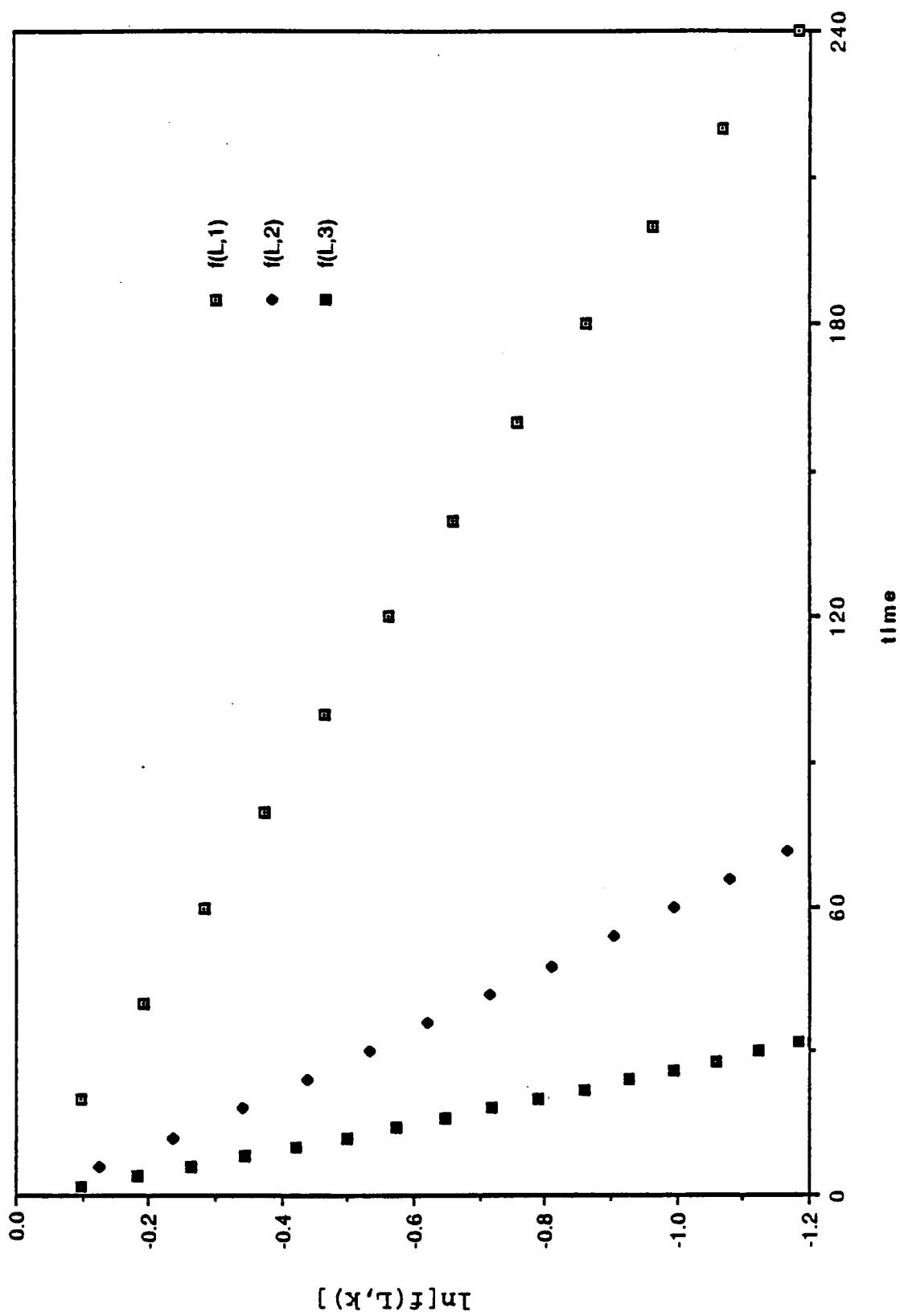


Figure 26. Semi-log plot of the autocorrelation functions of the first three normal modes for $E_r = .34$. SC model.

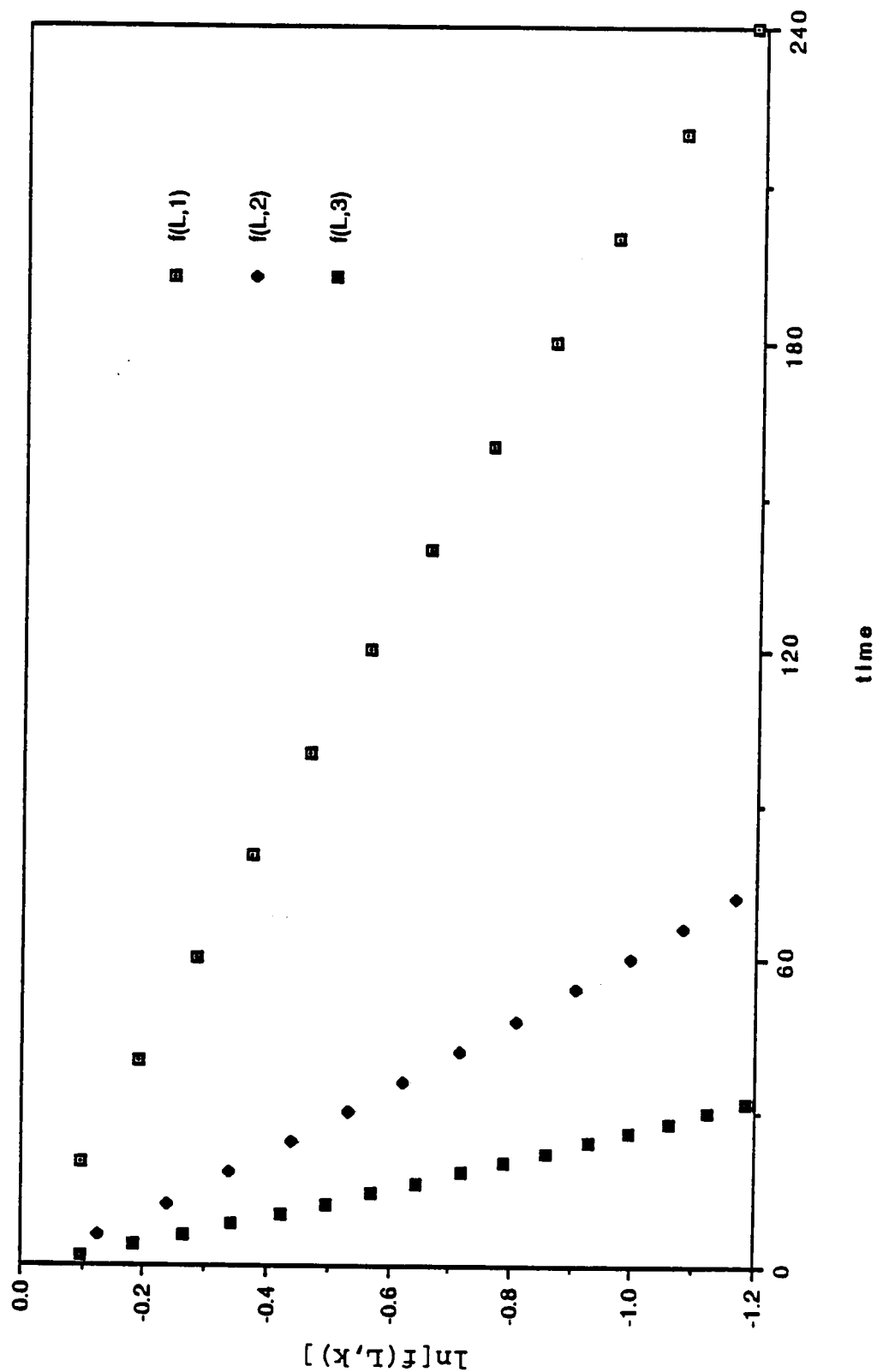


Figure 27. Semi-log plot of the autocorrelation functions of the first three normal modes for $E_F=0.16$. FCC model

The average values found for the relaxation times and the mean square-end-to-end distance are shown in Tables 8-12 (pp 108-112) for the SC chains at a variety of values of E_r where E_r has been previously defined as the negative of the minimum of the square-well potential divided by $k_B T$. E_r is referred to here as the reduced potential. Likewise the values of the relaxation times and the mean square end-to-end distance for the FCC model are listed in Tables 13-17 (pp 113-117).

In the good solvent regime, the relaxation times decrease with increasingly attractive pair interactions. This can be easily understood in terms of the dynamic scaling hypothesis. The attractive interactions reduce the chain's dimensions and therefore the relaxation times. However, the data shows that when the attraction becomes strong enough, the relaxation times of the third mode begin to increase for both the SC and FCC lattices.

To test the dynamic scaling hypothesis, the mean-square end-to-end distances for the chains were used to find the static scaling exponents, 2ν , for each potential and lattice model. The values of 2ν are given in Tables 18 and 19 for the SC and FCC models respectively. Likewise, the relaxation times were used to find the dynamic scaling exponents $a(k)$ and w . These exponents are also found in Tables 18 (p 118) and 19 (p 119).

In the last two columns of the table the values of w -

Table 8. Data for the Chain Length $L=23$ for the SC Model as
a Function of the Reduced Pair Potential, E_r .^{a,b}

E_r	$\langle R^2 \rangle$	$t_R(23)$	$t(23,1)$	$t(23,2)$	$t(23,3)$
-.20	53.7 (.4)	315 (5)	317 (9)	70.0 (2.7)	27.1 (.6)
-.10	51.4 (1.2)	328 (23)	326 (26)	66.4 (1.8)	26.0 (.7)
0.00	48.4 (.5)	257 (33)	268 (28)	65.1 (5.9)	26.5 (1.0)
.10	45.2 (.9)	255 (21)	284 (14)	65.4 (4.1)	25.9 (1.8)
.20	40.9 (.9)	244 (37)	244 (31)	61.3 (4.0)	25.4 (.8)
.30	36.8 (.7)	220 (17)	229 (17)	60.4 (2.1)	28.1 (1.5)
.32	36.1 (.4)	209 (11)	216 (10)	63.8 (2.7)	29.8 (1.8)
.34	35.0 (.7)	210 (6)	216 (11)	62.7 (4.0)	29.9 (1.5)
.36	34.0 (.9)	209 (18)	220 (15)	65.3 (5.0)	31.1 (2.1)
.38	33.1 (.9)	204 (16)	216 (16)	66.0 (4.7)	32.2 (2.2)
.40	31.9 (1.4)	190 (63)	209 (16)	64.3 (3.5)	31.8 (1.4)
.50	26.3 (.8)	163 (8)	186 (8)	75.8 (7.1)	39.0 (2.3)

^a $\langle R^2 \rangle$ data for the values of $E_r = 0.0, .10, \text{ and } .20$
was obtained from data collected for References 34 and 35.

^b Standard deviations of the runs are in parentheses.

Table 9. Data for the Chain Length $L=35$ for the SC Model as
a Function of the Reduced Pair Potential, E_R .^{a,b}

E_R	$\langle R^2 \rangle$	$t_R(35)$	$t(35,1)$	$t(35,2)$	$t(35,3)$
-.20	90.7 (2.8)	930 (100)	921 (87)	187 (10)	76.9 (4)
-.10	87.8 (3.1)	770 (74)	785 (80)	177 (22)	70.0 (5.2)
.00	79.6 (3.2)	704 (33)	722 (29)	173 (5.9)	72.0 (1.0)
.10	73.3 (3.3)	725 (130)	708 (100)	166 (4)	66.4 (1.8)
.20	65.7 (1.8)	572 (69)	591 (67)	149 (11)	66.5 (4.9)
.30	55.8 (1.3)	547 (17)	562 (17)	156 (2)	70.5 (1.5)
.32	54.3 (1.7)	504 (17)	542 (30)	158 (11)	71.0 (3.9)
.34	52.5 (2.1)	489 (26)	516 (30)	156 (11)	74.3 (5.1)
.36	53.1 (2.2)	487 (51)	496 (37)	160 (22)	74.9 (3.4)
.38	47.7 (2.0)	464 (21)	491 (23)	156 (6)	81.0 (5.5)
.40	46.5 (2.4)	450 (37)	490 (28)	156 (9)	77.9 (4.5)
.50	36.2 (2.1)	390 (47)	442 (47)	178 (7)	94.1 (20)

^a $\langle R^2 \rangle$ data for the values of $E_R = 0.0, .10, \text{ and } .20$
was obtained from data collected for References 34 and 35.

^b Standard deviations of the runs are in parentheses.

Table 10. Data for the Chain Length $L=47$ for the SC Model as
a Function of the Reduced Pair Potential, E_R .^{a,b}

E_R	$\langle R^2 \rangle$	$t_R(47)$	$t(47,1)$	$t(47,2)$	$t(47,3)$
-.20	129 (2)	1750 (170)	1750 (170)	352 (14)	142 (2)
-.10	120 (3)	1650 (130)	1630 (340)	336 (15)	139 (4)
.00	114 (7)	1260 (50)	1320 (110)	317 (26)	134 (17)
.10	105 (3)	1230 (110)	1230 (93)	301 (14)	122 (3)
.20	90.2 (6.4)	1040 (50)	1080 (30)	293 (13)	125 (7)
.30	77.5 (4.4)	993 (142)	1010 (110)	288 (22)	137 (8)
.32	74.6 (1.5)	928 (64)	975 (53)	283 (11)	130 (6)
.34	68.0 (98)	899 (90)	949 (28)	299 (28)	141 (8)
.36	66.8 (1.1)	855 (51)	910 (25)	270 (15)	148 (10)
.38	62.8 (2.2)	855 (65)	928 (58)	300 (16)	151 (7)
.40	60.9 (4.1)	812 (66)	879 (70)	289 (9)	146 (7)
.50	41.4 (1.9)	601 (61)	720 (32)	358 (23)	195 (19)

^a $\langle R^2 \rangle$ data for the values of $E_R = 0.0, .10, \text{ and } .20$
was obtained from data collected for References 34 and 35.

^b Standard deviations of the runs are in parentheses.

Table 11. Data for the Chain Length $L=59$ for the SC Model as
a Function of the Reduced Pair Potential, E_R .^{a,b}

E_R	$\langle R^2 \rangle$	$t_R(59)$	$t(59,1)$	$t(59,2)$	$t(59,3)$
-.20	172 (3.6)	2900 (220)	2860 (200)	574 (20)	237 (16)
-.10	157 (1.4)	2270 (110)	2340 (170)	539 (24)	219 (4)
.00	153 (7)	2270 (110)	2260 (180)	553 (22)	225 (15)
.10	139 (3)	1930 (100)	1940 (90)	499 (36)	211 (10)
.20	115 (3.8)	1910 (190)	1920 (180)	475 (52)	210 (10)
.30	95.6 (4.6)	1560 (150)	1620 (150)	428 (16)	223 (11)
.32	92.0 (1.8)	1480 (210)	1540 (160)	466 (25)	215 (9)
.34	80.7 (1.7)	1440 (110)	1520 (90)	468 (22)	226 (25)
.36	80.9 (2.1)	1400 (90)	1450 (60)	473 (17)	241 (18)
.38	77.3 (2.7)	1320 (90)	1420 (90)	451 (14)	235 (9)
.40	71.2 (3.8)	1260 (90)	1360 (80)	473 (35)	247 (22)
.50	47.7 (2.2)	928 (28)	1220 (61)	537 (37)	330 (39)

^a $\langle R^2 \rangle$ data for the values of $E_R = 0.0, .10, \text{ and } .20$
was obtained from data collected for References 34 and 35.

^b Standard deviations of the runs are in parentheses.

Table 12. Data for the Chain Length $L=71$ for the SC Model as
a Function of the Reduced Pair Potential, E_R .^a

E_R	$\langle R^2 \rangle$	$t_R(71)$	$t(71,1)$	$t(71,2)$	$t(71,3)$
-.20	216 (430)	4310 (430)	4300 (220)	920 (30)	367 (10)
-.10	201 (4)	3670 (170)	3660 (100)	855 (24)	345 (8)
.00	---	3780 (240)	3740 (190)	788 (68)	335 (16)
.10	---	3370 (210)	3400 (230)	747 (40)	331 (16)
.20	---	2770 (145)	2830 (165)	675 (35)	283 (47)
.30	114 (4)	2320 (120)	2400 (140)	677 (22)	322 (19)
.32	112 (1)	2150 (150)	2230 (150)	688 (55)	328 (20)
.34	106 (5)	2070 (270)	2190 (240)	651 (29)	328 (13)
.36	96.3 (1.5)	1940 (140)	2051 (150)	684 (28)	335 (18)
.38	89.6 (3.1)	1900 (200)	2110 (160)	664 (40)	361 (30)
.40	82.1 (2.5)	1870 (160)	2090 (150)	688 (74)	390 (29)
.50	51.2 (2.2)	1160 (100)	1550 (110)	822 (68)	510 (24)

^a Standard deviations of the runs are in parentheses.

Table 13. Data for the Chain Length $L=23$ for the FCC Model
as a Function of the Reduced Pair Potential, E_r .^a

E_r	$\langle R^2 \rangle$	$t_R(23)$	$t(23,1)$	$t(23,2)$	$t(23,3)$
-.10	44.5 (1.4)	400 (84)	403 (80)	82.1 (5.7)	29.9 (.7)
-.05	43.1 (1.1)	327 (18)	330 (19)	75.6 (4.3)	28.2 (1.4)
0.00	39.3 (1.4)	323 (29)	310 (13)	70.1 (4.6)	26.6 (1.0)
.05	36.1 (.5)	302 (33)	308 (20)	68.2 (3.4)	27.9 (1.0)
.10	33.5 (1.5)	249 (19)	255 (18)	66.7 (4.2)	26.0 (2.7)
.12	31.3 (.8)	254 (18)	259 (20)	61.8 (3.1)	28.5 (2.3)
.14	29.6 (1.3)	231 (13)	228 (26)	63.4 (5.5)	27.3 (2.1)
.16	26.9 (1.1)	201 (19)	216 (24)	66.8 (7.2)	28.8 (1.5)
.18	26.2 (.3)	203 (9)	217 (7)	61.1 (4.3)	27.9 (.4)
.20	24.1 (.6)	191 (16)	207 (22)	65.3 (.8)	30.1 (2.7)
.25	20.3 (.9)	160 (12)	183 (18)	65.1 (7.2)	37.8 (4.3)

^a Standard deviations of the runs are in parentheses.

Table 14. Data for the Chain Length $L=35$ for the FCC Model
as a Function of the Reduced Pair Potential, E_r .^a

E_r	$\langle R^2 \rangle$	$t_R(35)$	$t(35,1)$	$t(35,2)$	$t(35,3)$
-0.10	77.2 (4.0)	895 (95)	925 (101)	220 (8)	83.6 (5.3)
-0.05	71.8 (2.1)	790 (37)	832 (43)	189 (6)	81.9 (4.3)
0.00	65.6 (1.9)	823 (35)	873 (29)	177 (17)	74.9 (1.1)
.05	58.4 (1.7)	698 (45)	700 (47)	175 (9)	75.5 (4.0)
.10	51.5 (2.2)	586 (28)	593 (17)	155 (15)	69.1 (7.5)
.12	48.5 (1.8)	614 (44)	621 (54)	161 (13)	71.5 (4.2)
.14	45.5 (.7)	531 (88)	567 (84)	158 (10)	72.8 (4.7)
.16	41.2 (1.7)	459 (15)	490 (21)	156 (11)	74.3 (7.5)
.18	40.3 (1.7)	553 (40)	584 (46)	155 (17)	72.4 (6.1)
.20	36.3 (1.1)	450 (19)	502 (35)	154 (10)	72.2 (7.0)
.25	26.8 (1.9)	348 (36)	447 (44)	181 (22)	100 (19)

^a Standard deviations of the runs are in parentheses.

Table 15. Data for the Chain Length $L=47$ for the FCC Model
as a Function of the Reduced Pair Potential, E_r .^a

E_r	$\langle R^2 \rangle$	$t_R(47)$	$t(47,1)$	$t(47,2)$	$t(47,3)$
-0.10	102 (3)	1940 (230)	1900 (200)	423 (53)	166 (9)
-0.05	97.2 (3.6)	1620 (220)	1620 (200)	412 (30)	158 (17)
0.00	92.8 (1.1)	1490 (130)	1500 (180)	341 (18)	152 (7)
.05	85.8 (1.1)	1240 (46)	1280 (63)	342 (26)	138 (3)
.10	72.2 (2.0)	1140 (80)	1120 (70)	301 (20)	136 (15)
.12	67.1 (3.2)	1060 (178)	1090 (210)	286 (34)	130 (10)
.14	60.2 (1.9)	977 (128)	1050 (60)	285 (11)	139 (3)
.16	70.0 (2.4)	953 (59)	1020 (100)	268 (5)	137 (5)
.18	50.2 (3.2)	794 (63)	850 (17)	287 (21)	144 (8)
.20	43.4 (2.5)	720 (29)	794 (46)	291 (7)	149 (9)
.25	32.2 (.8)	553 (51)	698 (92)	283 (16)	170 (19)

^a Standard deviations of the runs are in parentheses.

Table 16. Data for the Chain Length $L=59$ for the FCC Model
as a Function of the Reduced Pair Potential, E_r .^a

E_r	$\langle R^2 \rangle$	$t_R(59)$	$t(59,1)$	$t(59,2)$	$t(59,3)$
-.10	145 (8)	3060 (370)	2970 (300)	669 (63)	290 (8)
-.05	135 (5)	2900 (440)	2950 (340)	634 (47)	263 (18)
0.00	121 (2)	2760 (160)	2440 (250)	597 (90)	238 (17)
.05	113 (5)	2420 (210)	2470 (130)	520 (59)	243 (5)
.10	93.2 (2.3)	1880 (230)	1870 (180)	491 (18)	224 (15)
.12	85.6 (1.3)	1860 (250)	1900 (190)	474 (28)	210 (15)
.14	79.7 (3.9)	1550 (120)	1600 (90)	447 (29)	215 (9)
.16	70.0 (2.5)	1600 (210)	1620 (200)	469 (18)	221 (16)
.18	60.4 (2.0)	1200 (120)	1300 (70)	447 (34)	217 (12)
.20	52.7 (2.5)	1120 (29)	1250 (46)	428 (21)	235 (3)
.25	33.2 (1.2)	714 (37)	943 (64)	454 (26)	304 (30)

^a Standard deviations of the runs are in parentheses.

Table 17. Data for the Chain Length $L=71$ for the FCC Model
as a Function of the Reduced Pair Potential, E_r .^a

E_r	$\langle R^2 \rangle$	$t_R(71)$	$t(71,1)$	$t(71,2)$	$t(71,3)$
-.10	176 (5)	4250 (1100)	4440 (990)	1100 (45)	437 (22)
-.05	168 (11)	4030 (530)	4100 (480)	969 (80)	395 (33)
0.00	154 (7)	3920 (600)	3810 (350)	887 (31)	387 (38)
.05	138 (2)	3250 (190)	3370 (130)	829 (32)	355 (24)
.10	114 (5)	2890 (270)	3070 (220)	714 (30)	308 (23)
.12	97.4 (5.7)	2350 (150)	2520 (140)	721 (29)	339 (19)
.14	93.8 (6.0)	2350 (160)	2390 (170)	682 (34)	310 (12)
.16	83.7 (3.7)	2110 (170)	2200 (110)	696 (47)	306 (14)
.18	67.8 (3.2)	1680 (160)	1900 (140)	636 (43)	363 (27)
.20	58.7 (.8)	1490 (120)	1710 (130)	647 (37)	380 (28)
.25	34.8 (1.9)	860 (100)	1250 (100)	660 (52)	394 (16)

^a Standard deviations of the runs are in parentheses.

Table 18. Values of the Scaling Exponents $2v$, w , and $a(k)$ as a Function of the Reduced Pair Potential, E_r , for the SC model.

E_r	$2v$	w	$a(1)$	$a(2)$	$a(3)$	$w-2v$	$a(1)-2v$
-.20	2.31	2.30	2.26	2.29	1.23	1.08	1.07
-.10	2.13	2.14	2.24	2.28	1.19	1.06	.95
0.00	2.35	2.30	2.22	2.25	1.22	1.13	1.08
.10	2.21	2.14	2.15	2.24	1.19	1.02	.95
.20	2.17	2.18	2.15	2.16	1.10	1.07	1.08
.30	2.08	2.07	2.11	2.18	1.01	1.07	1.06
.32	2.07	2.06	2.10	2.12	1.00	1.07	1.06
.34	2.04	2.05	2.09	2.13	.98	1.06	1.07
.36	1.99	1.99	2.08	2.14	.93	1.06	1.07
.38	1.98	2.02	2.05	2.13	.89	1.09	1.13
.40	1.92	2.02	2.08	2.15	.84	1.08	1.18
.50	1.74	1.90	2.12	2.30	---	---	---

Table 19. Values of the Scaling Exponents $2v$, w , and $a(k)$ as a Function of the Reduced Pair Potential, E_r , for the FCC model.

E_r	$2v$	w	$a(1)$	$a(2)$	$a(3)$	$w-2v$	$a(1)-2v$
-.10	2.15	2.15	2.27	2.39	1.22	.93	.93
-.05	2.28	2.27	2.28	2.33	1.20	1.08	1.07
0.00	2.23	2.18	2.26	2.35	1.21	1.02	.97
.05	2.15	2.13	2.19	2.26	1.20	.95	.93
.10	2.18	2.19	2.12	2.22	1.10	1.08	1.09
.12	2.01	2.05	2.16	2.17	1.03	.98	1.02
.14	2.05	2.07	2.09	2.15	1.03	1.02	1.04
.16	2.15	2.11	2.07	2.11	1.01	1.14	1.10
.18	1.82	1.86	2.08	2.24	.84	.98	1.02
.20	1.82	1.86	2.07	2.24	.78	1.04	1.08
.40	1.92	2.02	2.08	2.15	.84	1.08	1.18
.50	1.74	1.90	2.12	2.30	---	---	---

2ν and $a(1)-2\nu$ are listed. According to the dynamic scaling hypothesis these values should be equal to 1.0. It can be seen that the data gives values very close to the predicted value of 1.0 for repulsive potentials and temperatures above the theta point. Therefore, it seems that the dynamic scaling hypothesis holds quite well for extended chains.

Below the theta point the data for the mean-square end-to-end distance did not fit the static scaling law given by Equation 14 (p 12) well and therefore no value is given for 2ν . The absence of a good scaling relation for $\langle R^2 \rangle$ just below the theta point has been reported before and other researchers' data suggests that the radius of gyration may be a more useful measure of a chain's dimensions below the theta point.^{37,68} This should be investigated in future work.

Mazur and McCrackin had previously found that the static scaling exponent, 2ν , found for the FCC and SC lattice models was the same for a given value of q^*E_r .¹¹ We find that this is true for the data collected in this study as can be seen from Figure 28 (p 121). Since the chains obey the dynamic scaling hypothesis in the good solvent region, this implies that $a(k)$ values obtained for the two lattices are also equal for a given value of q^*E_r . From Figure 29 (p 122), we can see this graphically. Since the models have the same scaling behavior for a given value of q^*E_r , this quantity is referred to here as the effective potential.

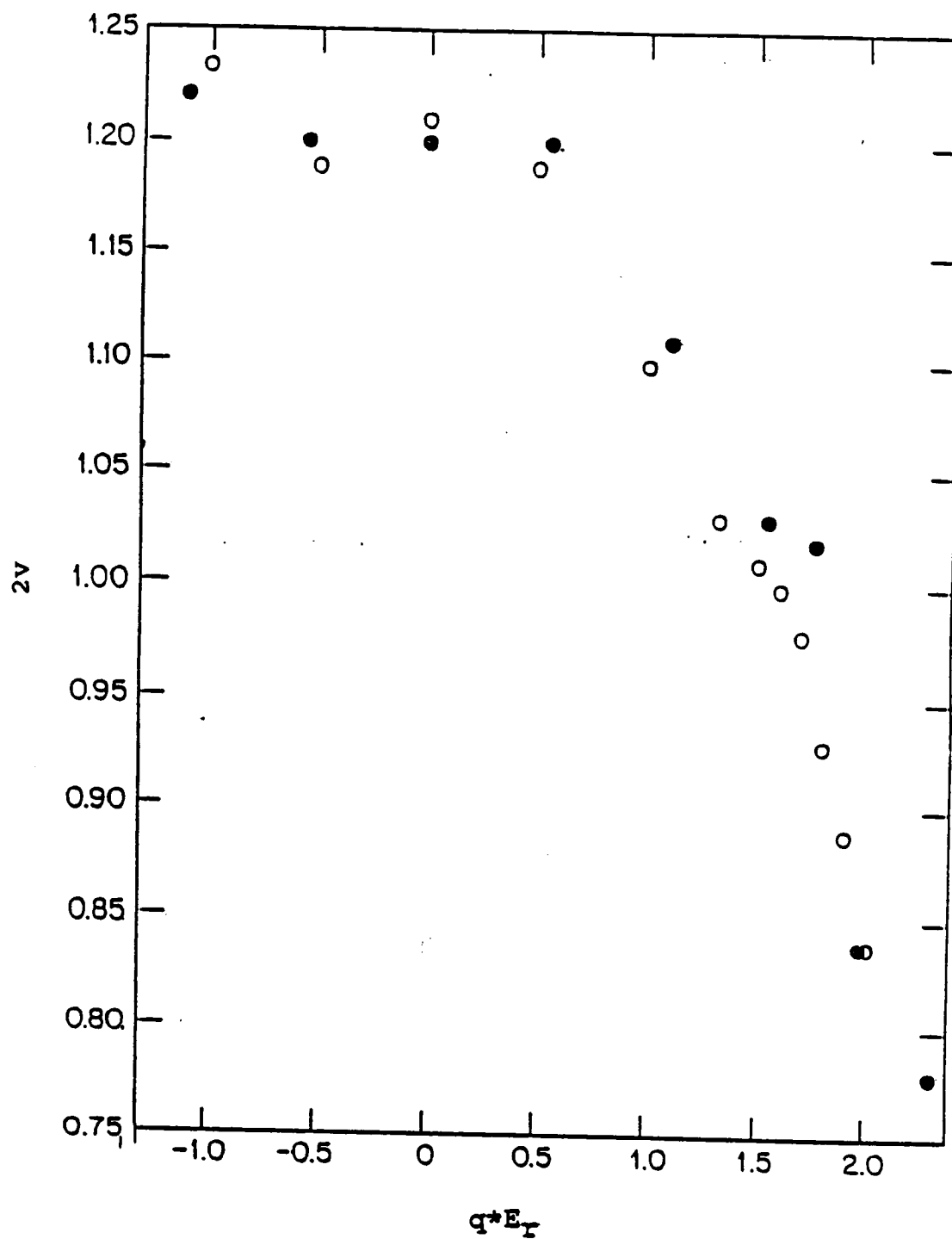


Figure 28. The scaling exponent $2v$ as a function of the effective potential, $q \cdot E_r$.

Open symbols are for the SC model. Closed symbols are for the FCC model.

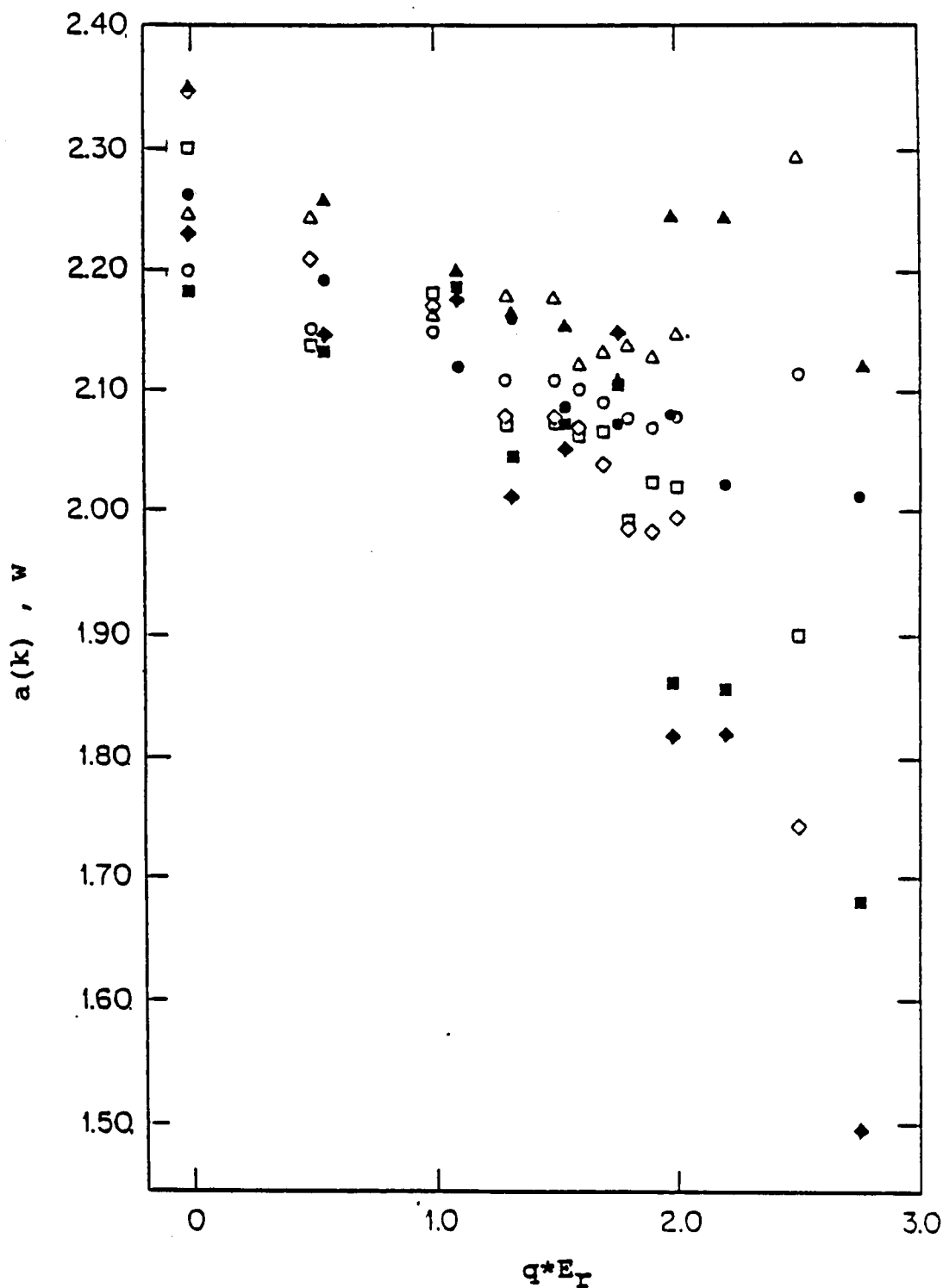


Figure 29. The scaling exponents w and $a(k)$ as a function of the effective potential, $q \cdot E_r$.

Open symbols are for the SC model. Closed symbols are for the FCC model. $w = (\diamond)$, $a(1) = (\square)$, $a(2) = (\circ)$, and $a(3) = (\triangle)$.

The values of $a(k)$ increase with increasing k for both lattice models. There are a few exceptions to this rule, but these are almost certainly the result of statistical scatter. The increase of $a(k)$ with k was previously observed for the athermal models. In good solvent conditions, the differences between $a(1)$, $a(2)$, and $a(3)$ found here are about the same magnitude as was found for the athermal model. In terms of the dynamic scaling hypothesis, the increase of $a(k)$ with k would mean that short segments are increasing in scale at a faster rate than the longer segments when the chain is increased in length. This is not possible for infinitely long chains, but cannot be ruled out for the short chains used in this study.

The two models give $a(k)$ values with very different behavior below the theta point. As the attraction increases, the SC lattice value of $a(3)$ increases sharply, while $a(2)$ shows a small increase, and $a(1)$ continues to decrease. For the FCC model $a(1)$ and $a(2)$ decrease, while $a(3)$ remains approximately constant.

Monte Carlo studies of highly concentrated systems have shown that increasing density causes an increase in $a(k)$.^{57,58} This increase is particularly great for the SC lattice since its crankshaft motions are frozen out at high concentration. Still, concentration effects cannot fully account for the observed behavior of $a(k)$. The chains being studied here are not very collapsed since we are observing

conditions near the theta point. Also, the high concentration studies have shown that increasing concentration effects all $a(k)$ in approximately the same manner.

Short range expansions of the chains which increase in scale more rapidly than the overall chain dimensions as the chain length is increased could also account for these observations, but it is unlikely that any such thing would happen. Such an expansion could not occur as the chain became infinitely long. To explain the data observed here, it would require that the chain lengths used here were of a particularly short magnitude for which this expansion occurs. If there was little difference between $a(1)$, $a(2)$, and $a(3)$, then this may be credible, but not for the large differences seen here, especially since the chains used here are of similar length. It is also debatable as to whether short range expansions occur below the theta point. In Curro and Schaefer's study, there was no expansion observed for a chain just below the theta temperature.⁴⁵ For future work it would be interesting to see how the internal segment distances scale in comparison with the overall chain dimensions for these chain lengths and potentials.

The most likely cause for the k dependence of $a(k)$ observed in the theta region is the effect of the increasing attractions on the lifetime of pair contacts. As the attraction increases the mean lifetime of a pair contact

should also increase. If the mean lifetime of a pair contact begins to approach the relaxation time of a normal mode, then the relaxation time of that normal mode should begin to increase dramatically. This is the physical basis of the concept of gel modes given by Brochard and deGennes.¹ Gel modes may explain much of the difference between the values of $a(k)$ obtained for the different lattices since the two-bead, crankshaft motions of the SC model are likely to be somewhat more effected by long pair lifetimes than single bead motions.

The values obtained for t_r and w below the theta point are of debatable merit. As the theta point is passed, the relaxation times of the normal modes begin to converge. The relaxation of the end-to-end vector is the result of contributions from the motion of all the modes. The linear region from which its relaxation times are found should be selected at long times since at long times the contributions of all but the first mode have died out. If the relaxation times of the modes are all approaching the same value, then the linear region will occur at much longer times. Indeed it was found that below the theta point the autocorrelation functions of the end-to-end vector lose their linearity over the region from which the relaxation times were calculated.

The relaxation times of the normal modes were also used to obtain the values of the scaling exponent $b(L)$. These values are listed in Tables 20 (p 126) and 21 (p 127)

Table 20. Values of the Scaling Exponent, $b(L)$, as a Function of Chain Length, L , and the Reduced Pair Potential, E_r , for the SC Model.

E_r	$b(23)$	$b(35)$	$b(47)$	$b(59)$	$b(71)$
-.20	2.23	2.26	2.29	2.27	2.24
-.10	2.30	2.20	2.25	2.15	2.14
0.00	2.10	2.09	2.06	2.10	2.20
.10	2.17	2.15	2.09	2.10	2.13
.20	1.91	1.99	1.96	2.01	2.09
.30	1.91	1.89	1.80	1.78	1.79
.32	1.80	1.84	1.83	1.79	1.74
.34	1.80	1.76	1.73	1.73	1.73
.36	1.78	1.71	1.66	1.63	1.64
.38	1.73	1.64	1.65	1.64	1.61
.40	1.71	1.67	1.63	1.55	1.53
.50	1.41	1.40	1.17	1.19	1.00

Table 21. Values of the Scaling Exponent, $b(L)$, as a Function of Chain Length, L , and the Reduced Pair Potential, E_r , for FCC Model.

E_r	$b(23)$	$b(35)$	$b(47)$	$b(59)$	$b(71)$
-.10	2.36	2.18	2.21	2.12	2.10
-.05	2.19	2.02	2.11	2.20	2.13
0.00	2.23	2.24	2.09	2.11	2.08
.05	2.19	2.02	2.01	2.13	2.05
.10	2.06	1.96	1.92	1.93	2.09
.12	2.02	2.00	1.93	2.00	1.83
.14	1.92	1.87	1.84	1.83	1.86
.16	1.82	1.71	1.84	1.81	1.78
.18	1.86	1.90	1.61	1.62	1.51
.20	1.75	1.76	1.52	1.52	1.37
.25	1.46	1.35	1.29	1.03	1.04
.50	1.41	1.40	1.17	1.19	1.00

for the SC and FCC models respectively. For expanded chains, the exponents for the two models are equal for a given value of the scaled potential as is shown in Figure 30 (p 129).

From the figure, it can be seen that the SC model gives smaller values of $b(L)$ for a given value of $q \cdot E_r$ in the theta region. The reason for this may simply be that the crankshaft motions are rarely performed in the interior of a somewhat collapsed chain, thus slowing the relaxations. The motions in the interior of the coil are crucial for the relaxation of the higher modes, but seem to be less important to the relaxation of the first mode.

As the theta point is approached the values of $b(L)$ decrease for increasing L . Decreasing values of $b(L)$ indicate that the short range motions within the chain are becoming more inhibited relative to the long range motions. This is consistent with the concept of gel modes since the longer chains have more nearest-neighbor pair contacts per segment as a result of their comparatively smaller surface area. Therefore, the gel mode hypothesis predicts that the higher modes are particularly slow for the long chains. This accounts for the decrease in $b(L)$. This is not to imply that the decrease in $b(L)$ is a simple density effect. It has been shown that $b(L)$ is only weakly dependent on density and that at high densities $b(L)$ approaches the Rouse value of 2.0.^{57,58}

Internal expansion effects are also unlikely to cause

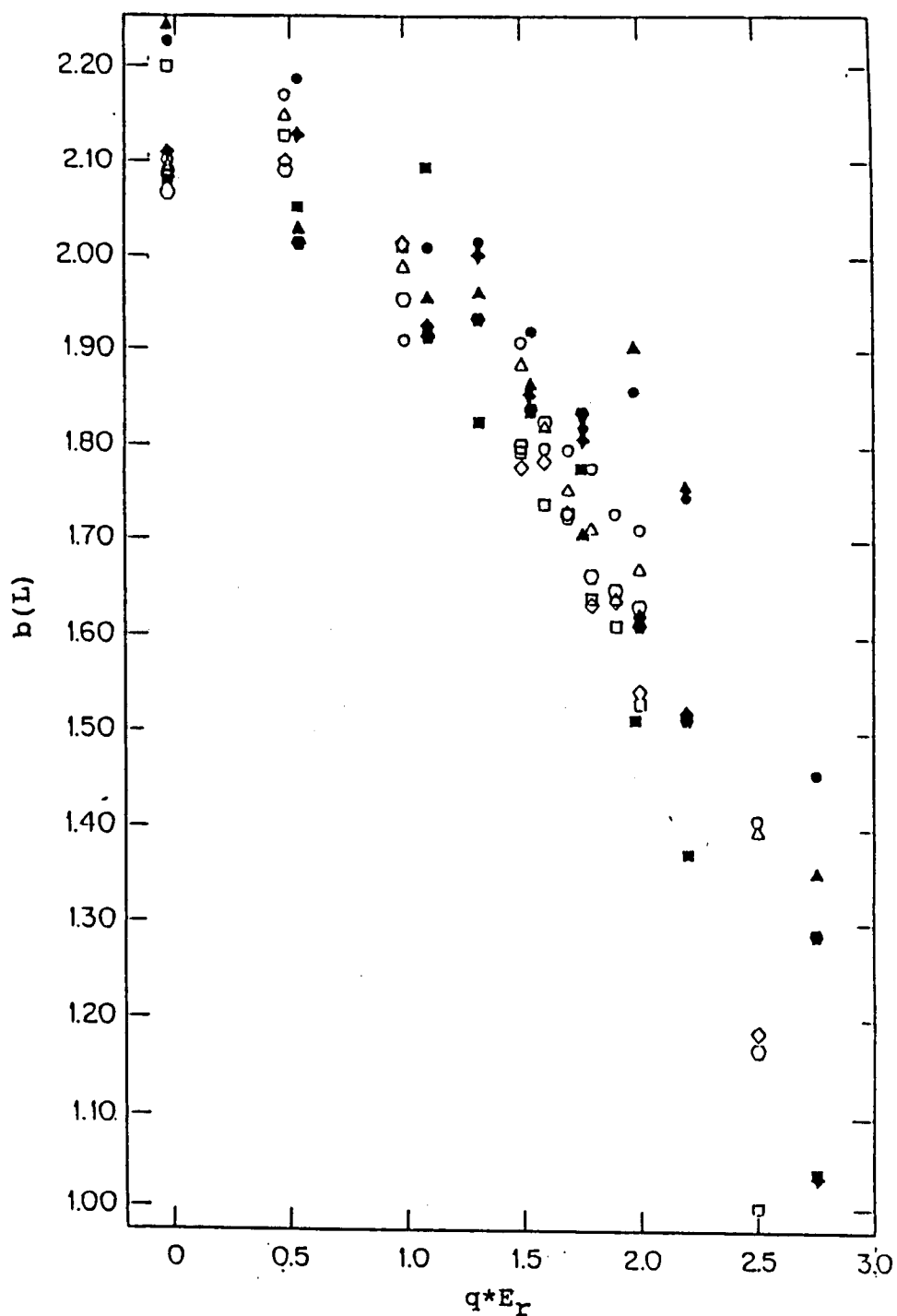


Figure 30. The scaling exponents $b(L)$ as a function of the effective potential, $q \cdot E_r$.

Open symbols are for the SC model. Closed symbols are for the FCC model. $L = 23(\bigcirc)$, $35(\triangle)$, $47(\hexagon)$, $59(\diamond)$, and $71(\square)$.

$b(L)$ to decrease with increasing L . Curro and Schaefer observed that internal segments of a given length are approximately the same size as an isolated chain of the same length for a chain just below the theta point, i.e. the chain is self-similar. This indicates that the expansion caused by the excluded volume condition has been effectively overcome by the attractive interaction. If a chain is self-similar, then the structure of the chain would affect all ranges of motion in a similar manner.

The theta point is defined to be the temperature at which a self-avoiding chain's attractive self-interactions cause it to behave as an ideal coil. It has been recognized that it is unlikely a potential could be found at which all the characteristics of an ideal chain would appear simultaneously. Therefore, the term theta region has been used to describe a temperature region where various of characteristics of an ideal coil can be found. In this work the theta point has been located for a number of different properties.

For an ideal chain, the values of $a(1)$, w , and $2v$ should be equal to 2.0, 2.0, and 1.0 respectively. From Tables 18 (p 118) and 19 (p 119), we find that for the FCC lattice these characteristics occur at about $q \cdot E_r = 1.87$, while for the SC lattice these characteristics occur approximately $q \cdot E_r = 1.7$. The reason for this difference is not known. It seems odd that the more flexible of the two

lattices would have the theta point requiring a greater attractive force. The flexibility should allow its dimensions to contract more easily since the correlation between successive bond vectors will die off more quickly. Therefore, it would seem that the difference in the observed theta values is likely to be the result of statistical errors inherent in any Monte Carlo study.

Another measure of the theta point is given by the quantity $\langle R^2 \rangle / L$. Domb and Fisher⁹³ have predicted that at the theta point this quantity will be equal to 1.5 and 1.2 for self-avoiding chains on the SC and FCC lattices respectively. This quantity is plotted vs. $q \cdot E_r$ for the SC and FCC lattices in Figures 31 (p 132) and 32 (p 133) respectively. From the figures we find that the SC lattice has its theta point value at $q \cdot E_r = 1.7$. For the FCC lattice the theta point value occurs at $q \cdot E_r = 1.76$.

The figures do not show any obvious chain length dependence of the theta point. However, a previous study using the SC model used center-of-mass diffusion data to estimate the theta point for infinitely long chains to be $q \cdot E_r = 1.5$.³⁵ For short chains, the study found the theta point to be at $q \cdot E_r = 1.7$ in agreement with the values obtained in this work.

The previously mentioned measures of the theta point all reach their theta point values at approximately the same values of the scaled potential. Thus it is tempting to refer

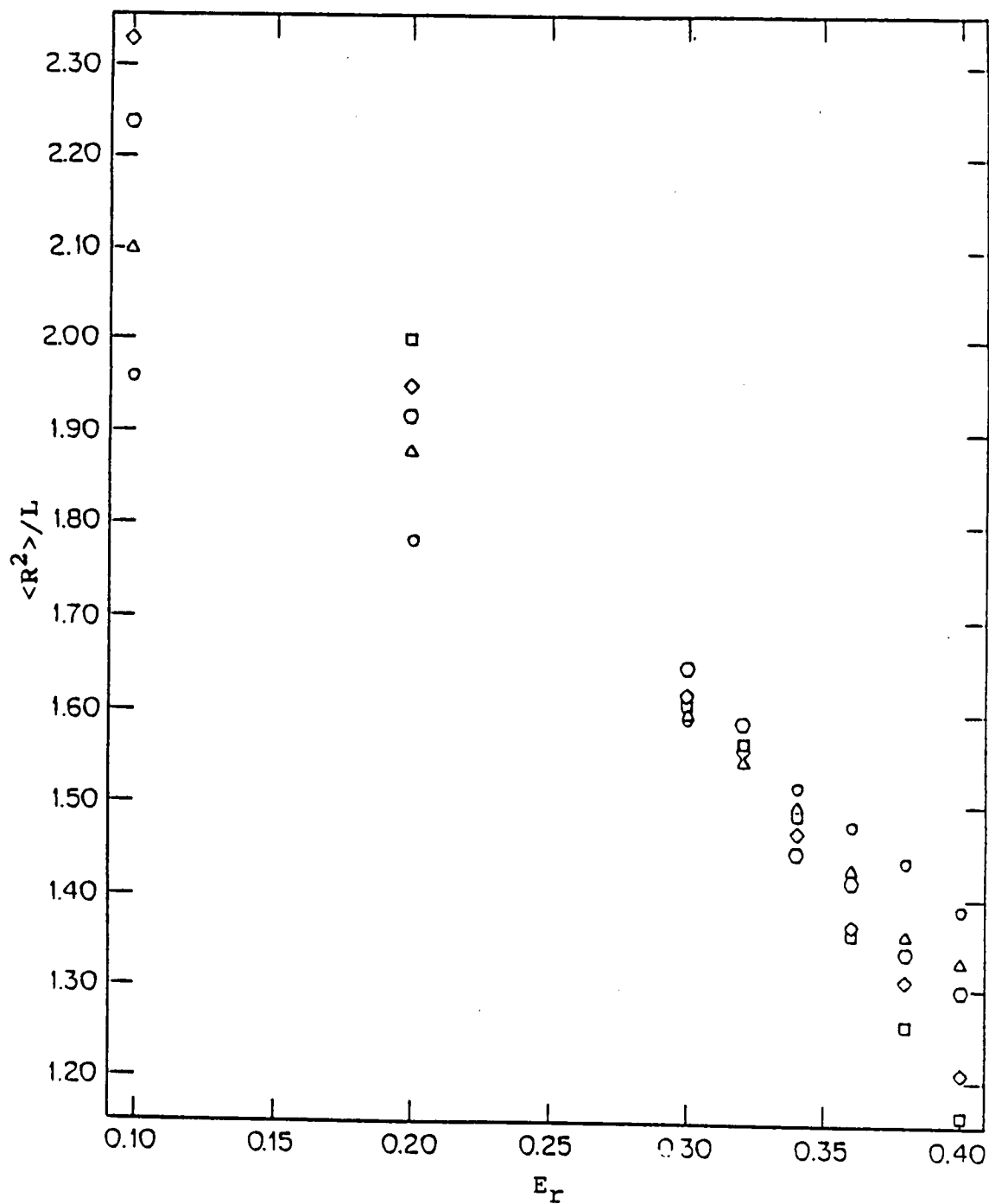


Figure 31. $\langle R^2 \rangle / L$ as a function of the reduced potential, E_r , for the SC model.

$L = 23(\bigcirc)$, $35(\triangle)$, $47(\odot)$, $59(\diamond)$, and $71(\square)$.

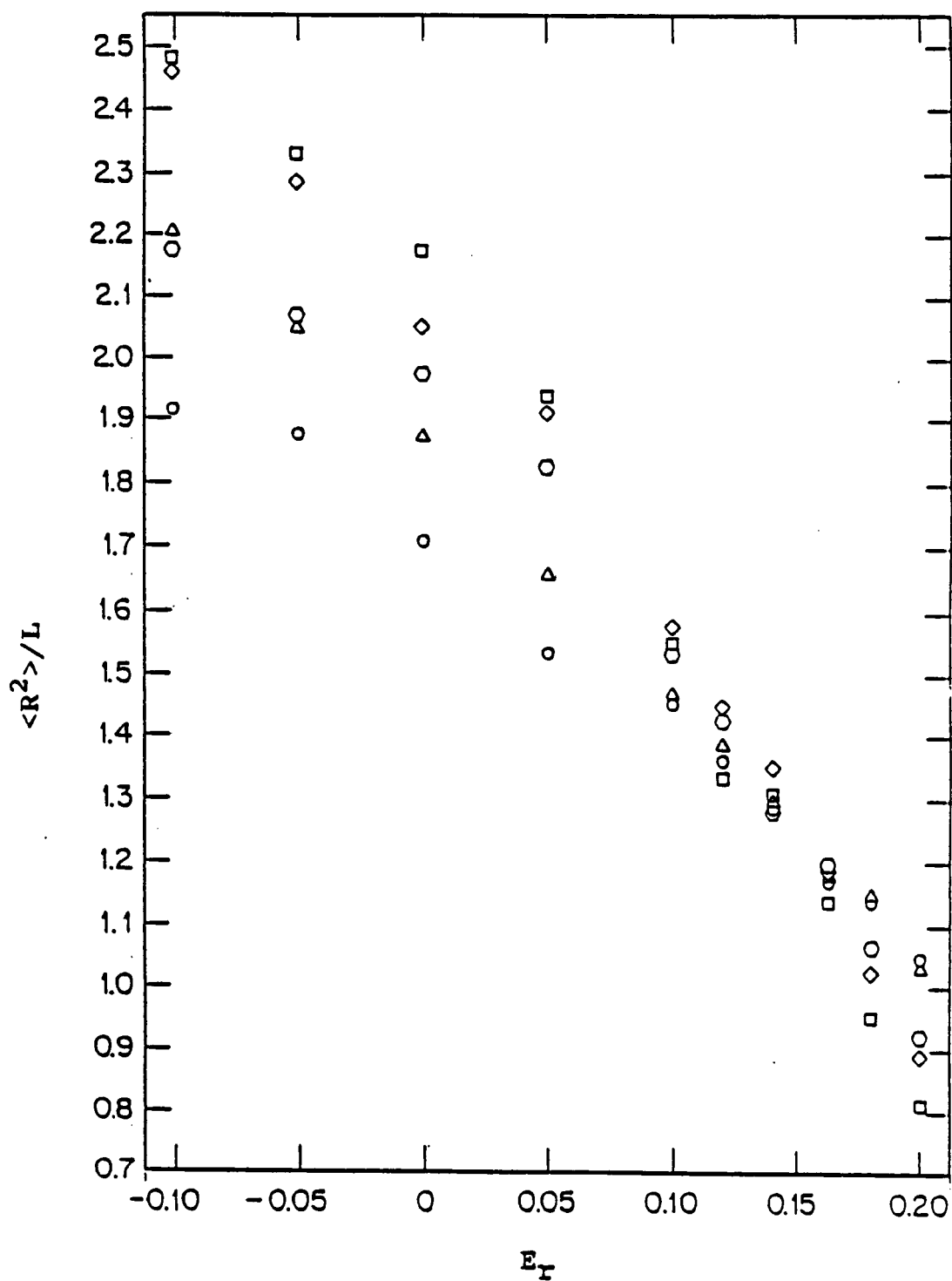


Figure 32. $\langle R^2 \rangle / L$ as a function of the reduced potential, E_r , for the FCC model.

$L = 23(\bigcirc)$, $35(\triangle)$, $47(\diamond)$, $59(\diamond)$, and $71(\square)$.

to a specific theta point rather than a theta region. However, there are some obvious quantities which do not reach their theta point values in this area. Both $b(L)$ and all $a(k)$ values should be equal to 2.0 at the theta point. From the values of $b(L)$ in Tables 20 (p 126) and 21 (p 127) it can be seen that $b(L)$ reaches its theta point value at much less attractive interactions than the previously discussed measures of the theta point. From Tables 18 (p 118) and 19 (p 119), it is apparent that as k increases, $a(k)$ reaches its theta point value of 2.0 at progressively, less attractive potentials.

To show the approach to the theta point in terms of the scaling exponents $a(k)$ and $b(L)$, plots were constructed of $a(k)$ vs. b , where b is the average of $b(60)$ and $b(72)$. This was done for both the SC and the FCC data. Figures 33 (p 135) and 34 (p 136) show that the true Rouse spectrum of dynamic scaling exponents is not even approximately obtained by a single value of the pair potential. This shows that no chain with excluded volume should be regarded as a truly ideal chain.

The difference between the lattice models in the poor solvent regime raises questions as to the credibility of the results of either lattice model. Hopefully, the differences are due to the two-bead elementary motions required for the SC model. If this is the case, then the data obtained for the FCC model may still provide an accurate representation

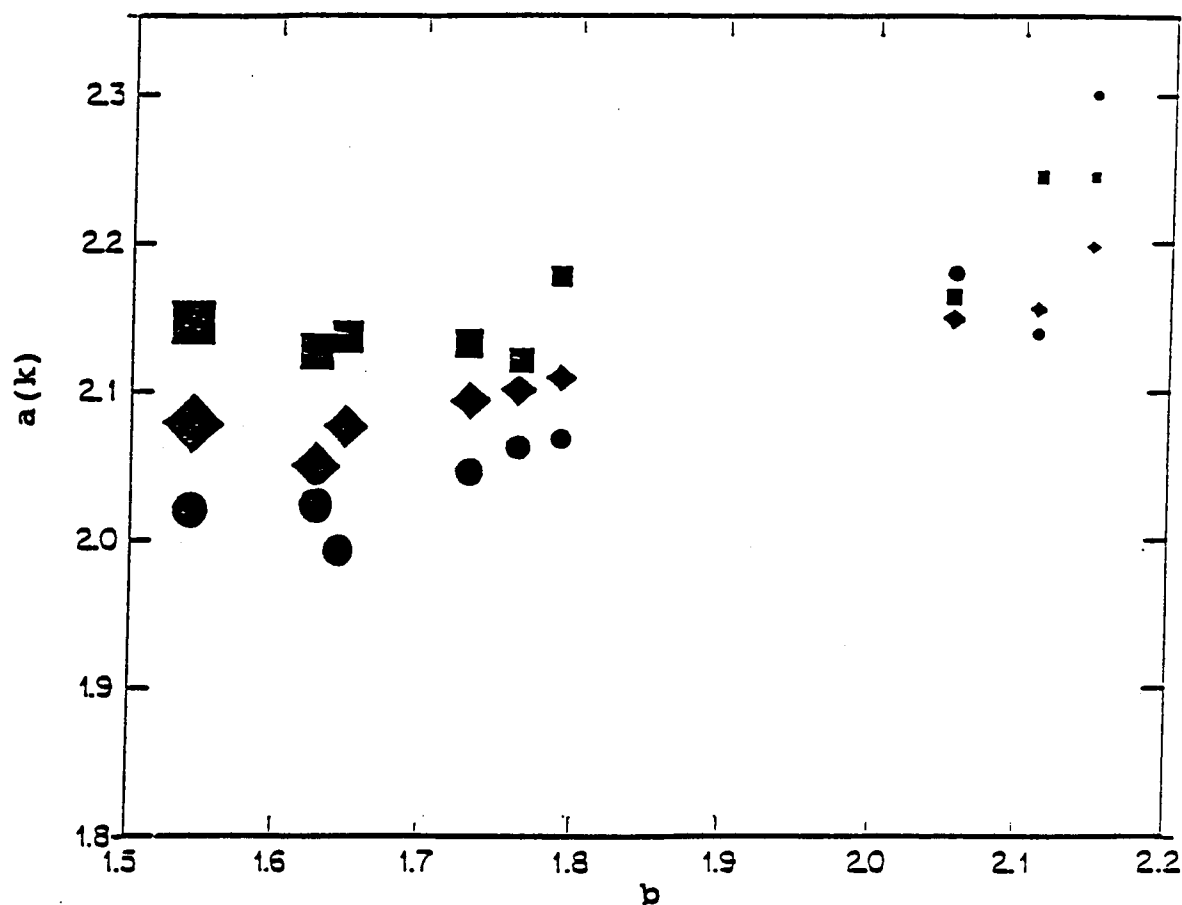


Figure 33. The scaling exponents $a(k)$ as a function of the scaling exponent b for the SC model.

$k = 1(\bullet)$, $2(\blacklozenge)$, and $3(\blacksquare)$. Increasingly large symbols indicate increasingly attractive pair interaction.

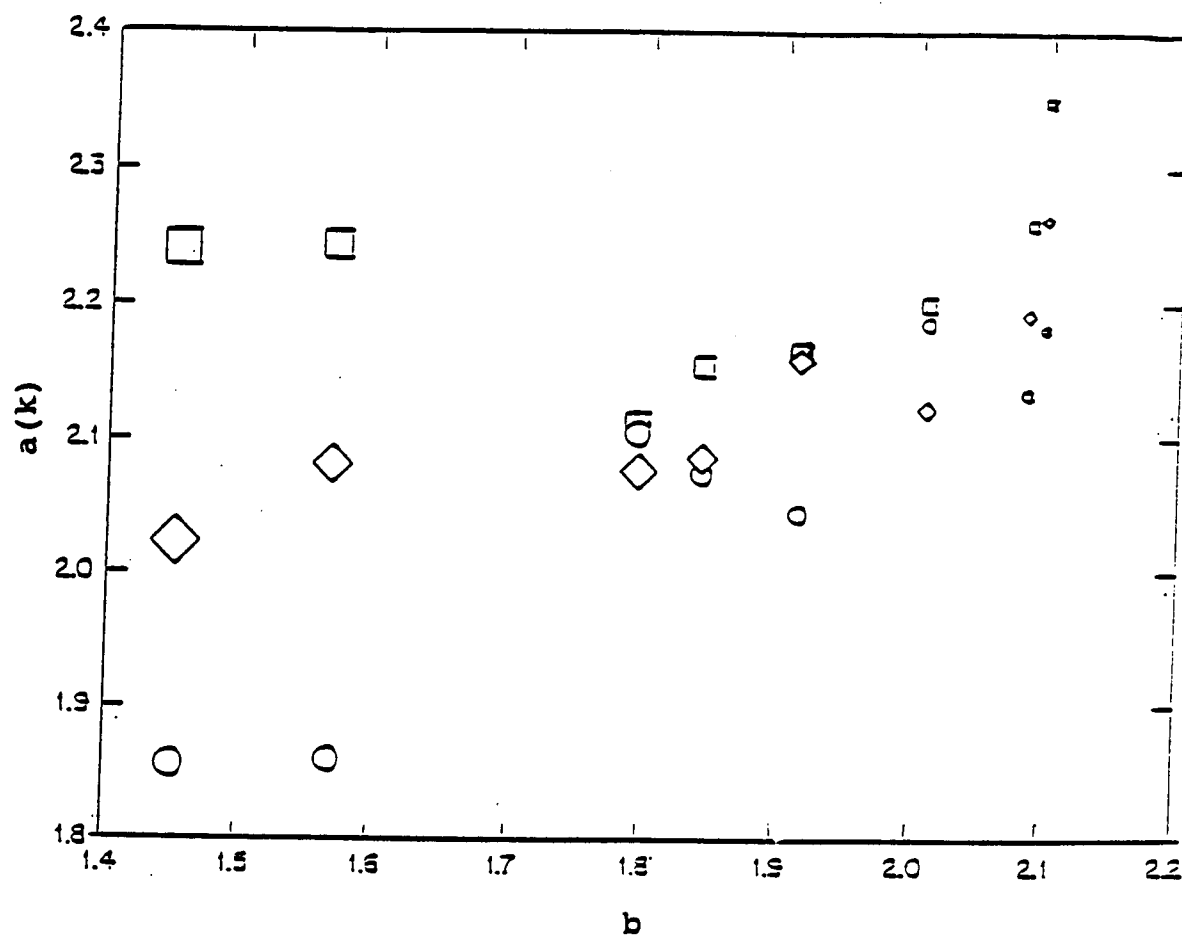


Figure 34. The scaling exponents $a(k)$ as a function of the scaling exponent b for the FCC model.

$k = 1(\bigcirc)$, $2(\diamond)$, and $3(\square)$. Increasingly large symbols indicate increasingly attractive pair interaction.

of polymer dynamics in this regime. In order to investigate this further, simulations should be performed for FCC and BCC models. Since both of these models require only one-bead elementary motions, the dynamics should be similar. If they are not, it is unlikely that lattice models can provide useful information on polymers in poor solvent conditions. If the simulations provide similar results in this regime, then they should provide evidence as to the existence of gel modes. In the next section, the results obtained for simulations in the poor solvent regime using the FCC and BCC models are presented.

C. The Poor Solvent Regime

Simulations were conducted using the thermal FCC and BCC models for chains of 24, 36, 48, and 60 beads, at three potentials below the theta point. 30,000 sample coordinates were recorded in each computer run. The relaxation times were obtained from the autocorrelation functions of the first three normal modes. Each relaxation time reported here is the average of the values obtained from four runs. Typical plots of the autocorrelation functions are shown in Figures 35 (p 138) and 36 (p 139) for a chain 24 beads.

The average values for the relaxation times are found in Tables 22-24 (pp 140-142). For both lattices the relaxation times are increasing in value for both the second and third modes. The relaxation times for the first mode

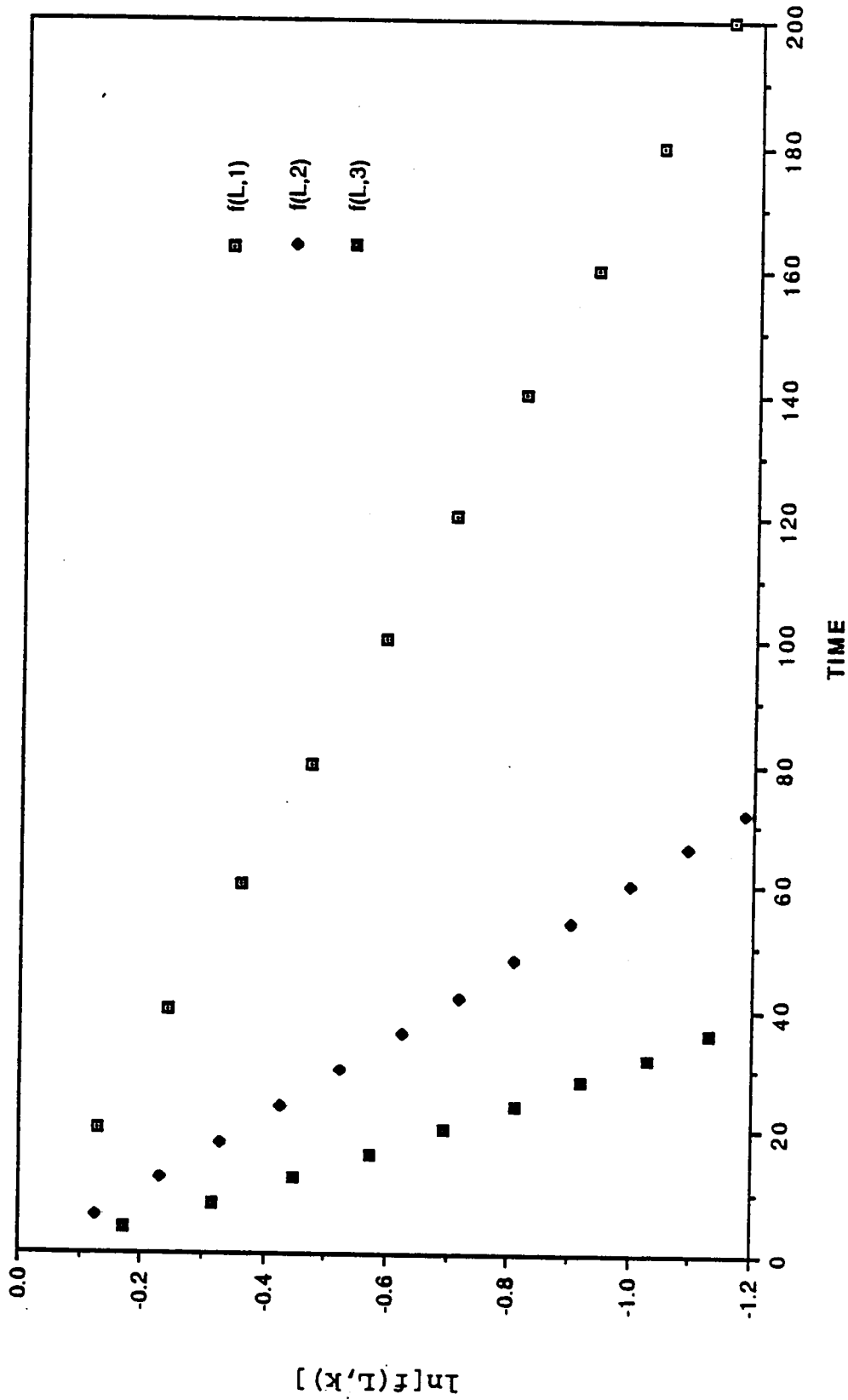


Figure 35. Semi-log plot of the autocorrelation functions of the first three normal modes for $E_F = 0.25$. FCC model

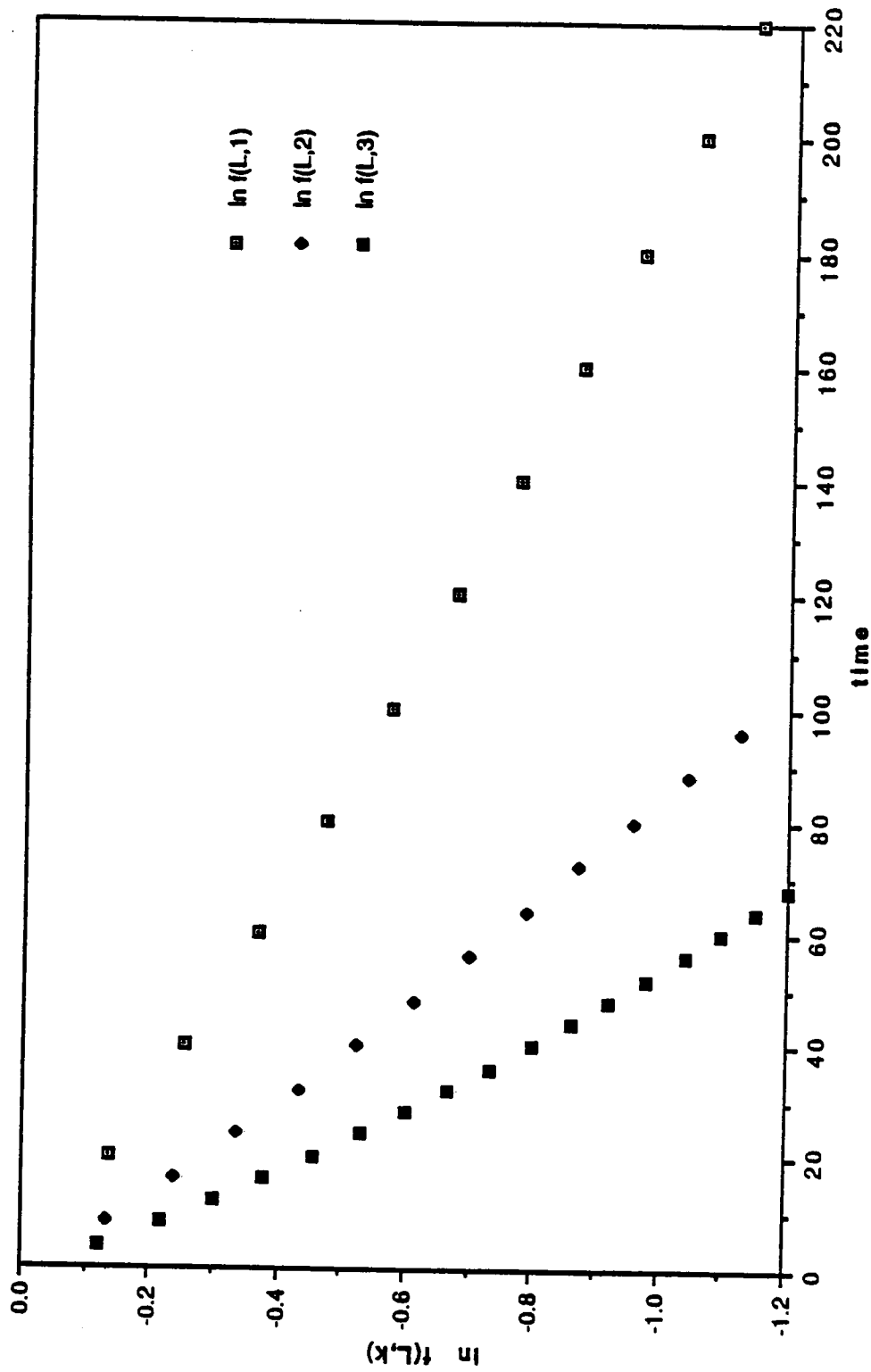


Figure 36. Semi-log plot of the autocorrelation functions of the first three normal modes for $E_F=0.55$. BCC model.

Table 22. Relaxation Times of the First Three Normal Modes, $t(L,k)$, as a Function of Chain Length, L , for the FCC [BCC] Model Obtained at $q \cdot E_r = 2.75$.^{a,b,c}

Chain Length	$t(L,1)$	$t(L,2)$	$t(L,3)$
23	180 (5) [212 (23)]	64.4 (1.8) [79.5 (3.1)]	33.6 (.5) [42.2 (2.1)]
35	399 (12) [511 (54)]	157 (3) [197 (13)]	88.4 (3.0) [110 (4)]
47	641 (30) [815 (53)]	285 (10) [363 (30)]	173 (2) [208 (12)]
59	920 (11) [1230 (110)]	471 (12) [546 (29)]	288 (9) [353 (18)]

^a Values of the relaxation times for the BCC model are listed in brackets below the respective values obtained for the FCC model.

^b Standard deviations of the runs are in parentheses.

^c E_r is the reduced pair potential and q is the coordination number of the lattice minus one.

Table 23. Relaxation Times of the First Three Normal Modes, $t(L,k)$, as a Function of Chain Length, L , for the FCC [BCC] Model Obtained at $q \cdot E_r = 3.30$.^{a,b,c}

Chain Length	$t(L,1)$	$t(L,2)$	$t(L,3)$
23	167 (7) [211 (11)]	69.2 (1.2) [85.8 (2.2)]	38.7 (.7) [47.9 (3.7)]
35	346 (7) [418 (48)]	172 (7) [215 (11)]	107 (1) [138 (5)]
47	540 (38) [697 (20)]	311 (15) [414 (14)]	216 (4) [273 (9)]
59	819 (19) [956 (46)]	510 (28) [658 (36)]	360 (13) [467 (33)]

^a Values of the relaxation times for the BCC model are listed in brackets below the respective values obtained for the FCC model.

^b Standard deviations of the runs are in parentheses.

^c E_r is the reduced pair potential and q is the coordination number of the lattice minus one.

Table 24. Relaxation Times of the First Three Normal Modes, $t(L,k)$, as a Function of Chain Length, L , for the FCC [BCC] Model Obtained at $q \cdot E_r = 3.85$.^{a,b,c}

Chain Length	$t(L,1)$	$t(L,2)$	$t(L,3)$
23	154 (4) [197 (10)]	76.1 (2.8) [95.5 (5.3)]	46.0 (.9) [58.2 (3.5)]
35	324 (11) [400 (26)]	196 (5) [230 (26)]	137 (7) [167 (8)]
47	522 (26) [629 (45)]	353 (12) [490 (26)]	273 (273) [384 (15)]
59	792 (13) [1080 63)]	627 (26) [812 (80)]	460 (13) [633 (31)]

^a Values of the relaxation times for the BCC model are listed in brackets below the respective values obtained for the FCC model.

^b Standard deviations of the runs are in parentheses.

^c E_r is the reduced pair potential and q is the coordination number of the lattice minus one.

show a slight decrease. The convergence of the relaxation times of the modes indicates that the chain is behaves very much like a single, solid unit.

The fact that the relaxation times are converging towards one another raises the question of whether correlations are developing between the motions of the modes. Verdier had reported that the normal modes of his model had correlations between the motions of the modes, and therefore did not give linear plots of $\ln\{F_k(t)\}$ vs. t . To investigate this possibility, the average of the cross-correlation between modes, $\langle U_i(0)U_j(0) \rangle$, was calculated. This had previously been done for the athermal SC model of Gurler et al.³¹ The earlier study had found no cross-correlation between the modes. In this work, it was found that the cross-correlation between the modes was statistically equal to zero for all the data studied below the theta point. This means that the normal modes are still a good set of coordinates for studying dynamics below the theta point.

The relaxation times were fit to the scaling law given by Equation 53 (p 74) to give the scaling exponents, $a(k)$. There is no lattice dependence found for the data as the values of $a(k)$ obtained from each model are approximately equal for a given value of the effective potential, $q \cdot E_r$. This can be seen from Figure 37 (p 144) and Table 25 (p 145).

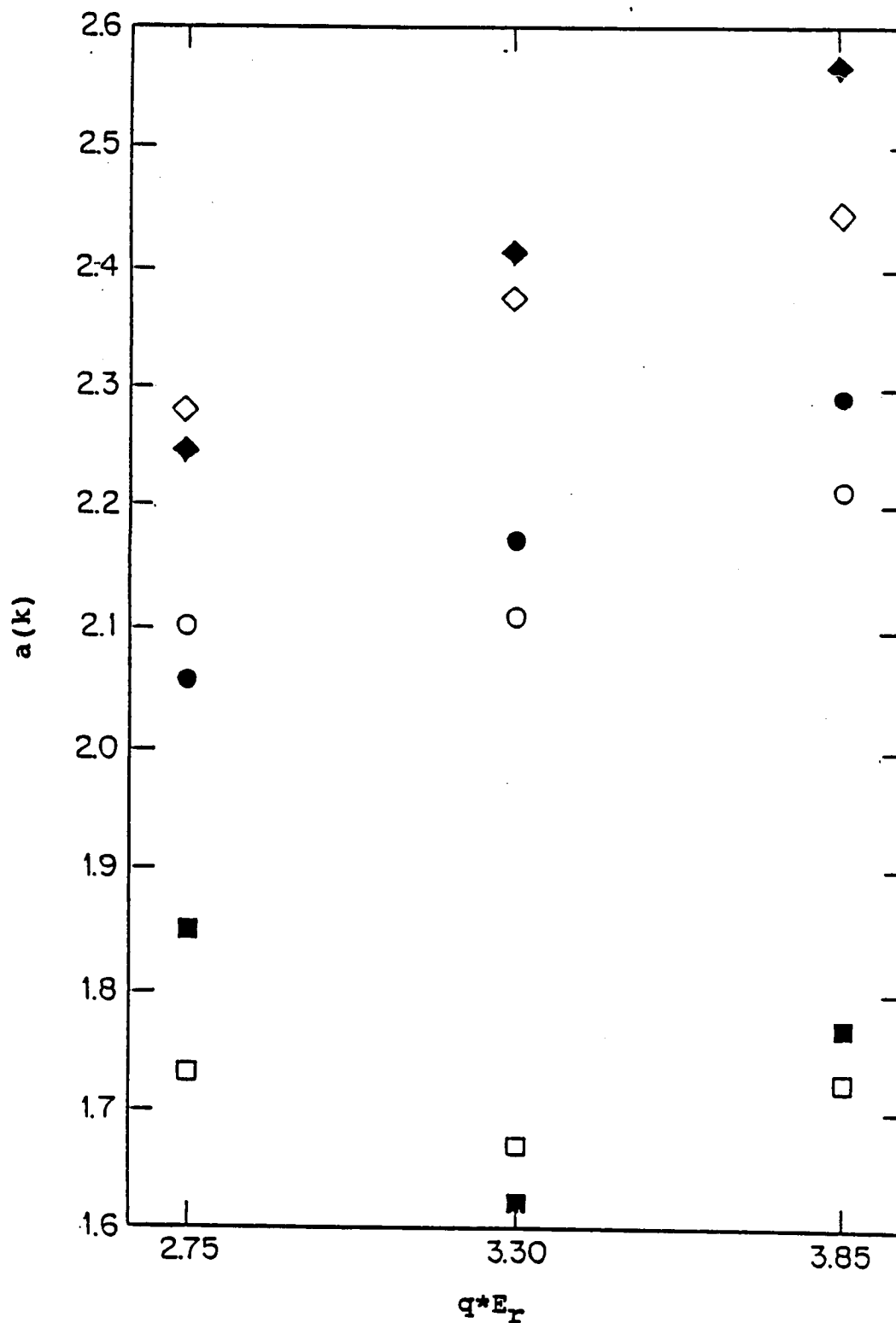


Figure 37. The scaling exponents $a(k)$ as a function of the effective potential, q^*E_r , in the poor solvent regime.

Open symbols are for the FCC model. Closed symbols are for the BCC model. $k = 1(\square)$, $2(\circ)$, and $3(\diamond)$.

Table 25. The Scaling Exponents $a(k)$ for the FCC (BCC) Model
as a Function of $q \cdot E_r$.^{a,b}

$q \cdot E_r$	$a(1)$	$a(2)$	$a(3)$
2.75	1.73 (1.85)	2.10 (2.06)	2.28 (2.25)
3.30	1.67 (1.62)	2.11 (2.17)	2.37 (2.41)
3.85	1.73 (1.77)	2.12 (2.29)	2.57 (2.57)

^a Values of the relaxation times for the BCC model are listed in parentheses below the respective values obtained for the FCC model.

^b E_r is the reduced pair potential and q is the coordination number of the lattice minus one.

The values obtained for $a(1)$ are quite close to $5/3$. The dynamic scaling hypothesis predicts this value for collapsed chains since for such chains $2\nu=2/3$. Unfortunately, the chains studied did not give a good fit for the scaling law relating $\langle R^2 \rangle$ and L . This has been observed previously.^{35,37,68} For future work, the radius of gyration may be the more appropriate measure of a collapsed chains dimensions at least in terms of scaling. Previous studies have suggested this.^{37,68}

The data shows large differences in $a(1)$, $a(2)$, and $a(3)$ values for a given potential, such that $a(k)$ increases with increasing k . This indicates that the relaxation of the short range motions are becoming more inhibited relative to the long range motions as the chain length increases. If this is to be explained by application of the dynamic scaling hypothesis to the internal motions of the chains, then the dimensions of internal segments must be scaling faster than the overall chain dimensions as the chain length is increased. It seems unlikely that differences in the chains' internal expansions large enough to account for the differences found in $a(k)$ values could occur for chains of such similar length.

Furthermore, Curro and Schaefer have observed that the internal segments of the chains have the same dimensions as an isolated chain just below the theta point.⁴⁵ This lack of internal expansion may continue below the theta point. A

study of internal chain expansions in the poor solvent regime has not yet been done, but would be of some interest.

If the increase in $a(k)$ with k cannot be explained by internal expansions within the chains, neither can this behavior be explained simply by the increasing density of the chains. It has been found that $a(k)$ increases for increasingly dense systems, but the increase is approximately the same for all values of k .^{57,58}

It seems that the more likely explanation for the observed increase of $a(k)$ with k is the increase in the lifetime of nearest-neighbor pair contacts for the increasingly collapsed long chains. Brochard and deGennes have predicted that as the mean lifetime of the contacts approaches the relaxation time of a mode, the relaxation time of that mode should increase dramatically, resulting in the creation of what Brochard and deGennes have referred to as gel modes.¹ In Table 26 (p 148) are listed the coil densities as determined from the measurements of the mean-square end-to-end distance by the equation

$$C_D = (3N/4\pi) \langle R^2 \rangle^{-3/2}. \quad (57)$$

From the table it can be readily seen that the longer chains are much more tightly coiled than the shorter ones, and therefore should have long-lived nearest-neighbor contacts. If Brochard and deGennes are correct, this would result in unusually large values for the relaxation times of the higher modes in the longer (more dense) chains, which in

Table 26. The Values obtained for the Mean Coil Densities, C_D , as a Function of Chain Length and the Effective Potential, $q \cdot E_r$, for the FCC (BCC) Model.^{a,b}

Chain Length	$q \cdot E_r = 2.75$	$q \cdot E_r = 3.30$	$q \cdot E_r = 3.85$
23	.0613 (.0580)	.0811 (.0731)	.1118 (.0986)
35	.0615 (.0567)	.0980 (.0930)	.1447 (.1384)
47	.0682 (.0628)	.1180 (.1078)	.1839 (.1657)
59	.0773 (.0681)	.1370 (.1355)	.2087 (.1967)

^a C_D Values for the BCC model are listed in parentheses below the respective values obtained for the FCC model.

^b E_r is the reduced pair potential and q is the coordination number of the lattice minus one.

turn implies an increase in $a(k)$ with increasing k . The large dependence of $a(k)$ on k observed here is strong evidence for the existence of these gel modes.

The relaxation times were also fit to the scaling relation given by Equation 54 (p 74). The values of $b(L)$ obtained for the two models are listed in Table 27 (p 150) and plotted vs. $q \cdot E_r$ in Figure 38 (p 151). From the figure it is apparent that, within the limits of the study, the two models give the same value of $b(L)$ for a given value of the scaled potential. We also see that as the attraction is increased the dependence of $b(L)$ on L increases; for larger L , $b(L)$ is smaller. This data indicates that the higher coil densities result in greater inhibition of shorter range motions relative to the longer range motions which is consistent with the existence of gel modes.

A comparison of the $b(L)$ values in Table 27 (p 150) with the coil densities in Table 26 (p 148) shows a strong correlation between $b(L)$ and C_D . This is even more evident in the plot of $b(L)$ vs. C_D in Figure 39 (p 152). From the plot it can be seen that there is a nearly linear relationship between $b(N)$ and C_D which is only weakly dependent on chain length or potential. Most of the data points lie relatively close to the same straight line. This correlation between the static property, segment density, and the dynamic property, the scaling exponent $b(L)$ has not been reported before, to the best of our knowledge.

Table 27. The Values of the Scaling Exponent, $b(L)$, as a Function of Chain Length and the Effective Potential, $q \cdot E_r$, for the FCC (BCC) Model.^{a,b}

Chain Length	$q \cdot E_r = 2.75$	$q \cdot E_r = 3.30$	$q \cdot E_r = 3.85$
23	1.520 (1.462)	1.325 (1.345)	1.093 (1.102)
35	1.369 (1.398)	1.058 (1.001)	.778 (.797)
47	1.190 (1.236)	.831 (.843)	.589 (.440)
59	1.048 (1.138)	.740 (.644)	.478 (.482)

^a Values of the relaxation times for the BCC model are listed in parentheses below the respective values obtained for the FCC model.

^b E_r is the reduced pair potential and q is the coordination number of the lattice minus one.

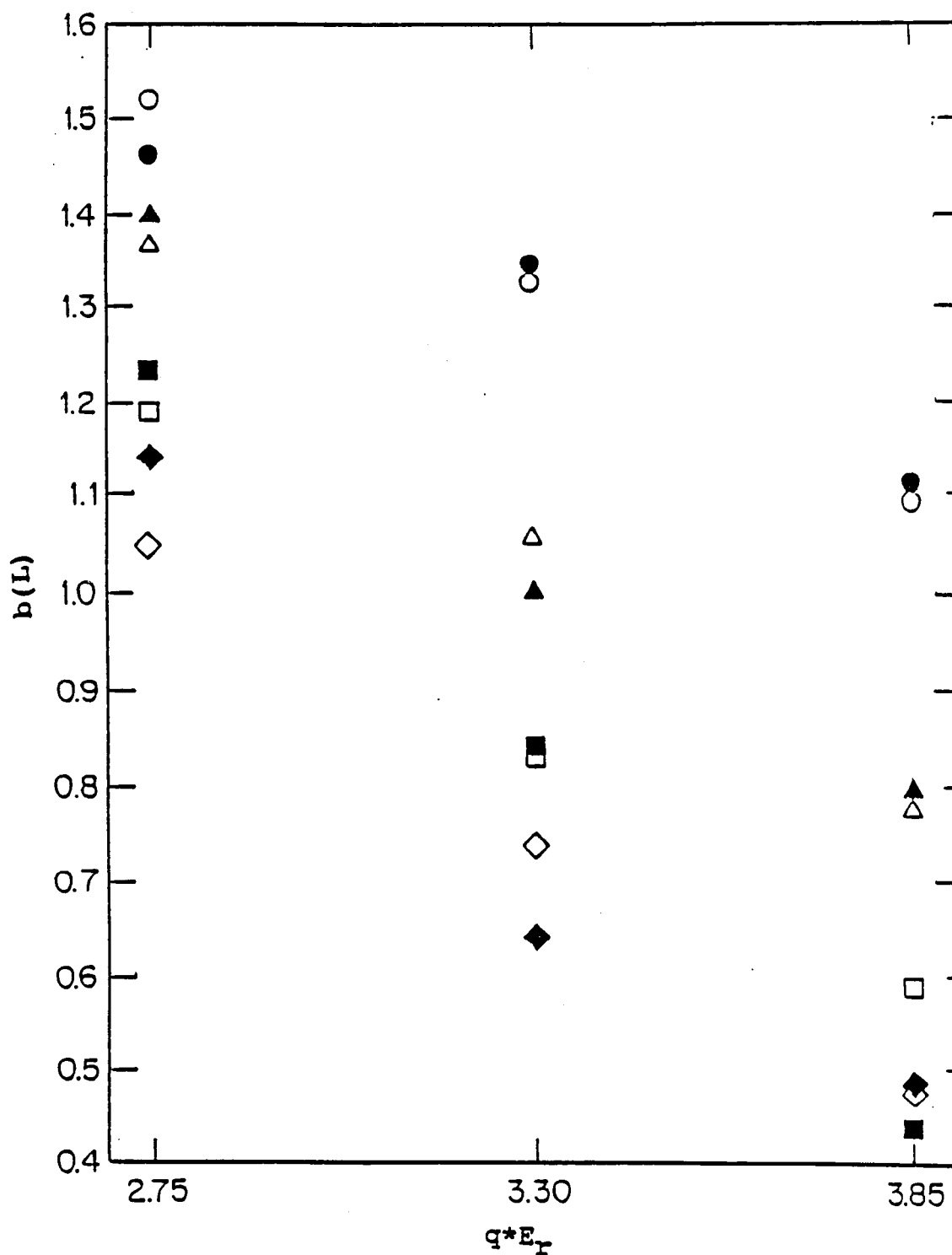


Figure 38. The scaling exponents $b(L)$ as a function of the effective potential, $q \cdot E_r$, in the poor solvent regime.

Open symbols are for the FCC model. Closed symbols are for the BCC model. $L = 23(\bigcirc)$, $35(\triangle)$, $47(\square)$, and $59(\diamond)$.

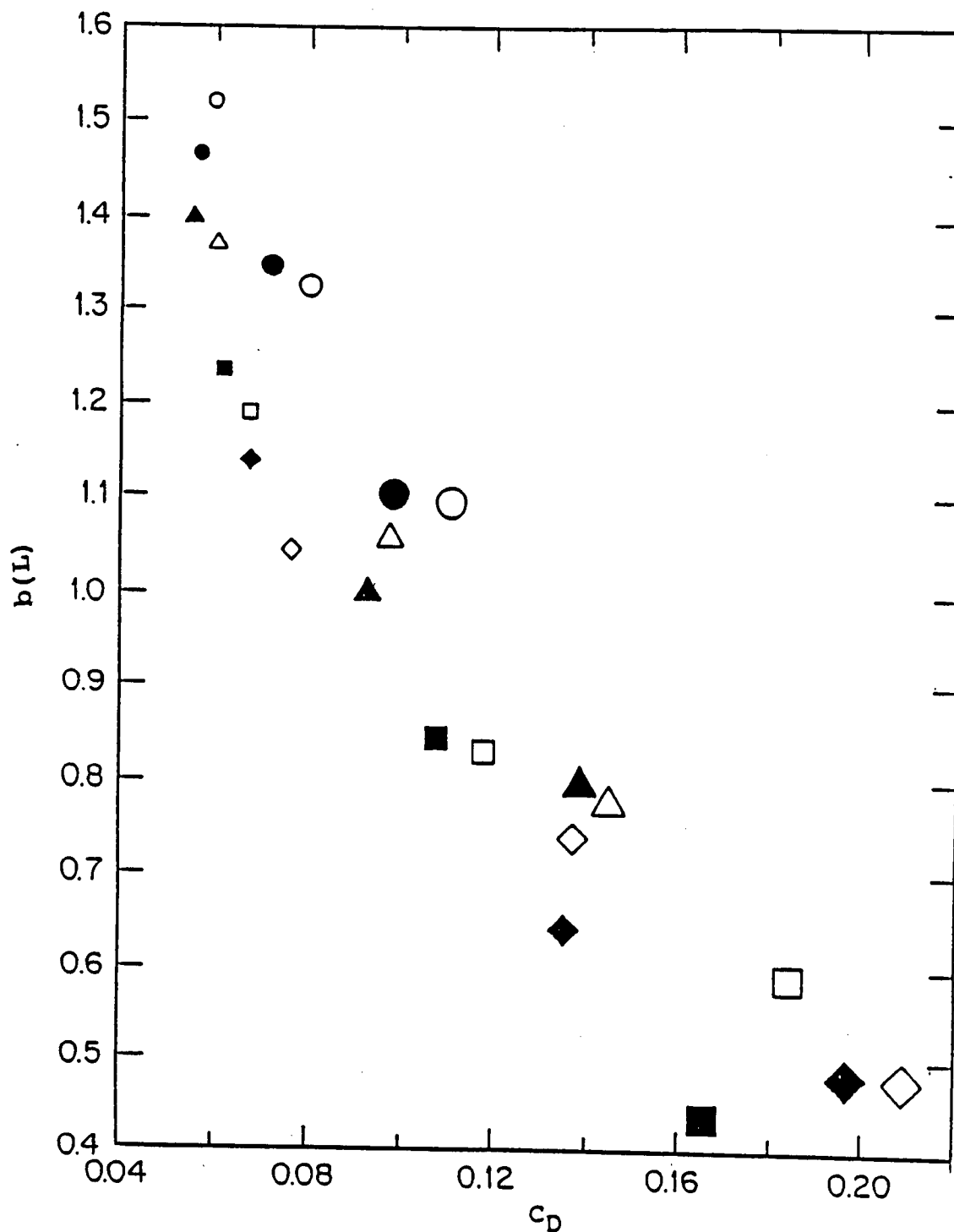


Figure 39. The scaling exponents $b(L)$ as a function of the coil density, c_D , in the poor solvent regime.

Open symbols are for the FCC model. Closed symbols are for the BCC model. $L = 23(\bigcirc)$, $35(\triangle)$, $47(\square)$, and $59(\diamond)$. Increasingly large symbols indicate increasingly attractive pair interactions.

CHAPTER IV

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The results for athermal simulations indicate that the FCC and BCC models all give dynamic scaling results which show good agreement with the bead-spring predictions for self-avoiding chains. These results show that, for athermal models, the dynamics are not dependent on the coordination number of the lattice. The SC model had one- and two-bead elementary motions, yet gave the same scaling results as the BCC and FCC models which had only one-bead elementary motions. This indicates that models such as these will give reasonable dynamic scaling results as long as out-of-plane motions are possible. The differences in the dynamic scaling observed here and the scaling observed by Verdier appear to be the result of the lack of out-of-plane motions in Verdier's simulations.

The thermal models also indicate that lattice restrictions do not affect the dynamic scaling in any fundamental way. Both the SC and FCC models gave dynamics consistent with bead-spring predictions in good and theta solvent conditions. This implies that dynamic and static scaling properties are intimately related via the dynamic scaling hypothesis.

For extended chains, the two models gave the same dynamic scaling exponents for a given value of $q \cdot E_r$. The

differences in the collapsed state found the two models were due to the preferential suppression of the two-bead motions required for out-of-plane motions in the SC model. For the short chains studied here, the value of the pair potential for which the theta point occurred was found by a number of measures to be approximately $q \cdot E_r = 1.75$.

It was found that the dynamic scaling exponent, $a(k)$, increased slightly with increasing k in athermal and good solvents and for repulsive potentials. This was observed for athermal SC, FCC, and BCC models and for thermal SC and FCC models. Whether this is the result of internal segments scaling faster than the overall chain dimensions as chain length is increased should be investigated.

The thermal FCC and BCC models gave the same scaling exponents for a given value of $q \cdot E_r$ in the poor solvent regime. This indicates that the differences in lattice coordination number do not effect the dynamic scaling properties even for collapsed chains. The dependence of $a(k)$ on k became great in this region. Also, it was found that the scaling exponent $b(L)$ decreased with increasing L in this regime. $b(L)$ values were found to be highly correlated with coil density in this region.

The observed behavior of the chains' dynamics in the theta region and below seems to be best explained by the formation of gel modes as predicted by Brochard and deGennes. In the future, it would be interesting to measure

the actual lifetime of pair contacts for chains in the theta and poor solvent regimes in order to further test Brochard and deGennes hypothesis. An examination of the scaling properties of internal segments would also be useful in that it may eliminate the question as to whether this has a significant effect on the dynamics.

The success of the bead-spring models in explaining the results obtained from the computer simulations indicates that bead-spring theories and simulations are in good agreement with one another. This means that simulations using these models may be used to simulate real polymer behavior in conditions where the hydrodynamic interaction is negligible. One such situation is the demixing of polymers in bulk and grain growth. Further study investigating the reptation model in the bulk phase is also worth pursuing. However, the computer time required to investigate bulk properties would be considerable.

Another possible use for these models would be a study of the effect of surfaces on polymer dynamics. A potential such as the one used in this study could be used to simulate a polymer's attraction to a surface. This could be used to investigate the properties of polymers on thin films.

Finally, the dynamics of a single polymer chain have not been studied for a strictly two-dimensional simulation. The bead-spring models and the dynamic scaling hypothesis do

make predictions for two-dimensional systems, but these have not been investigated. Unfortunately, simulations such as these are not able to simulate two-dimensional dynamics due to the fixed length of the bonds. This means, that in a two-dimensional simulation, structures would have to diffuse out the ends of the chain. This would affect the dynamics in an unreasonable way.

Recently, Carmesin and Kremer⁹⁴ have developed Monte Carlo simulations of polymers with flexible bonds. This would allow study of a two-dimensional system. It is currently being used to study star polymers.⁹⁵ This could not be done by previous simulation models due to the immobility of the star in models with inflexible bonds. This flexible bond model also has the primarily aesthetic advantage of allowing a dynamic transition to every state where the excluded volume constraint is not violated.

Madras and Sokal⁹⁶ have severely criticized inflexible bond models because these models have states which are dynamically inaccessible, although energetically allowed. Therefore, in this sense the simulations are not ergodic. However, these states are very few in number, particularly for the highest coordination number lattices. In fact, it has apparently never been shown that either the FCC or BCC lattice would have states which were energetically allowed but not dynamically accessible for a single chain. The criticism of Sokal and Madras is of concern

only for the lowest coordination number lattices when used to study the most highly concentrated systems. In a concentrated system, the excluded volume effects are quite likely to prevent the chain from having an allowed pathway to certain states. The number of these inaccessible states will increase with increasing concentration.

In conclusion, it is safe to say that the study polymer dynamics via computer simulation is in a relative state of infancy. New uses of Monte Carlo methods for dynamic studies are common-place. Recent reports include studies of spinodal decomposition in a two-dimensional system⁹⁷, reports of simulations of the dynamic behavior of the folding of different proteins,^{98,99} and a study of the dynamics of ring polymers.¹⁰⁰ Previous work and the observations reported here have shown that Monte Carlo simulations can be a valuable tool in the study of polymer dynamics. The models developed in this work should be useful in simulating systems with temperature dependent effects, and the high-coordination number models should be particularly useful in investigating dense systems.

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APPENDICES

APPENDIX I

FORTTRAN CODE FOR THE FCC ATHERMAL MODEL

This program writes the sampled coordinates to a tape through the buffer arrays TPX, TPY, and TPZ. The length of the buffer must be declared. If the array dimensions are a and b, then the buffer length (BUFLEN) is $a*b$. The maximum value of the first dimension, a, is the number of beads in the chain. b should be chosen to be a relatively large value so that a significant number of samples are written to the tape. This value is selected so that $a*b \leq 1536$. 1536 is three blocks on the tape. This basic procedure is used for all the simulations in this work. The following code is for a chain of 24 beads, and this chain length is used for all the codes in each of the succeeding appendices. The code in this and all the other appendices is written for an HP 1000 series computer, which was used exclusively throughout this study.

```

C THIS PROGRAM WAS USED TO GENERATE THE DATA FOR THE
C ATHERMAL FCC MODEL.
C THIS IS AN INEFFICIENT PROGRAM AND THE THERMAL FCC
C MODEL WHICH EVOLVED FROM THIS IS A BETTER ALGORITHM
C TO WORK WITH.
C UNLIKE THE LATER MODEL, THE COORDINATE COR AND RCOR
C ARE NOT CARTESIAN IN THIS PROGRAM.
C IN THIS PROGRAM RLCOR IS A CARTESIAN SET OF
C CARTESIAN SET OF COORDINATES.
C TO PERFORM SIMULATIONS WITHOUT THE EXCLUDED VOLUME
C CHECK ELEMENTS THE LINES WHERE THIS IS CHECKED
C WHICH ARE ENCLOSED BY COMMENT LINES OF DASHES, I.E.--
FTN7X,Q
$FILES 1,4
$CDS ON
      PROGRAM FCC121
      EMA HOME,X,Y,Z
      LOGICAL HOME(60,60,60)
      INTEGER*4 DBLOCK,SUM
      REAL JTIME
      INTEGER COR(12,3),RCOR(12,3),RLCOR(12,3)
      INTEGER TPZ(12,128),DEL(3),BLOCK(2),ITIME(6)
      INTEGER X(30000),Y(30000),Z(30000)
      INTEGER TPY(12,128),BUFLEN, EL(3),MOVE(3,3)
      INTEGER V(12,3),VEC(3),TPX(12,128)
      EQUIVALENCE (BLOCK(1),DBLOCK)
      DATA SUM/0/
C THE ARRAY V HAS THE NON-CARTESIAN VECTORS WHICH LOCATE
C A CHAIN'S NEAREST-NEIGHBORS
      DATA V/1,0,0,-1,0,0,1,1,0,-1,-1,0,0,1,0,0,-1,0,-1
      *,0,1,1,0,-1,0,0,1,0,0,-1,0,-1,-1,0,1,1/
      LU=24
      BUFLen=3072
      I9=0
      DBLOCK=0
      OPTION=100001B
      CALL LURQ(OPTION,LU)
50    FORMAT(I2,I3,F15.7,6I6)
C SET PERIODIC BOX TO BE EMPTY, THE PERIODIC BOX IS
C NON-CARTESIAN
      DO 909 I1=1,60
      DO 909 I2=1,60
      DO 909 I3=1,60
909    HOME(I1,I2,I3)=.FALSE.
C*****
      OPEN(UNIT=5,FILE='N121')
      READ(5,50)LENGTH,NUM,R2,ITIME(1)
      WRITE(1,50)LENGTH,NUM,R2
      READ(5,FMT=129)((COR(I,J),RCOR(I,J),J=1,3)
      *,I=1,LENGTH)
      DO 303 I=1,LENGTH
      IF(HOME(COR(I,1),COR(I,2),COR(I,3)))GOTO 632
      HOME(COR(I,1),COR(I,2),COR(I,3))=.TRUE.

```

```

303      CONTINUE
        CLOSE(5)
        GO TO 118
632      WRITE(1,365)I
365      FORMAT(' ERROR IN DATA',215)
        STOP
C
118      WRITE(1,33)
33      FORMAT(' DATA OK')
C
C SAMPLING INTERVAL IS 1/2 A BEAD CYCLE
C*****
      JK=LENGTH*NUM*.5
C INITIALIZE THE RANDOM NUMBER GENERATORS
      A=ARAN(1)
      A=BRAN(1)
C THIS LOOP CONTAINS THE SIMULATIONS OF ATTEMPTED
C MOTIONS
      DO 2800 I1=1,30000
      DO 2700 I2=1,JK
      J=BRAN(0)*LENGTH+1
      IF((J.EQ.1).OR.(J.EQ.LENGTH)) GO TO 1000
      J1=J-1
      J2=J+1
      RLCOR(J2,1)=RCOR(J2,1)+RCOR(J2,2)
      RLCOR(J2,2)=RCOR(J2,1)+RCOR(J2,3)
      RLCOR(J2,3)=RCOR(J2,2)+RCOR(J2,3)
      RLCOR(J1,1)=RCOR(J1,1)+RCOR(J1,2)
      RLCOR(J1,2)=RCOR(J1,1)+RCOR(J1,3)
      RLCOR(J1,3)=RCOR(J1,2)+RCOR(J1,3)
      IDEL=((RLCOR(J1,1)-RLCOR(J2,1))**2
*      +(RLCOR(J1,2)-RLCOR(J2,2))**2
*      +(RLCOR(J1,3)-RLCOR(J2,3))**2)/2
C 2000, 2000, AND 4000 ARE FOR THE 60, 90, AND 120
C DEGREE ANGLES RESPECTIVELY
      GO TO (2000,2000,4000,2700) IDEL
C
C END ROUTINE
C
1000    IF(J.EQ.1)THEN
      J1=2
    ELSE
      J1=LENGTH-1
    ENDIF
      IX=RCOR(J,1)-RCOR(J1,1)
      IY=RCOR(J,2)-RCOR(J1,2)
      IZ=RCOR(J,3)-RCOR(J1,3)
C RANDOMLY PICK ONE OF 11 NEIGHBORING POSITIONS TO
C ATTEMPT TO MOVE TO
      K=ARAN(0)*11+1
C IF THE POSITION IS THE SAME AS THE ORIGINAL,
C REJECT THIS AND USE K=12

```

```

      IF((IX.EQ.V(K,1)).AND.(IY.EQ.V(K,2)).AND.
* (IZ.EQ.V(K,3))) K=12
      DO 1010 K1=1,3
        DEL(K1)=COR(J1,K1)+V(K,K1)
        IF(DEL(K1).EQ.61)DEL(K1)=1
        IF(DEL(K1).EQ.0) DEL(K1)=60
1010 CONTINUE
C-----
      IF(HOME(DEL(1),DEL(2),DEL(3)))GO TO 2700
C-----
      HOME(DEL(1),DEL(2),DEL(3))=.TRUE.
      HOME(COR(J,1),COR(J,2),COR(J,3))=.FALSE.
      DO 1020 K2=1,3
        COR(J,K2)=DEL(K2)
        RCOR(J,K2)=RCOR(J1,K2)+V(K,K2)
1020 CONTINUE
      GO TO 2700
C
C 120 DEGREE ROUTINE, AN ATTEMPTED BOND VECTOR EXCHANGE
C
      4000 DO 4010 K1=1,3
        DEL(K1)=RCOR(J1,K1)-RCOR(J,K1)+COR(J2,K1)
        IF(DEL(K1).EQ.61) DEL(K1)=1
        IF(DEL(K1).EQ.0) DEL(K1)=60
      4010 CONTINUE
C-----
      IF(HOME(DEL(1),DEL(2),DEL(3)))GO TO 2700
C-----
      HOME(DEL(1),DEL(2),DEL(3))=.TRUE.
      HOME(COR(J,1),COR(J,2),COR(J,3))=.FALSE.
      DO 4020 K2=1,3
        COR(J,K2)=DEL(K2)
        RCOR(J,K2)=RCOR(J1,K2)+RCOR(J2,K2)-RCOR(J,K2)
      4020 CONTINUE
      GO TO 2700
C
C 90 AND 60 DEGREE ROUTINES, RANDOMLY PICK ONE OF
C THREE DIFFERENT MOVES
      2000 K=3*ARAN(0)+1
      RLCOR(J,1)=RCOR(J,1)+RCOR(J,2)
      RLCOR(J,2)=RCOR(J,1)+RCOR(J,3)
      RLCOR(J,3)=RCOR(J,2)+RCOR(J,3)
C THIS IS THE 60 DEGREE ROUTINE (IDEL=1)
      IF(IDEL.EQ.1)THEN
        DO 2010 K1=1,3
          VEC(K1)=RLCOR(J1,K1)+RLCOR(J2,K1)-2*RLCOR(J,K1)
          IF(K.EQ.1)THEN
            IF(ABS(VEC(K1)).EQ.2) VEC(K1)=0
          ENDIF
          IF(K.EQ.2)THEN
            IF(ABS(VEC(K1)).EQ.1) VEC(K1)=0
          ENDIF
        ENDIF

```

```

2010  CONTINUE
      EL(1)=(VEC(1)+VEC(2)-VEC(3))/2
      EL(2)=(VEC(1)-VEC(2)+VEC(3))/2
      EL(3)=(VEC(2)+VEC(3)-VEC(1))/2
      ELSE
C THIS IS THE 120 DEGREE ROUTINE
      DO 3010 K1=1,3
        VEC(K1)=(RLCOR(J1,K1)+RLCOR(J2,K1))/2
        *      -RLCOR(J,K1)
        MOVE(1,K1)=VEC(K1)
        IF(RLCOR(J1,K1).NE.RLCOR(J,K1))THEN
          MOVE(2,K1)=0
          MOVE(3,K1)=0
        ELSE
          MOVE(2,K1)=1
          MOVE(3,K1)=-1
        ENDIF
3010  CONTINUE
      EL(1)=(VEC(1)+MOVE(K,1)+VEC(2)+MOVE(K,2)-VEC(3)
        *      -MOVE(K,3))/2
      EL(2)=(VEC(1)+MOVE(K,1)-VEC(2)-MOVE(K,2)+VEC(3)
        *      +MOVE(K,3))/2
      EL(3)=(VEC(2)+MOVE(K,2)+VEC(3)+MOVE(K,3)-VEC(1)
        *      -MOVE(K,1))/2
      ENDIF
      DO 2030 K2=1,3
        DEL(K2)=EL(K2)+COR(J,K2)
        IF(DEL(K2).GE.61) DEL(K2)=DEL(K2)-60
        IF(DEL(K2).LE.0) DEL(K2)=DEL(K2)+60
2030  CONTINUE
C-----
      IF(HOME(DEL(1),DEL(2),DEL(3)))GO TO 2700
C-----
      HOME(DEL(1),DEL(2),DEL(3))=.TRUE.
      HOME(COR(J,1),COR(J,2),COR(J,3))=.FALSE.
      DO 3030 K3=1,3
        COR(J,K3)=DEL(K3)
        RCOR(J,K3)=RCOR(J,K3)+EL(K3)
3030  CONTINUE
2700  CONTINUE
C*****
C RECORD COR TO TAPE
C
      I9=I9+1
      IF (I9.EQ.129) THEN
        CALL EXEC(2,24+1008,TPX,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+1008,TPY,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+1008,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
      I9=1

```

```

ENDIF
DO 2753 I8=1,LENGTH
  TPX(I8,I9)=RCOR(I8,1)+RCOR(I8,2)
  TPY(I8,I9)=RCOR(I8,1)+RCOR(I8,3)
  TPZ(I8,I9)=RCOR(I8,2)+RCOR(I8,3)
2753 CONTINUE
C SINGLE CHAIN WORKUP
  SUM=SUM+(TPX(1,I9)-TPX(LENGTH,I9))**2
  *      +(TPY(1,I9)-TPY(LENGTH,I9))**2
  *      +(TPZ(1,I9)-TPZ(LENGTH,I9))**2
  X(I1)=TPX(1,I9)-TPX(LENGTH,I9)
  Y(I1)=TPY(1,I9)-TPY(LENGTH,I9)
  Z(I1)=TPZ(1,I9)-TPZ(LENGTH,I9)
2800 CONTINUE
  CALL EXEC(2,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  CALL EXEC(2,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  CALL EXEC(2,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  WRITE(1,10)DBLOCK
10  FORMAT(' NEXT AVAILABLE BLOCK IS ',I110)
C*****
C      RECORD DATA
      R2=SUM/30000.
      JTIME=0
      OPEN(UNIT=8,FILE='HEX12')
      WRITE(8,50)LENGTH,NUM,R2
C THIS LOOP CALCULATES THE AUTOCORRELATION FUNCTION OF
C THE END-TO-END VECTOR
      DO 1301 I2=1,200
        SUM=0
        MAXI=30000-I2
        DO 1401 I3=1,MAXI
          J=I2+I3
          SUM=SUM+X(I3)*X(J)+Y(I3)*Y(J)+Z(I3)*Z(J)
1401 CONTINUE
        TAU=DBLE(SUM)/DBLE(MAXI)/R2
        JTIME=JTIME+.5
        WRITE(8,1402)JTIME,TAU
1402 FORMAT(' TIME=',F7.3,5X,'TAU=',PE13.6)
1301 CONTINUE
        CLOSE(8)
C*****
C RECORD FINAL COORDINATES
C
125  OPEN(UNIT=6,FILE='N121')
      REWIND(6)
      WRITE(6,50)LENGTH,NUM,R2,ITIME(1),ITIME(4)
      WRITE(6,129)((COR(I,J),RCOR(I,J),J=1,3),
  *      I=1,LENGTH
      CLOSE(6)

```

```

129    FORMAT(2014)
      STOP
      END

C
      FUNCTION ARAN(I)
      SAVE
      REAL*8 IRAND,MULT,LARGE
      INTEGER ITIME(5)
      DATA IRAND/14532./,MULT/65539./
      DATA LARGE/2147483647./
      IF(I.EQ.0)GOTO 1
      CALL EXEC(11,ITIME)
      IRAND=IRAND*DBLE(ITIME(1)+ITIME(2)+ITIME(3)
*      +ITIME(4))
      WRITE(1,393)IRAND
393    FORMAT(F10.2)
      GOTO 2

C
1      IRAND=IRAND*MULT
2      IRAND=DMOD(IRAND,LARGE)+1
      ARAN=(IRAND)/(LARGE+1)
      K=ARAN*30000
      ARAN=FLOAT(K)/30000.
      IF(ARAN.GE.1)ARAN=.999
      IF(ARAN.LE.0)ARAN=.001
      RETURN
      END

C
      FUNCTION BRAN(I)
      SAVE
      REAL*8 IRAND,MULT,LARGE
      INTEGER ITIME(5)
      DATA IRAND/123479./,MULT/65539./
      DATA LARGE/2147483647./
      IF(I.EQ.0)GOTO 1
      CALL EXEC(11,ITIME)
      IRAND=IRAND*DBLE(ITIME(1)+ITIME(2))
      GOTO 2
1      IRAND=IRAND*MULT
2      IRAND=DMOD(IRAND,LARGE)+1
      BRAN=(IRAND)/(LARGE+1)
      K=BRAN*30000
      BRAN=FLOAT(K)/30000.
      IF(BRAN.GE.1)BRAN=.999
      IF(BRAN.LE.0)BRAN=.001
      RETURN
      END

```

APPENDIX II

FORTRAN CODE FOR THE ATHERMAL BCC MODEL

```

C FOR A SIMULATION WITHOUT THE EXCLUDED VOLUME CONDITION
C SIMPLY REMOVE THE TWO LINES IN WHICH THE EXCLUDED
C VOLUME IS CHECKED THESE ARE WITHIN COMMENT LINES OF
C DASHES, I.E. -----

```

```

FTN7X,Q

```

```

$FILES 1,4

```

```

$CDS ON

```

```

PROGRAM BCC241
EMA HOME,X,Y,Z
LOGICAL HOME(60,60,60)
INTEGER*4 DBLOCK,SUM
DOUBLE PRECISION DSEED,DR
INTEGER COR(24,3,1),RCOR(24,3,1),KRX(8),KRY(8)
INTEGER ITIME(5),BLOCK(2),BUFLEN,TPZ(24,64)
INTEGER X(30000),Y(30000),Z(30000),TPX(24,64)
INTEGER TPY(24,64),CN, KRZ(8)
EQUIVALENCE (BLOCK(1),DBLOCK)

```

```

C*****

```

```

DATA SUM/0/

```

```

C KR ARRAYS GIVE THE COMPONENTS OF THE VECTORS TO THE
C EIGHT NEAREST-NEIGHBORS

```

```

DATA KRX/1,1,1,1,-1,-1,-1,-1/

```

```

DATA KRY/1,-1,1,-1,1,-1,1,-1/

```

```

DATA KRZ/1,1,-1,-1,1,1,-1,-1/

```

```

LU=24

```

```

OPTION=100001B

```

```

CALL LURQ(OPTION,LU)

```

```

C WRITE(1,15)

```

```

15 FORMAT(' ENTER STARTING BLOCK')

```

```

DBLOCK=28000

```

```

C READ(1,25)DBLOCK

```

```

25 FORMAT(1110)

```

```

BUFLEN=1536

```

```

50 FORMAT(12,13,F15.7,6I6)

```

```

C SET THE PERIODIC BOX TO BE UNOCCUPIED

```

```

DO 909 I1=1,60

```

```

DO 909 I2=1,60

```

```

DO 909 I3=1,60

```

```

909 HOME(I1,I2,I3)=.FALSE.

```

```

C*****

```

```

C READ IN FILE WITH LATTICE

```

```

C*****

```

```

OPEN(UNIT=5,FILE='B241')

```

```

READ(5,50)LENGTH,NUM,R2,ITIME(1)

```

```

WRITE(1,50)LENGTH,NUM,R2

```

```

DO 303 I0=1,NUM

```

```

WRITE(1,32)I0

```

```

32 FORMAT(13)

```

```

READ(5,FMT=129)((COR(I,J,I0),RCOR(I,J,I0),J=1,3)
*,I=1,LENGTH)

```

```

DO 303 I=1,LENGTH

```

```

IF(HOME(COR(I,1,I0),COR(I,2,I0),COR(I,3,I0)))

```

```

* GO TO 632

```

```

        HOME(COR(1,1,10),COR(1,2,10),COR(1,3,10))=.TRUE.
303      CONTINUE
        CLOSE(5)
        GOTO 118
632      WRITE(1,365)1,10
365      FORMAT(' ERROR IN DATA',2I5)
        STOP

C
  118    WRITE(1,33)
33      FORMAT(' DATA OK')
C
C*****
C INITIALIZE RANDOM NUMBER GENERATORS AND VARIABLES,
C KJ IS THE SAMPLING INTERVAL.
C 2 IS THE NUMBER OF BEAD CYCLES BETWEEN SAMPLES
      JK=LENGTH*NUM*2
C
      A=ARAN(1)
      A=BRAN(1)
      I9=0
C ATTEMPTED MOTIONS
      DO 2800 I1=1,30000
      DO 2700 I2=1,JK
      CN=1
C
C PICK A BEAD
C
      J=BRAN(0)*LENGTH+1
C CHECK FOR END BEADS
      IF(J.EQ.1)GOTO 140
      IF(J.EQ.LENGTH)GOTO 150
C
      J1=J-1
      J2=J+1
C DETERMINE ORIENTATION
      NDSQ=((RCOR(J1,1,CN)-RCOR(J2,1,CN))**2
      * +(RCOR(J1,2,CN)-RCOR(J2,2,CN))**2
      * +(RCOR(J1,3,CN)-RCOR(J2,3,CN))**2)/4+1
C*****
      GO TO (160,300,300,2700) NDSQ
C SPIKE,60,120,LINEAR
C*****
C
C 60 AND 120 DEGREE MOVES
C
C FIRST DETERMINE AVERAGE POSITION OF THE BEADS
C BONDED NEIGHBORS AND THEN THE VECTOR FROM THE BEAD
C TO THIS POSITION
300      IAX=(RCOR(J2,1,CN)+RCOR(J1,1,CN))/2
      IAY=(RCOR(J2,2,CN)+RCOR(J1,2,CN))/2
      IAZ=(RCOR(J2,3,CN)+RCOR(J1,3,CN))/2
      IRX=(IAX-RCOR(J,1,CN))*2

```

```

      IRY=(IAY-RCOR(J,2,CN))*2
      IRZ=(IAZ-RCOR(J,3,CN))*2
C DETERMINE WHICH OF THREE POSSIBLE VECTORS WILL BE
C TRIED FOR THE 60 DEGREE CASE.
C SETTING A COMPONENT OF THE BOND VECTOR EXCHANGE TO
C BE ZERO WILL GIVE ONE OF THE OTHER TWO POSSIBILITIES
C IF THE COMPONENT IS ONE OF THE TWO NON-ZERO ONES
C RANDOMLY SELECTING A COMPONENT WILL GIVE A RANDOM
C CHOICE BETWEEN THE POSSIBILITIES
      IF(NDSQ.EQ.2)THEN
        K1=ARAN(0)*3+1
        IF(K1.EQ.1)IRX=0
        IF(K1.EQ.2)IRY=0
        IF(K1.EQ.3)IRZ=0
      ENDIF
      IX=COR(J,1,CN)+IRX
      IY=COR(J,2,CN)+IRY
      IZ=COR(J,3,CN)+IRZ
      IF(IX.GT.60) IX=IX-60
      IF(IY.GT.60) IY=IY-60
      IF(IZ.GT.60) IZ=IZ-60
      IF(IX.LT.1) IX=IX+60
      IF(IY.LT.1) IY=IY+60
      IF(IZ.LT.1) IZ=IZ+60
C-----
      IF(HOME(IX,IY,IZ))GO TO 2700
C-----
      HOME(IX,IY,IZ)=.TRUE.
      HOME(COR(J,1,CN),COR(J,2,CN),COR(J,3,CN))=.FALSE.
      COR(J,1,CN)=IX
      COR(J,2,CN)=IY
      COR(J,3,CN)=IZ
      RCOR(J,1,CN)=IRX+RCOR(J,1,CN)
      RCOR(J,2,CN)=IRY+RCOR(J,2,CN)
      RCOR(J,3,CN)=IRZ+RCOR(J,3,CN)
      GO TO 2700
C *****
C BEAD IS END BEAD
C
150   J1=LENGTH-1
      GO TO 160
C
C BEAD IS FIRST BEAD
140   J1=2
C*****
C END AND SPIKE ROUTINE(MORE OF THE SAME)
C
160   NRX=RCOR(J,1,CN)-RCOR(J1,1,CN)
      NRY=RCOR(J,2,CN)-RCOR(J1,2,CN)
      NRZ=RCOR(J,3,CN)-RCOR(J1,3,CN)
C
C DETERMINE THE VECTOR MOVE ATTEMPTED

```

```

C
170 K2=ARAN(0)*8+1
C CHECK TO SEE IT IS NOT THE SAME VECTOR AS IS
C BETWEEN THE BEAD AND ITS NEIGHBOR
  IF((KRX(K2).EQ.NRX).AND.(KRY(K2).EQ.NRY).AND.
  * (KRZ(K2).EQ.NRZ))GO TO 170
  KX=KRX(K2)+COR(J1,1,CN)
  KY=KRY(K2)+COR(J1,2,CN)
  KZ=KRZ(K2)+COR(J1,3,CN)
  IF(KX.GT.60)KX=KX-60
  IF(KY.GT.60)KY=KY-60
  IF(KZ.GT.60)KZ=KZ-60
  IF(KX.LT.1)KX=KX+60
  IF(KY.LT.1)KY=KY+60
  IF(KZ.LT.1)KZ=KZ+60
C-----
  IF(HOME(KX,KY,KZ))GO TO 2700
C-----
  HOME(KX,KY,KZ)=.TRUE.
  HOME(COR(J,1,CN),COR(J,2,CN),COR(J,3,CN))=.FALSE.
  COR(J,1,CN)=KX
  COR(J,2,CN)=KY
  COR(J,3,CN)=KZ
  RCOR(J,1,CN)=RCOR(J1,1,CN)+KRX(K2)
  RCOR(J,2,CN)=RCOR(J1,2,CN)+KRY(K2)
  RCOR(J,3,CN)=RCOR(J1,3,CN)+KRZ(K2)
2700 CONTINUE
C*****
C RECORD COR TO TAPE
C
  I9=I9+1
  IF (I9.EQ.65) THEN
    CALL EXEC(2,24+1008,TPX,BUFLEN,BLOCK(1),BLOCK(2))
    DBLOCK=DBLOCK+3
    CALL EXEC(2,24+1008,TPY,BUFLEN,BLOCK(1),BLOCK(2))
    DBLOCK=DBLOCK+3
    CALL EXEC(2,24+1008,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
    DBLOCK=DBLOCK+3
    I9=1
  ENDIF
  DO 2753 I8=1,LENGTH
    TPX(I8,I9)=RCOR(I8,1,1)
    TPY(I8,I9)=RCOR(I8,2,1)
    TPZ(I8,I9)=RCOR(I8,3,1)
2753 CONTINUE
C
  SUM=SUM+(RCOR(1,1,1)-RCOR(LENGTH,1,1))*2
  *      +(RCOR(1,2,1)-RCOR(LENGTH,2,1))*2
  *      +(RCOR(1,3,1)-RCOR(LENGTH,3,1))*2
  X(I1)=RCOR(1,1,1)-RCOR(LENGTH,1,1)
  Y(I1)=RCOR(1,2,1)-RCOR(LENGTH,2,1)
  Z(I1)=RCOR(1,3,1)-RCOR(LENGTH,3,1)

```

```

2800      CONTINUE
C RECORD WHAT IS LEFT TO TAPE
      CALL EXEC(2,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
      DBLOCK=DBLOCK+3
      CALL EXEC(2,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
      DBLOCK=DBLOCK+3
      CALL EXEC(2,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
      DBLOCK=DBLOCK+3
      WRITE(1,10)DBLOCK
      10  FORMAT(' NEXT AVAILABLE BLOCK IS ',I110)
C*****
C RECORD DATA
C
      R2=SUM/30000.
      JTIME=0
      OPEN(UNIT=8,FILE='B0D24')
      WRITE(8,50)LENGTH,NUM,R2
C LOOP CALCULATES THE AUTOCORRELATION FUNCTION OF
C THE END-TO-END VECTOR
      DO 1301 I2=1,200
        SUM=0
        MAXI=30000-I2
        DO 1401 I3=1,MAXI
          J=I2+I3
          SUM=SUM+X(I3)*X(J)+Y(I3)*Y(J)+Z(I3)*Z(J)
1401    CONTINUE
        TAU=DBLE(SUM)/DBLE(MAXI)/R2
        JTIME=JTIME+2
        WRITE(8,1402)JTIME,TAU
1402    FORMAT(' TIME='1F7.2,5X,'TAU=',PE13.6)
1301    CONTINUE
        CLOSE(8)
C RECORD CHAIN'S COORDINATES TO THE DISK
C
125      OPEN(UNIT=6,FILE='B241')
      REWIND(6)
      WRITE(6,50)LENGTH,NUM,R2,ITIME(1)
      DO 1011 I1=1,NUM
        WRITE(6,129)((COR(I,J,I1),RCOR(I,J,I1),J=1,3)
          * ,I=1,LENGTH)
1011    CONTINUE
      WRITE(6,50)LENGTH,NUM,R2,ITIME(1)
      CLOSE(6)
      129  FORMAT(20I4)
      STOP
      END
C ARAN AND BRAN ARE RANDOM NUMBER GENERATORS
      FUNCTION ARAN(I)
      SAVE
      REAL*8 IRAND,MULT,LARGE
      INTEGER ITIME(5)
      DATA IRAND/14532.,MULT/65539./

```

```

DATA LARGE/2147483647./
IF(I.EQ.0)GOTO 1
CALL EXEC(11,ITIME)
IRAND=IRAND*DBLE(ITIME(1)+ITIME(2))
*      +ITIME(3)+ITIME(4))
WRITE(1,393)IRAND
393    FORMAT(F10.2)
GOTO 2
1      IRAND=IRAND*MULT
2      IRAND=DMOD(IRAND,LARGE)+1
      ARAN=(IRAND)/(LARGE+1)
      K=ARAN*30000
      ARAN=FLOAT(K)/30000.
      IF(ARAN.GE.1)ARAN=.999
      IF(ARAN.LE.0)ARAN=.001
      RETURN
      END

C
FUNCTION BRAN(I)
SAVE
REAL*8 IRAND,MULT,LARGE
INTEGER ITIME(5)
DATA IRAND/123479./,MULT/65539./
DATA LARGE/2147483647./
IF(I.EQ.0)GOTO 1
CALL EXEC(11,ITIME)
IRAND=IRAND*DBLE(ITIME(1)+ITIME(2))
GOTO 2
1      IRAND=IRAND*MULT
2      IRAND=DMOD(IRAND,LARGE)+1
      BRAN=(IRAND)/(LARGE+1)
      K=BRAN*30000
      BRAN=FLOAT(K)/30000.
      IF(BRAN.GE.1)BRAN=.999
      IF(BRAN.LE.0)BRAN=.001
      RETURN
      END

```

APPENDIX III
FORTRAN CODE FOR THE THERMAL SC MODEL

```

FTN7X,Q
$FILES 1,4
$CDS ON
      PROGRAM S241
      EMA HOME,X,Y,Z
      LOGICAL HOME(60,60,60)
      INTEGER*4 DBLOCK,SUM
      INTEGER CORX(24),CORY(24),CORZ(24),RCORX(24)
      INTEGER RCORZ(24),BLOCK(2),NRMX(2),NRMZ(2)
      INTEGER POX(6),POY(6),POZ(6),DELX(6),DELY(6)
      INTEGER RCORY(24),NRMZ(2),DELZ(6),CRNKLY3(2)
      INTEGER NXTX(6),NXTY(6),NXTZ(6),ITIME(5)
      INTEGER TPX(24,64),TPY(24,64),TPZ(24,64),BUFLEN
      INTEGER CRNKLY2(2),CRNKLY3(2),CRNKLY2(2)
      INTEGER CRNKLY2(2),CRNKLY3(2),CRNKLY2(2)
      REAL PR(6),OP(0:10),RND(5000)
      INTEGER X(30000),Y(30000),Z(30000)
      COMMON RND
      EQUIVALENCE (BLOCK(1),DBLOCK)
      DATA DELX/1,0,0,-1,0,0/
      DATA DELY/0,1,0,0,-1,0/
      DATA DELZ/0,0,1,0,0,-1/
      DATA I9/0/
      DATA LP/1,-1/
      DATA BUFLN/1536/
      DATA SUM/0/
      LU=24
      OPTION=000001B
      CALL LURQ(OPTION,LU)
      DBLOCK=0
C INITIALIZE THE PERIODIC BOX TO BE EMPTY
      DO 909 I1=1,60
      DO 909 I2=1,60
      DO 909 I3=1,60
      909 HOME(I1,I2,I3)=.FALSE.
C READ IN THE PERIODIC (COR) AND REAL (RCOR)
C COORDINATES. POT IS THE POTENTIAL
      15 FORMAT(' OK')
      OPEN(UNIT=5,FILE='S241')
      READ(5,55)LENGTH,NUM,R2,POT,ITIME(1)
      WRITE(1,55)LENGTH,NUM,R2,POT,ITIME(1)
      55 FORMAT(I2,I3,F15.7,F10.6,3I6)
      READ(5,FMT=129)(CORX(I),RCORX(I),CORY(I),
      * RCORY(I),CORZ(I),RCORZ(I),I=1,LENGTH)
      DO 303 I=1,LENGTH
      IF (HOME(CORX(I),CORY(I),CORZ(I)))GO TO 632
      HOME(CORX(I),CORY(I),CORZ(I))=.TRUE.
      303 CONTINUE
      CLOSE(5)
      GO TO 118
      632 WRITE(1,365)I
      365 FORMAT(' ERROR IN DATA',I5)
      STOP

```

```

118 WRITE(1,33)
33  FORMAT(' DATA OK')
    LNP1=LENGTH+1
C CALCULATE THE BOLTZMANN FACTORS
    DO 600 I=0,10
        OP(I)=EXP(POT*I)
    600 CONTINUE
C SET THE SAMPLING INTERVAL TO BE 4 BEAD CYCLES
    JK=LENGTH*4
C INITIALIZE THE RANDOM NUMBER GENERATOR
    CALL INIT(IPOINT)
C THIS LOOP PERFORMS THE ATTEMPTED MOTIONS
    DO 2800 I1=1,30000
        DO 2700 I2=1,JK
C RANDOMLY PICK A BEAD, i.e.J
            J=R250(IPOINT)*LENGTH+1
            IF(J.EQ.1)GO TO 900
            IF(J.NE.LENGTH)GO TO 1500
            J1=LENGTH-1
            GO TO 1000
        900 J1=2
C *****
C END ROUTINE
C *****
    1000 TOT=0.0
        HOME(CORX(J),CORY(J),CORZ(J))=.FALSE.
        IX=CORX(J1)-CORX(J)
        IY=CORY(J1)-CORY(J)
        IZ=CORZ(J1)-CORZ(J)
        DO 30 M1=1,6
            NO=-1
            POX(M1)=CORX(J1)+DELX(M1)
            IF(POX(M1).EQ.61) POX(M1)=1
            IF(POX(M1).EQ.0) POX(M1)=60
            POY(M1)=CORY(J1)+DELY(M1)
            IF(POY(M1).EQ.61) POY(M1)=1
            IF(POY(M1).EQ.0) POY(M1)=60
            POZ(M1)=CORZ(J1)+DELZ(M1)
            IF(POZ(M1).EQ.61) POZ(M1)=1
            IF(POZ(M1).EQ.0) POZ(M1)=60
C DON'T ALLOW MOTIONS WHERE THE EXCLUDED VOLUME
C CONSTRAINT IS VIOLATED
C OR A 180 DEGREE FLIP OF A BEAD'S BOND IS MADE
            IF(((IX.EQ.DELX(M1)).AND.(IY.EQ.DELY(M1)).AND.
            * (IZ.EQ.DELZ(M1))).OR.(HOME(POX(M1),POY(M1),
            * POZ(M1))))THEN
                PR(M1)=0.0
            ELSE
C SEE HOW MANY NEAREST-NEIGHBORS ARE OCCUPIED
                DO 50 M3=1,6
                    NXTX(M3)=POX(M1)+DELX(M3)
                    IF(NXTX(M3).EQ.61) NXTX(M3)=1

```

```

        IF(NXTX(M3).EQ.0) NXTX(M3)=60
        NXTY(M3)=POY(M1)+DELY(M3)
        IF(NXTY(M3).EQ.61) NXTY(M3)=1
        IF(NXTY(M3).EQ.0) NXTY(M3)=60
        NXTZ(M3)=POZ(M1)+DELZ(M3)
        IF(NXTZ(M3).EQ.61) NXTZ(M3)=1
        IF(NXTZ(M3).EQ.0) NXTZ(M3)=60
        IF(HOME(NXTX(M3),NXTY(M3),NXTZ(M3)))NO=NO+1
50    CONTINUE
        PR(M1)=OP(NO)
        ENDIF
        TOT=TOT+PR(M1)
30    CONTINUE
        A=R250(IPOINT)*TOT
        SM=0.0
C    PICK A LOCATION TO MOVE TO
        DO 80 M6=1,6
            SM=SM+PR(M6)
            IF(SM.GT.A)THEN
                CORX(J)=POX(M6)
                RCORX(J)=RCORX(J1)+DELX(M6)
                CORY(J)=POY(M6)
                RCORY(J)=RCORY(J1)+DELY(M6)
                CORZ(J)=POZ(M6)
                RCORZ(J)=RCORZ(J1)+DELZ(M6)
                HOME(CORX(J),CORY(J),CORZ(J))=.TRUE.
                GO TO 2700
            ENDIF
80    CONTINUE
C
C*****
C    NORMAL ROUTINE
C
1500  J1=J-1
        J2=J+1
        M=(RCORX(J1)-RCORX(J2))*2+(RCORY(J1)
        * -RCORY(J2))*2+(RCORZ(J1)-RCORZ(J2))*2
C    A LINEAR CONFORMATION MEANS NO MOVE IS POSSIBLE
        IF(M.EQ.4)GO TO 2700
        NRMX(2)=CORX(J2)+RCORX(J1)-RCORX(J)
        IF(NRMX(2).EQ.61) NRMX(2)=1
        IF(NRMX(2).EQ.0) NRMX(2)=60
        NRMY(2)=CORY(J2)+RCORY(J1)-RCORY(J)
        IF(NRMY(2).EQ.61) NRMY(2)=1
        IF(NRMY(2).EQ.0) NRMY(2)=60
        NRMZ(2)=CORZ(J2)+RCORZ(J1)-RCORZ(J)
        IF(NRMZ(2).EQ.61) NRMZ(2)=1
        IF(NRMZ(2).EQ.0) NRMZ(2)=60
C    IF THE NORMAL MOTION CANNOT BE PERFORMED DUE TO THE
C    SITE BEING OCCUPIED, TRY A CRANKSHAFT
        IF(HOME(NRMX(2),NRMY(2),NRMZ(2)))GO TO 2000
        HOME(CORX(J),CORY(J),CORZ(J))=.FALSE.

```

```

      NRMX(1)=CORX(J)
      NRMY(1)=CORY(J)
      NRMZ(1)=CORZ(J)
C SEE HOW MANY NEAREST-NEIGHBOR SITES ARE OCCUPIED
      DO 120 N3=1,2
        NO=-2
        DO 130 N4=1,6
          NXTX(N4)=NRMX(N3)+DELX(N4)
          IF(NXTX(N4).EQ.61) NXTX(N4)=1
          IF(NXTX(N4).EQ.0) NXTX(N4)=60
          NXTY(N4)=NRMY(N3)+DELY(N4)
          IF(NXTY(N4).EQ.61) NXTY(N4)=1
          IF(NXTY(N4).EQ.0) NXTY(N4)=60
          NXTZ(N4)=NRMZ(N3)+DELZ(N4)
          IF(NXTZ(N4).EQ.61) NXTZ(N4)=1
          IF(NXTZ(N4).EQ.0) NXTZ(N4)=60
          IF(HOME(NXTX(N4),NXTY(N4),NXTZ(N4)))NO=NO+1
130    CONTINUE
        PR(N3)=OP(NO)
120    CONTINUE
C SELECT EITHER REMAINING IN PLACE OR A NORMAL MOTION
      A=R250(IPOINT)*(PR(1)+PR(2))
      IF(PR(2).GT.A)THEN
        RCORX(J)=RCORX(J2)+RCORX(J1)-RCORX(J)
        CORX(J)=NRMX(2)
        RCORY(J)=RCORY(J2)+RCORY(J1)-RCORY(J)
        CORY(J)=NRMY(2)
        RCORZ(J)=RCORZ(J2)+RCORZ(J1)-RCORZ(J)
        CORZ(J)=NRMZ(2)
      ENDIF
      HOME(CORX(J),CORY(J),CORZ(J))=.TRUE.
      GO TO 2700
C*****
C CRANKSHAFT ROUTINE
C FIRST SEE IF THERE IS A CRANKSHAFT STRUCTURE
2000 L1=0
      J3=J1-1
      J4=J2+1
      IF(J3.NE.0)THEN
        IF((NRMX(2).EQ.CORX(J3)).AND.(NRMY(2).EQ.
* CORY(J3)).AND.(NRMZ(2).EQ.CORZ(J3)))THEN
          L1=J3
          L2=J1
          L3=J
          L4=J2
        ENDIF
      ENDIF
      IF(J4.NE.LNP1)THEN
        IF((NRMX(2).EQ.CORX(J4)).AND.(NRMY(2).EQ.
* CORY(J4)).AND.(NRMZ(2).EQ.CORZ(J4)))THEN
          L1=J1
          L2=J

```

```

      L3=J2
      L4=J4
    ENDIF
  ENDIF
  IF(L1.EQ.0)GO TO 2700
C L2 AND L3 ARE THE BEADS FOR WHICH THE MOTION WILL
C BE ATTEMPTED
  HOME(CORX(L2),CORY(L2),CORZ(L2))=.FALSE.
  HOME(CORX(L3),CORY(L3),CORZ(L3))=.FALSE.
  NO=-2
C FIND THE NUMBER OF PAIR INTERACTIONS FOR L2 AND L3
C AT THEIR PRESENT LOCATIONS
  DO 200 K1=1,6
    POX(K1)=CORX(L2)+DELX(K1)
    IF(POX(K1).EQ.61) POX(K1)=1
    IF(POX(K1).EQ.0) POX(K1)=60
    NXTX(K1)=CORX(L3)+DELX(K1)
    IF(NXTX(K1).EQ.61) NXTX(K1)=1
    IF(NXTX(K1).EQ.0) NXTX(K1)=60
    POY(K1)=CORY(L2)+DELY(K1)
    IF(POY(K1).EQ.61) POY(K1)=1
    IF(POY(K1).EQ.0) POY(K1)=60
    NXTY(K1)=CORY(L3)+DELY(K1)
    IF(NXTY(K1).EQ.61) NXTY(K1)=1
    IF(NXTY(K1).EQ.0) NXTY(K1)=60
    POZ(K1)=CORZ(L2)+DELZ(K1)
    IF(POZ(K1).EQ.61) POZ(K1)=1
    IF(POZ(K1).EQ.0) POZ(K1)=60
    NXTZ(K1)=CORZ(L3)+DELZ(K1)
    IF(NXTZ(K1).EQ.61) NXTZ(K1)=1
    IF(NXTZ(K1).EQ.0) NXTZ(K1)=60
    IF(HOME(POX(K1),POY(K1),POZ(K1))) NO=NO+1
    IF(HOME(NXTX(K1),NXTY(K1),NXTZ(K1))) NO=NO+1
  200 CONTINUE
  PR(3)=OP(NO)
  TOT=PR(3)
C FIND THE TWO POSSIBLE 90 DEGREE CRANKSHAFT LOCATIONS
  DO 230 K4=1,2
    PR(K4)=1.0
    CRNKX2(K4)=CORX(L1)
    CRNKX3(K4)=CORX(L4)
    IF(CORX(L1).EQ.CORX(L3))THEN
      CRNKX2(K4)=CRNKX2(K4)+LP(K4)
      CRNKX3(K4)=CRNKX3(K4)+LP(K4)
    IF(CRNKLX2(K4).EQ.61) CRNKX2(K4)=1
    IF(CRNKLX2(K4).EQ.0) CRNKX2(K4)=60
    IF(CRNKLX3(K4).EQ.61) CRNKX3(K4)=1
    IF(CRNKLX3(K4).EQ.0) CRNKX3(K4)=60
    ID=1
  ENDIF
  CRNKY2(K4)=CORY(L1)
  CRNKY3(K4)=CORY(L4)

```

```

      IF(CORY(L1).EQ.CORY(L3))THEN
        CRNKLY2(K4)=CRNKLY2(K4)+LP(K4)
        CRNKLY3(K4)=CRNKLY3(K4)+LP(K4)
        IF(CRNKLY2(K4).EQ.61) CRNKLY2(K4)=1
        IF(CRNKLY2(K4).EQ.0) CRNKLY2(K4)=60
        IF(CRNKLY3(K4).EQ.61) CRNKLY3(K4)=1
        IF(CRNKLY3(K4).EQ.0) CRNKLY3(K4)=60
        ID=2
      ENDIF
      CRNKLZ2(K4)=CORZ(L1)
      CRNKLZ3(K4)=CORZ(L4)
      IF(CORZ(L1).EQ.CORZ(L3))THEN
        CRNKLZ2(K4)=CRNKLZ2(K4)+LP(K4)
        CRNKLZ3(K4)=CRNKLZ3(K4)+LP(K4)
        IF(CRNKLZ2(K4).EQ.61) CRNKLZ2(K4)=1
        IF(CRNKLZ2(K4).EQ.0) CRNKLZ2(K4)=60
        IF(CRNKLZ3(K4).EQ.61) CRNKLZ3(K4)=1
        IF(CRNKLZ3(K4).EQ.0) CRNKLZ3(K4)=60
        ID=3
      ENDIF
C DETERMINE IF THE PROSPECTIVE CRANKSHFT POSITION IS
C OCCUPIED
      IF((HOME(CRNKLX2(K4),CRNKLY2(K4),CRNKLZ2(K4)))
      * .OR.(HOME(CRNKLX3(K4),CRNKLY3(K4)
      * CRNKLZ3(K4))))PR(K4)=0.0
230 CONTINUE
C FIND THE NUMBER OF PAIR INTERACTIONS FOR THE BEADS
DO 250 K6=1,2
  IF(PR(K6).NE.0.0)THEN
    NO=-2
    DO 260 K7=1,6
      POX(K7)=CRNKLY2(K6)+DELX(K7)
      NXTX(K7)=CRNKLY3(K6)+DELX(K7)
      IF(POX(K7).EQ.61) POX(K7)=1
      IF(POX(K7).EQ.0) POX(K7)=60
      IF(NXTX(K7).EQ.61) NXTX(K7)=1
      IF(NXTX(K7).EQ.0) NXTX(K7)=60
      POY(K7)=CRNKLY2(K6)+DELY(K7)
      NXTY(K7)=CRNKLY3(K6)+DELY(K7)
      IF(POY(K7).EQ.61) POY(K7)=1
      IF(POY(K7).EQ.0) POY(K7)=60
      IF(NXTY(K7).EQ.61) NXTY(K7)=1
      IF(NXTY(K7).EQ.0) NXTY(K7)=60
      POZ(K7)=CRNKLZ2(K6)+DELZ(K7)
      NXTZ(K7)=CRNKLZ3(K6)+DELZ(K7)
      IF(POZ(K7).EQ.61) POZ(K7)=1
      IF(POZ(K7).EQ.0) POZ(K7)=60
      IF(NXTZ(K7).EQ.61) NXTZ(K7)=1
      IF(NXTZ(K7).EQ.0) NXTZ(K7)=60
      IF(HOME(POX(K7),POY(K7),POZ(K7))) NO=NO+1
      IF(HOME(NXTX(K7),NXTY(K7),NXTZ(K7))) NO=NO+1
260 CONTINUE

```

```

        PR(K6)=OP(NO)
        TOT=TOT+PR(K6)
    ENDIF
250 CONTINUE
    A=R250(IPOINT)*TOT
    SM=0.0
C PICK THE FINAL LOCATION OF THE CRANKSHAFT
    DO 300 K11=1,2
        SM=SM+PR(K11)
        IF(SM.GT.A)THEN
            CORX(L2)=CRNK LX2(K11)
            RCORX(L2)=RCORX(L1)
            CORX(L3)=CRNK LX3(K11)
            RCORX(L3)=RCORX(L4)
            IF(ID.EQ.1)THEN
                RCORX(L2)=RCORX(L2)+LP(K11)
                RCORX(L3)=RCORX(L3)+LP(K11)
            ENDIF
            CORY(L2)=CRNK LY2(K11)
            RCORY(L2)=RCORY(L1)
            CORY(L3)=CRNK LY3(K11)
            RCORY(L3)=RCORY(L4)
            IF(ID.EQ.2)THEN
                RCORY(L2)=RCORY(L2)+LP(K11)
                RCORY(L3)=RCORY(L3)+LP(K11)
            ENDIF
            CORZ(L2)=CRNK LZ2(K11)
            RCORZ(L2)=RCORZ(L1)
            CORZ(L3)=CRNK LZ3(K11)
            RCORZ(L3)=RCORZ(L4)
            IF(ID.EQ.3)THEN
                RCORZ(L2)=RCORZ(L2)+LP(K11)
                RCORZ(L3)=RCORZ(L3)+LP(K11)
            ENDIF
            GO TO 2300
        ENDIF
    300 CONTINUE
2300 HOME(CORX(L2),CORY(L2),CORZ(L2))=.TRUE.
    HOME(CORX(L3),CORY(L3),CORZ(L3))=.TRUE.
2700 CONTINUE
C*****
C RECORD TO TAPE
C
    I9=I9+1
    IF(I9.EQ.65)THEN
        CALL EXEC(2,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
    I9=1

```

```

ENDIF
DO 2753 I8=1,LENGTH
  TPX(I8,I9)=RCORX(I8)
  TPY(I8,I9)=RCORY(I8)
  TPZ(I8,I9)=RCORZ(I8)
2753 CONTINUE
C SINGLE CHAIN WORKUP
  SUM=SUM+(RCORX(1)-RCORX(LENGTH))**2
  *      +(RCORY(1)-RCORY(LENGTH))**2
  *      +(RCORZ(1)-RCORZ(LENGTH))**2
  X(I1)=RCORX(1)-RCORX(LENGTH)
  Y(I1)=RCORY(1)-RCORY(LENGTH)
  Z(I1)=RCORZ(1)-RCORZ(LENGTH)
2800 CONTINUE
  CALL EXEC(2,24+1008,TPX,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  CALL EXEC(2,24+1008,TPY,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  CALL EXEC(2,24+1008,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  WRITE(1,10)DBLOCK
  10 FORMAT(' NEXT AVAILABLE BLOCK IS ',I110)
C*****
C RECORD DATA
  R2=SUM/30000.
  JTIME=0
65  FORMAT(I2,I3,1F15.7)
  OPEN(UNIT=8,FILE='SIMP24')
  WRITE(8,65)LENGTH,NUM,R2
C CALCULATE THE AUTOCORRELATION FUNCTION OF THE
C END-TO-END VECTOR
  DO 1301 I2=1,200
    SUM=0
    MAXI=30000-I2
    DO 1401 I3=1,MAXI
      J=I2+I3
      SUM=SUM+X(I3)*X(J)+Y(I3)*Y(J)+Z(I3)*Z(J)
1401 CONTINUE
      TAU=DBLE(SUM)/DBLE(MAXI)/R2
      JTIME=JTIME+4
      WRITE(8,1402)JTIME,TAU
1402 FORMAT(' TIME=',F7.3,5X,'TAU=',PE13.6)
1301 CONTINUE
      CLOSE(8)
C*****
C PRINT OUT FINAL COORDINATES OF THE CHAIN
  125 OPEN(UNIT=5,FILE='S241')
  REWIND(5)
  WRITE(5,55)LENGTH,NUM,R2,POT,ITIME(1)
  WRITE(5,129)(CORX(I),RCORX(I),CORY(I),RCORY(I),
  * CORZ(I),RCORZ(I),I=1,LENGTH)
  WRITE(5,55)LENGTH,NUM,R2,POT,ITIME(1)

```

```

        CLOSE(5)
129  FORMAT(20I4)
        CALL FMPRUNPROGRAM(STRING,0,0,0,0,0,NAME)
        STOP
        END
C*****
C THIS IS THE SHIFT RANDOM NUMBER GENERATOR
      FUNCTION R250(IPOINT)
        INTEGER*4 IRND(5000),MASK,I
        DIMENSION RND(5000)
        EQUIVALENCE (IRND(1),RND(1))
        COMMON IRND
        DATA MASK/1073742082/
        IPOINT=IPOINT+1
        IF(IPOINT.GT.5000)CALL REINT(IPOINT)
        I=IEOR(IRND(IPOINT-250),IRND(IPOINT-103))
        IRND(IPOINT)=IOR(I,MASK)
        R250=RND(IPOINT)-1.0
        RETURN
      END
C REINT REINITIALIZES R250
      SUBROUTINE REINT(IPOINT)
        INTEGER*4 IRND(5000),IRND2(250)
        EQUIVALENCE (IRND(4751),IRND2(1))
        COMMON IRND
        DO 1 I=1,250
          IRND(I)=IRND2(I)
1      CONTINUE
        IPOINT=251
        RETURN
      END
C INIT INITIALIZES R250 USING ARAN
      SUBROUTINE INIT(IPOINT)
        DIMENSION RND(5000)
        INTEGER*4 IRND(5000),MASK
        EQUIVALENCE (RND(1),IRND(1))
        COMMON RND
        DATA MASK/1073741568/
        A=ARAN(1)
        DO 1 I=1,250
          RND(I)=ARAN(0)
          IRND(I)=IAND(IRND(I),MASK)
1      CONTINUE
        IPOINT=250
        RETURN
      END
C ARAN PROVIDES A SEED OF 250 RANDOM NUMBERS TO R250.
C ARAN USES THE HP CLOCK AS A SEED
      FUNCTION ARAN(I)
        SAVE
        REAL*8 IRAND,MULT,LARGE
        INTEGER ITIME(5)

```

```

DATA IRAND/15893./,MULT/65539./,LARGE/2147483647./
IF(I.EQ.0)GO TO 1
CALL EXEC(11,ITIME)
IRAND=IRAND*DBLE(ITIME(1)+ITIME(2)+ITIME(3)+
* ITIME(4))
WRITE(1,393)IRAND
393 FORMAT(F10.2)
GO TO 2
1 IRAND=IRAND*MULT
2 IRAND=DIMOD(IRAND,LARGE)+1
ARAN=IRAND/(LARGE+1)
K=ARAN*30000
ARAN=FLOAT(K)/30000.
IF(ARAN.GE.1)ARAN=.999
IF(ARAN.LE.0)ARAN=.001
RETURN
END

```

APPENDIX IV
FORTRAN CODE FOR THE THERMAL FCC MODEL

```

FTN7X,Q
$FILES 1,4
$CDS ON
    PROGRAM F241
    EMA HOME,X,Y,Z
    LOGICAL HOME(90,90,90)
    INTEGER*4 DBLOCK,SUM
    REAL PR(12),OP(0:11)
    INTEGER VECX(3),DETX(12),NXTX(12),UX(12),MOVEX(3)
    INTEGER VECY(3),DELY(12),NXTY(12),UY(12),MOVEY(3)
    INTEGER VECZ(3),DELZ(12),NXTZ(12),UZ(12),MOVEZ(3)
    INTEGER CORX(24),RCORX(24),X(30000),TPX(24,64)
    INTEGER CORY(24),RCORY(24),Y(30000),TPY(24,64)
    INTEGER CORZ(24),RCORZ(24),Z(30000),TPZ(24,64)
    INTEGER BLOCK(2),ITIME(6),BUFLEN,NAME(3)
    CHARACTER*15 STRING
    EQUIVALENCE (BLOCK(1),DBLOCK)
C*****
    DATA NAME/'F361'/
    DATA STRING/'XQ F361::PATTON'/
    DATA SUM/0/
C THE (CARTESIAN) VECTORS BETWEEN A BEAD AND ITS
C NEAREST-NEIGHBORS
    DATA UX/1,1,1,1,-1,-1,-1,-1,0,0,0,0/
    DATA UY/1,-1,0,0,1,-1,0,0,1,1,-1,-1/
    DATA UZ/0,0,1,-1,0,0,1,-1,1,-1,1,-1/
    LU=24
    BUFLen=1536
    I9=0
    DBLOCK=0
    OPTION=000001B
    CALL LURQ(OPTION,LU)
50  FORMAT(I2,I3,F15.7,F10.6,6I6)
C SET THE PERIODIC BOX TO BE EMPTY
    DO 909 I1=1,90
    DO 909 I2=1,90
    DO 909 I3=1,90
    909  HOME(I1,I2,I3)=.FALSE.
C*****
C READ IN THE PERIODIC AND REAL COORDINATES*****
    OPEN(UNIT=5,FILE='F241')
    READ(5,50)LENGTH,NUM,R2,POT,ITIME(1)
    WRITE(1,50)LENGTH,NUM,R2,POT
    READ(5,FMT=129)(CORX(J),RCORX(J),CORY(J)
    * ,RCORY(J),CORZ(J),RCORZ(J),J=1,LENGTH)
    DO 303 I=1,LENGTH
        IF(HOME(CORX(I),CORY(I),CORZ(I)))GOTO 632
        HOME(CORX(I),CORY(I),CORZ(I))=.TRUE.
    303  CONTINUE
        CLOSE(5)
        GO TO 118
    632  WRITE(1,365)I
    365  FORMAT(' ERROR IN DATA',2I5)

```

```

      STOP
C
118  WRITE(1,33)
33   FORMAT(' DATA OK')
C
C CALCULATE THE BOLTZMANN FACTORS
      DO 606 I=0,11
          OP(I)=EXP(I*POT)
      606 CONTINUE
C SAMPLING INTERVAL IS 4 BEAD CYCLES
      JK=LENGTH*NUM*4
C INITIALIZE THE RANDOM NUMBER GENERATOR
      CALL INIT(IPOINT)
C THIS LOOP PERFORMS THE BEAD MOTIONS
      DO 2800 I1=1,30000
          DO 2700 I2=1,JK
              SM=0.0
              TOT=0.0
C A IS THE RANDOM NUMBER WHICH DETERMINES WHICH POSSIBLE
C MOTION WILL BE ACCEPTED
C J DETERMINES WHICH BEAD WILL BE SELECTED FOR ATTEMPTED
C MOTION
              A=R250(IPOINT)
              J=R250(IPOINT)*LENGTH+1
              HOME(CORX(J),CORY(J),CORZ(J))=.FALSE.
              IF((J.EQ.1).OR.(J.EQ.LENGTH)) GO TO 1000
              J1=J-1
              J2=J+1
              IDEL=((RCORX(J1)-RCORX(J2))**2
*                +(RCORY(J1)-RCORY(J2))**2
*                +(RCORZ(J1)-RCORZ(J2))**2)/2
              GO TO (2000,3000,4000,2700) IDEL
C
C END ROUTINE
C
1000  IF(J.EQ.1)THEN
          J1=2
      ELSE
          J1=LENGTH-1
      ENDIF
C DETERMINE THE RELATIVE PROBABILITIES OF EACH
C POSSIBLE MOTION
      DO 1010 K1=1,12
          NO=-1
          DELX(K1)=CORX(J1)+UX(K1)
          IF(DELX(K1).EQ.91)DELX(K1)=1
          IF(DELX(K1).EQ.0) DELX(K1)=90
          DELY(K1)=CORY(J1)+UY(K1)
          IF(DELY(K1).EQ.91)DELY(K1)=1
          IF(DELY(K1).EQ.0)DELY(K1)=90
          DELZ(K1)=CORZ(J1)+UZ(K1)
          IF(DELZ(K1).EQ.91)DELZ(K1)=1

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      IF(DELZ(K1).EQ.0)DELZ(K1)=90
C IF THE POSTION IS OCCUPPIED THEN THE PROBABILITY IS ZERO
      IF(HOME(DELX(K1),DELY(K1),DELZ(K1)))THEN
        PR(K1)=0.0
      ELSE
C FIND OUT HOW MANY NEAREST-NEIGHBORS ARE OCCUPPIED
        DO 1030 K3=1,12
          NXTX(K3)=DELX(K1)+UX(K3)
          IF(NXTX(K3).EQ.91)NXTX(K3)=1
          IF(NXTX(K3).EQ.0)NXTX(K3)=90
          NXTY(K3)=DELY(K1)+UY(K3)
          IF(NXTY(K3).EQ.91)NXTY(K3)=1
          IF(NXTY(K3).EQ.0)NXTY(K3)=90
          NXTZ(K3)=DELZ(K1)+UZ(K3)
          IF(NXTZ(K3).EQ.91)NXTZ(K3)=1
          IF(NXTZ(K3).EQ.0)NXTZ(K3)=90
          IF(HOME(NXTX(K3),NXTY(K3),NXTZ(K3)))NO=NO+1
1030    CONTINUE
        PR(K1)=OP(NO)
        ENDIF
        TOT=TOT+PR(K1)
1010    CONTINUE
        DO 1050 K5=1,12
          PR(K5)=PR(K5)/TOT
1050    CONTINUE
C SELECT A POSSIBILITY
        DO 1060 K6=1,12
          SM=SM+PR(K6)
          IF(SM.GE.A)THEN
            CORX(J)=DELX(K6)
            RCORX(J)=RCORX(J1)+UX(K6)
            CORY(J)=DELY(K6)
            RCORY(J)=RCORY(J1)+UY(K6)
            CORZ(J)=DELZ(K6)
            RCORZ(J)=RCORZ(J1)+UZ(K6)
            GO TO 2700
          ENDIF
1060    CONTINUE
C
C 120 DEGREE ROUTINE
C DEL (2) ARRAY IS THE LOCATION OF THE BEAD AFTER A
C BOND VECTOR EXCHANGE
      4000 DELX(2)=RCORX(J1)-RCORX(J)+CORX(J2)
        IF(DELX(2).EQ.91) DELX(2)=1
        IF(DELX(2).EQ.0) DELX(2)=90
        DELY(2)=RCORY(J1)-RCORY(J)+CORY(J2)
        IF(DELY(2).EQ.91) DELY(2)=1
        IF(DELY(2).EQ.0) DELY(2)=90
        DELZ(2)=RCORZ(J1)-RCORZ(J)+CORZ(J2)
        IF(DELZ(2).EQ.91) DELZ(2)=1
        IF(DELZ(2).EQ.0) DELZ(2)=90
C IF THE POSITION IS OCCUPIED NO MOTION IS POSSIBLE

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```

      IF (HOME (DELX (2), DELY (2), DELZ (2))) THEN
        GO TO 2700
      ELSE
        DELX (1) = CORX (J)
        DELY (1) = CORY (J)
        DELZ (1) = CORZ (J)
        DO 4020 K2 = 1, 2
          NO = -2
        C DETERMINE HOW MANY NEAREST-NEIGHBORS ARE OCCUPIED
          DO 4030 K3 = 1, 12
            NXTX (K3) = DELX (K2) + UX (K3)
            IF (NXTX (K3).EQ.91) NXTX (K3) = 1
            IF (NXTX (K3).EQ.0) NXTX (K3) = 90
            NXTY (K3) = DELY (K2) + UY (K3)
            IF (NXTY (K3).EQ.91) NXTY (K3) = 1
            IF (NXTY (K3).EQ.0) NXTY (K3) = 90
            NXTZ (K3) = DELZ (K2) + UZ (K3)
            IF (NXTZ (K3).EQ.91) NXTZ (K3) = 1
            IF (NXTZ (K3).EQ.0) NXTZ (K3) = 90
            IF (HOME (NXTX (K3), NXTY (K3), NXTZ (K3))) NO = NO + 1
          4030 CONTINUE
          PR (K2) = OP (NO)
        4020 CONTINUE
          PR (1) = PR (1) / (PR (1) + PR (2))
          IF (PR (1).LT.A) THEN
        C IF TRUE PERFORM THE BOND VECTOR EXCHANGE
          RCORX (J) = RCORX (J2) + RCORX (J1) - RCORX (J)
          RCORY (J) = RCORY (J2) + RCORY (J1) - RCORY (J)
          RCORZ (J) = RCORZ (J2) + RCORZ (J1) - RCORZ (J)
          CORX (J) = DELX (2)
          CORY (J) = DELY (2)
          CORZ (J) = DELZ (2)
          ENDIF
          GO TO 2700
        ENDIF
      C
      C 60 DEGREE ROUTINE
      C
      2000 DELX (4) = CORX (J)
          DELY (4) = CORY (J)
          DELZ (4) = CORZ (J)
          DO 2010 K1 = 1, 3
        C THIS CALCULATION THE VECTOR ALONG WHICH THE BEAD
        C WOULD MOVE FOR A BOND VECTOR EXCHANGE
          VECX (K1) = RCORX (J1) + RCORX (J2) - 2 * RCORX (J)
          VECY (K1) = RCORY (J1) + RCORY (J2) - 2 * RCORY (J)
          VECZ (K1) = RCORZ (J1) + RCORZ (J2) - 2 * RCORZ (J)
        C ELEMINATING THE PROPER COMPONENTS OF THE VECTOR
        C WILL GIVE THE VECTORS ALONG WHICH OUT-OF-PLANE MOTION
        C CAN OCCUR
          IF (K1.EQ.1) THEN

```

```

      IF(IABS(VECX(K1)).EQ.2)VECX(K1)=0
      IF(IABS(VECY(K1)).EQ.2)VECY(K1)=0
      IF(IABS(VE CZ(K1)).EQ.2)VE CZ(K1)=0
    ENDIF
    IF(K1.EQ.2)THEN
      IF(IABS(VECX(K1)).EQ.1)VECX(K1)=0
      IF(IABS(VECY(K1)).EQ.1)VECY(K1)=0
      IF(IABS(VE CZ(K1)).EQ.1)VE CZ(K1)=0
    ENDIF
    DELX(K1)=CORX(J)+VECX(K1)
    IF(DELX(K1).GE.91)DELX(K1)=DELX(K1)-90
    IF(DELX(K1).LE.0)DELX(K1)=DELX(K1)+90
    DELY(K1)=CORY(J)+VECY(K1)
    IF(DELY(K1).GE.91)DELY(K1)=DELY(K1)-90
    IF(DELY(K1).LE.0)DELY(K1)=DELY(K1)+90
    DELZ(K1)=CORZ(J)+VE CZ(K1)
    IF(DE LZ(K1).GE.91)DE LZ(K1)=DE LZ(K1)-90
    IF(DE LZ(K1).LE.0)DE LZ(K1)=DE LZ(K1)+90
  2010 CONTINUE
    DO 2040 K4=1,4
      NO=-2
    C IF OCCUPIED NO MOTION TO THIS LOCATION IS POSSIBLE
      IF(HOME(DE LX(K4),DE LY(K4),DE LZ(K4)))THEN
        PR(K4)=0.0
      ELSE
    C CHECK TO SEE THE NUMBER OF OCCUPIED NEAREST-NEIGHBORS
        DO 2050 K5=1,12
          NXTX(K5)=DE LX(K4)+UX(K5)
          IF(NXTX(K5).EQ.91)NXTX(K5)=1
          IF(NXTX(K5).EQ.0)NXTX(K5)=90
          NXTY(K5)=DE LY(K4)+UY(K5)
          IF(NXTY(K5).EQ.91)NXTY(K5)=1
          IF(NXTY(K5).EQ.0)NXTY(K5)=90
          NXTZ(K5)=DE LZ(K4)+UZ(K5)
          IF(NXTZ(K5).EQ.91)NXTZ(K5)=1
          IF(NXTZ(K5).EQ.0)NXTZ(K5)=90
          IF(HOME(NXTX(K5),NXTY(K5),NXTZ(K5)))NO=NO+1
        2050 CONTINUE
        PR(K4)=OP(NO)
        TOT=TOT+PR(K4)
      ENDIF
    2040 CONTINUE
    DO 2070 K7=1,4
      PR(K7)=PR(K7)/TOT
    2070 CONTINUE
  C SELECT A LOCATION TO MOVE TO
    DO 2080 K8=1,3
      SM=SM+PR(K8)
      IF(SM.GE.A)THEN
        CORX(J)=DE LX(K8)
        RCORX(J)=RCORX(J)+VECX(K8)
        CORY(J)=DE LY(K8)
        RCORY(J)=RCORY(J)+VECY(K8)

```

```

CORZ(J)=DELZ(K8)
RCORZ(J)=RCORZ(J)+UECZ(K8)
GO TO 2700
ENDIF
2080 CONTINUE
GO TO 2700
C
C 90 DEGREE ROUTINE
C
3000 MOVEX(1)=(RCORX(J1)+RCORX(J2))/2-RCORX(J)
MOVEY(1)=(RCORY(J1)+RCORY(J2))/2-RCORY(J)
MOVEZ(1)=(RCORZ(J1)+RCORZ(J2))/2-RCORZ(J)
C 2 TIMES MOVE (1) GIVES THE VECTOR FOR A BEAD'S
C MOTION IF IT UNDERGOES BOND VECTOR EXCHANGE.
C BOND VECTOR EXCHANGE MOVE (2) OR MOVE (3) PLUS
C MOVE (1) WILL GIVE THE OUT-OF-PLANE POSSIBILITIES
IF(RCORX(J1).NE.RCORX(J))THEN
MOVEX(2)=0
MOVEX(3)=0
ELSE
MOVEX(2)=1
MOVEX(3)=-1
ENDIF
IF(RCORY(J1).NE.RCORY(J))THEN
MOVEY(2)=0
MOVEY(3)=0
ELSE
MOVEY(2)=1
MOVEY(3)=-1
ENDIF
IF(RCORZ(J1).NE.RCORZ(J))THEN
MOVEZ(2)=0
MOVEZ(3)=0
ELSE
MOVEZ(2)=1
MOVEZ(3)=-1
ENDIF
DO 3020 K2=1,3
DELX(K2)=CORX(J)+MOVEX(K2)+MOVEX(1)
IF(DELX(K2).GE.91)DELX(K2)=DELX(K2)-90
IF(DELX(K2).LE.0)DELX(K2)=DELX(K2)+90
DELY(K2)=CORY(J)+MOVEY(K2)+MOVEY(1)
IF(DELY(K2).GE.91)DELY(K2)=DELY(K2)-90
IF(DELY(K2).LE.0)DELY(K2)=DELY(K2)+90
DELZ(K2)=CORZ(J)+MOVEZ(K2)+MOVEZ(1)
IF(DELZ(K2).GE.91)DELZ(K2)=DELZ(K2)-90
IF(DELZ(K2).LE.0)DELZ(K2)=DELZ(K2)+90
3020 CONTINUE
DELX(4)=CORX(J)
DELY(4)=CORY(J)
DELZ(4)=CORZ(J)
DO 3040 K4=1,4

```

```

      NO=-2
C IF THE POSITION IS OCCUPIED NO MOTION IS POSSIBLE
C TO THIS LOCATION
      IF(HOME(DE LX(K4),DE LY(K4),DE LZ(K4)))THEN
        PR(K4)=0.0
      ELSE
C CHECK TO SEE THE NUMBER OF OCCUPIED NEIGHBORS
        DO 3050 K5=1,12
          NXTX(K5)=DE LX(K4)+UX(K5)
          IF(NXTX(K5).EQ.91)NXTX(K5)=1
          IF(NXTX(K5).EQ.0)NXTX(K5)=90
          NXTY(K5)=DE LY(K4)+UY(K5)
          IF(NXTY(K5).EQ.91)NXTY(K5)=1
          IF(NXTY(K5).EQ.0)NXTY(K5)=90
          NXTZ(K5)=DE LZ(K4)+UZ(K5)
          IF(NXTZ(K5).EQ.91)NXTZ(K5)=1
          IF(NXTZ(K5).EQ.0)NXTZ(K5)=90
          IF(HOME(NXTX(K5),NXTY(K5),NXTZ(K5)))NO=NO+1
3050    CONTINUE
        PR(K4)=OP(NO)
        TOT=TOT+PR(K4)
      ENDIF
3040 CONTINUE
      DO 3070 K7=1,4
        PR(K7)=PR(K7)/TOT
3070 CONTINUE
C PICK A MOTION
      DO 3080 K8=1,3
        SM=SM+PR(K8)
        IF(SM.GE.A)THEN
          CORX(J)=DE LX(K8)
          RCORX(J)=RCORX(J)+MOVEX(K8)+MOVEX(1)
          CORY(J)=DE LY(K8)
          RCORY(J)=RCORY(J)+MOVEY(K8)+MOVEY(1)
          CORZ(J)=DE LZ(K8)
          RCORZ(J)=RCORZ(J)+MOVEZ(K8)+MOVEZ(1)
          GO TO 2700
        ENDIF
3080 CONTINUE
2700 HOME(CORX(J),CORY(J),CORZ(J))=.TRUE.
C *****
C RECORD COR TO TAPE
C
      I9=I9+1
      IF (I9.EQ.65) THEN
        CALL EXEC(2,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
      I9=1

```

```

ENDIF
DO 2753 I8=1,LENGTH
  TPX(I8,I9)=RCORX(I8)
  TPY(I8,I9)=RCORY(I8)
  TPZ(I8,I9)=RCORZ(I8)
2753 CONTINUE
C SINGLE CHAIN WORKUP
  SUM=SUM+(TPX(1,I9)-TPX(LENGTH,I9))**2
  *      +(TPY(1,I9)-TPY(LENGTH,I9))**2
  *      +(TPZ(1,I9)-TPZ(LENGTH,I9))**2
  X(I1)=TPX(1,I9)-TPX(LENGTH,I9)
  Y(I1)=TPY(1,I9)-TPY(LENGTH,I9)
  Z(I1)=TPZ(1,I9)-TPZ(LENGTH,I9)
2800 CONTINUE
  CALL EXEC(2,24+1008,TPX,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  CALL EXEC(2,24+1008,TPY,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  CALL EXEC(2,24+1008,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
  DBLOCK=DBLOCK+3
  OPTION=1000008
  CALL LURQ(OPTION)
  WRITE(1,10)DBLOCK
  10 FORMAT(' NEXT AVAILABLE BLOCK IS ',I110)
C*****
C      RECORD DATA
  R2=SUM/30000.
  RSQ=R2/2.
  JTIME=0
  OPEN(UNIT=8,FILE='HEX24')
  WRITE(8,50)LENGTH,NUM,RSQ,POT
C CALCULATE THE AUTOCORRELATION FUNCTION OF THE
C END-TO-END VECTOR
  DO 1301 I2=1,200
    SUM=0
    MAXI=30000-I2
    DO 1401 I3=1,MAXI
      J=I2+I3
      SUM=SUM+X(I3)*X(J)+Y(I3)*Y(J)+Z(I3)*Z(J)
1401 CONTINUE
    TAU=DBLE(SUM)/DBLE(MAXI)/R2
    JTIME=JTIME+4
    WRITE(8,1402)JTIME,TAU
1402 FORMAT(' TIME=',F7.3,5X,'TAU=',PE13.6)
1301 CONTINUE
    CLOSE(8)
C*****
C RECORD THE FINAL COORDINATES
C
125 OPEN(UNIT=6,FILE='FC241')
  REWIND(6)
  WRITE(6,50)LENGTH,NUM,RSQ,POT,ITIME(1)

```

```

        WRITE(6,129)(CORX(J),RCORX(J),CORY(J),RCORY(J),
*      CORZ(J),RCORZ(J),J=1,LENGTH)
        WRITE(6,50)LENGTH,NUM,RSQ,POT,ITIME(1)
        CLOSE(6)
129      FORMAT(20I4)
        CALL FMPRUNPROGRAM(STRING,0,0,0,0,0,NAME)
        STOP
        END

C
C ARAN PROVIDES THE SEED FOR R250, ARAN USES THE
C HP CLOCK AS ITS SEED
      FUNCTION ARAN(I)
        SAVE
        REAL*8 IRAND,MULT,LARGE
        INTEGER ITIME(5)
        DATA IRAND/14532./,MULT/65539./
        DATA LARGE/2147483647./
        IF(I.EQ.0)GOTO 1
        CALL EXEC(11,ITIME)
        IRAND=IRAND*DBLE(ITIME(1)+ITIME(2)
*      +ITIME(3)+ITIME(4))
        WRITE(1,393)IRAND
393      FORMAT(F10.2)
        GOTO 2

C
1      IRAND=IRAND*MULT
2      IRAND=DMOD(IRAND,LARGE)+1
        ARAN=(IRAND)/(LARGE+1)
        K=ARAN*30000
        ARAN=FLOAT(K)/30000.
        IF(ARAN.GE.1)ARAN=.999999
        IF(ARAN.LE.0)ARAN=.000001
        RETURN
        END

C
      FUNCTION R250(IPOINT)
        INTEGER*4 IRND(5000),MASK,I
        DIMENSION RND(5000)
        EQUIVALENCE (IRND(1),RND(1))
        COMMON IRND
        DATA MASK/1073742082/
        IPOINT=IPOINT+1
        IF(IPOINT.GT.5000)CALL REINT(IPOINT)
        I=IEOR(IRND(IPOINT-250),IRND(IPOINT-103))
        IRND(IPOINT)=IOR(I,MASK)
        R250=RND(IPOINT)-1.0
        RETURN
        END

C REINT REINIATIALIZES R250
      SUBROUTINE REINT(IPOINT)
        INTEGER*4 IRND(5000),IRND2(250)

```

```

      EQUIVALENCE (IRND(4751),IRND2(1))
      COMMON IRND
      DO 1 I=1,250
        IRND(I)=IRND2(I)
1      CONTINUE
      IPOINT=251
      RETURN
      END
C INIT INITIALIZES R250 USING ARAN
      SUBROUTINE INIT(IPOINT)
      DIMENSION RND(5000)
      INTEGER*4 IRND(5000),MASK
      EQUIVALENCE (RND(1),IRND(1))
      COMMON RND
      DATA MASK/1073741568/
      A=ARAN(1)
      DO 1 I=1,250
        RND(I)=ARAN(0)
        IRND(I)=IAND(IRND(I),MASK)
1      CONTINUE
      IPOINT=250
      RETURN
      END

```

APPENDIX V

FORTRAN CODE FOR THE THERMAL BCC MODEL

```

FTN7X,Q
$FILES 1,4
$CDS ON
      PROGRAM BOD24
      EMA HOME,X,Y,Z
      LOGICAL HOME(90,90,90)
      INTEGER*4 DBLOCK,SUM
      REAL PR(8),OP(0:7)
      INTEGER VECX(3),DELX(8),NXTX(8),UX(8),MOVEX(3)
      INTEGER VECY(3),DELY(8),NXTY(8),UY(8),MOVEY(3)
      INTEGER VECZ(3),DELZ(8),NXTZ(8),UZ(8),MOVEZ(3)
      INTEGER CORX(24),RCORX(24),X(30000),TPX(24,64)
      INTEGER CORY(24),RCORY(24),Y(30000),TPY(24,64)
      INTEGER CORZ(24),RCORZ(24),Z(30000),TPZ(24,64)
      INTEGER BLOCK(2),ITIME(6),BUFLEN,NAME(3)
      CHARACTER*16 STRING
      EQUIVALENCE (BLOCK(1),DBLOCK)
C*****
      DATA NAME/'BOD36'/
      DATA STRING/'XQ BOD36::PATTON'/
      DATA SUM/0/
C UX,UY,UZ ARE THE COMPONENTS OF THE VECTORFS TO
C THE NEAREST-NEIGHBOR LATTICE SITES
      DATA UX/1,1,1,1,-1,-1,-1,-1/
      DATA UY/1,-1,1,-1,1,-1,1,-1/
      DATA UZ/1,1,-1,-1,1,1,-1,-1/
      LU=24
      BUFLEN=1536
      I9=0
      DBLOCK=0
      OPTION=000001B
      CALL LURQ(OPTION,LU)
50      FORMAT(12,I3,F15.7,F10.6,6I6)
C SET THE PERIODIC BOX ARRAY TO BE EMPTY
      DO 909 I1=1,90
      DO 909 I2=1,90
      DO 909 I3=1,90
909      HOME(I1,I2,I3)=.FALSE.
C*****
C READ IN INITIAL COORDINATES BOTH PERIODIC AND REAL
C*****
      OPEN(UNIT=5,FILE='BODY241')
      READ(5,50)LENGTH,NUM,R2,POT,ITIME(1)
      WRITE(1,50)LENGTH,NUM,R2,POT
      READ(5,FMT=129)(CORX(J),RCORX(J),CORY(J),
      * RCORY(J),CORZ(J),RCORZ(J),J=1,LENGTH)
      DO 303 I=1,LENGTH
      IF(HOME(CORX(I),CORY(I),CORZ(I)))GOTO 632
      HOME(CORX(I),CORY(I),CORZ(I))=.TRUE.
303      CONTINUE
      CLOSE(5)
      GO TO 118
632      WRITE(1,365)I

```

```

365  FORMAT(' ERROR IN DATA',215)
    STOP
C
118  WRITE(1,33)
33   FORMAT(' DATA OK')
C
C CALUCULATE THE BOLTZMANN FACTORS
C*****
      DO 606 I=0,7
        OP(I)=EXP(I*POT)
606  CONTINUE
C JK IS THE NUMBER OF ATTEMPTED MOVES BETWEEN CYCLES
    JK=LENGTH*NUM*4
C INITIALIZE THE RANDOM NUMBER GENERATOR
    CALL INIT(IPOINT)
C BEGIN THE SIMULATION LOOP
      DO 2800 I1=1,30000
        DO 2700 I2=1,JK
          SM=0.0
          TOT=0.0
C A DETERMINES WHICH OF THE POSSIBLE MOVES IS CHOSEN
          A=R250(IPOINT)
C J IS THE BEAD FOR WHICH THE ATTEMPTED MOTION WILL
C OCCUR
          J=R250(IPOINT)*LENGTH+1
          HOME(CORX(J),CORY(J),CORZ(J))=.FALSE.
          IF((J.EQ.1).OR.(J.EQ.LENGTH)) GO TO 1000
          J1=J-1
          J2=J+1
          IDEL=((RCORX(J1)-RCORX(J2))**2
            *   +(RCORY(J1)-RCORY(J2))**2
            *   +(RCORZ(J1)-RCORZ(J2))**2)/4
C 3000 AND 4000 ARE THE 60 AND 120 DEGEREE ROUTINES
C RESPECTIVELY
          GO TO (3000,4000,2700) IDEL
C
C END ROUTINE
C
1000 IF(J.EQ.1)THEN
      J1=2
    ELSE
      J1=LENGTH-1
    ENDIF
C FIND OUT IF THE POSSIBLE LOCATION TO WHICH THE BEAD
C MAY MOVE IS OCCUPIED
      DO 1010 K1=1,8
        NO=-1
        DELX(K1)=CORX(J1)+UX(K1)
        IF(DELX(K1).EQ.91)DELX(K1)=1
        IF(DELX(K1).EQ.0) DELX(K1)=90
        DELY(K1)=CORY(J1)+UY(K1)
        IF(DELY(K1).EQ.91)DELY(K1)=1

```

```

        IF(DELX(K1).EQ.0)DELX(K1)=90
        DELZ(K1)=CORZ(J1)+UZ(K1)
        IF(DELZ(K1).EQ.91)DELZ(K1)=1
        IF(DELZ(K1).EQ.0)DELZ(K1)=90
C IF THE POSITION IS OCCUPIED THE PROBABILITY IS ZERO
        IF(HOME(DELX(K1),DELY(K1),DELZ(K1)))THEN
            PR(K1)=0.0
        ELSE
C FIND THE NUMBER OF NEAREST-NEIGHBOR PAIR INTERACTIONS
            DO 1030 K3=1,8
                NXTX(K3)=DELX(K1)+UX(K3)
                IF(NXTX(K3).EQ.91)NXTX(K3)=1
                IF(NXTX(K3).EQ.0)NXTX(K3)=90
                NXTY(K3)=DELY(K1)+UY(K3)
                IF(NXTY(K3).EQ.91)NXTY(K3)=1
                IF(NXTY(K3).EQ.0)NXTY(K3)=90
                NXTZ(K3)=DELZ(K1)+UZ(K3)
                IF(NXTZ(K3).EQ.91)NXTZ(K3)=1
                IF(NXTZ(K3).EQ.0)NXTZ(K3)=90
                IF(HOME(NXTX(K3),NXTY(K3),NXTZ(K3)))NO=NO+1
1030      CONTINUE
            PR(K1)=OP(NO)
        ENDIF
        TOT=TOT+PR(K1)
1010  CONTINUE
        A=A*TOT
        DO 1060 K6=1,8
            SM=SM+PR(K6)
C PICK A LOCATION TO MOVE TO
            IF(SM.GE.A)THEN
                CORX(J)=DELX(K6)
                RCORX(J)=RCORX(J1)+UX(K6)
                CORY(J)=DELY(K6)
                RCORY(J)=RCORY(J1)+UY(K6)
                CORZ(J)=DELZ(K6)
                RCORZ(J)=RCORZ(J1)+UZ(K6)
                GO TO 2700
            ENDIF
1060  CONTINUE
C
C 120 DEGREE ROUTINE
C
4000  DELX(2)=RCORX(J1)-RCORX(J)+CORX(J2)
        IF(DELX(2).EQ.91) DELX(2)=1
        IF(DELX(2).EQ.0) DELX(2)=90
        DELY(2)=RCORY(J1)-RCORY(J)+CORY(J2)
        IF(DELY(2).EQ.91) DELY(2)=1
        IF(DELY(2).EQ.0) DELY(2)=90
        DELZ(2)=RCORZ(J1)-RCORZ(J)+CORZ(J2)
        IF(DELZ(2).EQ.91) DELZ(2)=1
        IF(DELZ(2).EQ.0) DELZ(2)=90
        IF(HOME(DELX(2),DELY(2),DELZ(2)))THEN

```

```

        GO TO 2700
    ELSE
C DEL (1) AND DEL (2) ARE THE BOND VECTOR EXCHANGE
C POSITON AND THE ORIGINAL LOCATION IN THE PERIODIC
C BOX RESPECTIVELY
        DELX(1)=CORX(J)
        DELY(1)=CORY(J)
        DELZ(1)=CORZ(J)
        DO 4020 K2=1,2
            NO=-2
C COUNT NUMBER OF PAIR INTERACTIONS
        DO 4030 K3=1,8
            NXTX(K3)=DELX(K2)+UX(K3)
            IF(NXTX(K3).EQ.91)NXTX(K3)=1
            IF(NXTX(K3).EQ.0)NXTX(K3)=90
            NXTY(K3)=DELY(K2)+UY(K3)
            IF(NXTY(K3).EQ.91)NXTY(K3)=1
            IF(NXTY(K3).EQ.0)NXTY(K3)=90
            NXTZ(K3)=DELZ(K2)+UZ(K3)
            IF(NXTZ(K3).EQ.91)NXTZ(K3)=1
            IF(NXTZ(K3).EQ.0)NXTZ(K3)=90
            IF(HOME(NXTX(K3),NXTY(K3),NXTZ(K3)))NO=NO+1
4030    CONTINUE
        PR(K2)=OP(NO)
4020    CONTINUE
C PICK LOCATION TO MOVE TO
        A=A*(PR(1)+PR(2))
        IF(PR(1).LT.A)THEN
            RCORX(J)=RCORX(J2)+RCORX(J1)-RCORX(J)
            RCORY(J)=RCORY(J2)+RCORY(J1)-RCORY(J)
            RCORZ(J)=RCORZ(J2)+RCORZ(J1)-RCORZ(J)
            CORX(J)=DELX(2)
            CORY(J)=DELY(2)
            CORZ(J)=DELZ(2)
        ENDIF
        GO TO 2700
    ENDIF
C
C 60 DEGREE ROUTINE MOVE (1) IS FOR BOND VECTOR
C EXCHANGE MOTION. SETTING THE
C PROPER COMPONENTS OF MOVE (1) TO ZERO GIVES
C MOVE (2) AND MOVE (3), THE OTHER POSSIBLE MOTIONS
3000 MOVEX(1)=RCORX(J1)+RCORX(J2)-RCORX(J)*2
    MOVEY(1)=RCORY(J1)+RCORY(J2)-RCORY(J)*2
    MOVEZ(1)=RCORZ(J1)+RCORZ(J2)-RCORZ(J)*2
    IF(MOVEX(1).EQ.0)THEN
        MOVEY(2)=0
        MOVEZ(2)=MOVEZ(1)
        MOVEY(3)=MOVEY(1)
        MOVEZ(3)=0
        MOVEX(2)=0
        MOVEX(3)=0
    
```

```

ENDIF
IF(MOVEY(1).EQ.0)THEN
  MOVEZ(2)=0
  MOVEX(2)=MOVEX(1)
  MOVEZ(3)=MOVEZ(1)
  MOVEX(3)=0
  MOVEY(2)=0
  MOVEY(3)=0
ENDIF
IF(MOVEZ(1).EQ.0)THEN
  MOVEX(2)=0
  MOVEY(2)=MOVEY(1)
  MOVEX(3)=MOVEX(1)
  MOVEY(3)=0
  MOVEZ(2)=0
  MOVEZ(3)=0
ENDIF
C CHECK TO SEE IF THE POSSIBLE MOTION IS BLOCKED BY
C EXCLUDED VOLUME
DO 3020 K2=1,3
  DELX(K2)=CORX(J)+MOVEX(K2)
  IF(DELX(K2).GE.91)DELX(K2)=DELX(K2)-90
  IF(DELX(K2).LE.0)DELX(K2)=DELX(K2)+90
  DELY(K2)=CORY(J)+MOVEY(K2)
  IF(DELY(K2).GE.91)DELY(K2)=DELY(K2)-90
  IF(DELY(K2).LE.0)DELY(K2)=DELY(K2)+90
  DELZ(K2)=CORZ(J)+MOVEZ(K2)
  IF(DELZ(K2).GE.91)DELZ(K2)=DELZ(K2)-90
  IF(DELZ(K2).LE.0)DELZ(K2)=DELZ(K2)+90
3020 CONTINUE
C DEL (4) IS THE CURRENT POSITION
DELX(4)=CORX(J)
DELY(4)=CORY(J)
DELZ(4)=CORZ(J)
DO 3040 K4=1,4
  NO=-2
C IF POSITION IS OCCUPIED NO MOTION IS POSSIBLE
C TO THAT POSITION
  IF(HOME(DELX(K4),DELY(K4),DELZ(K4)))THEN
    PR(K4)=0.0
  ELSE
C FIND THE NUMBER OF PAIR INTERACTIONS
    DO 3050 K5=1,8
      NXTX(K5)=DELX(K4)+UX(K5)
      IF(NXTX(K5).EQ.91)NXTX(K5)=1
      IF(NXTX(K5).EQ.0)NXTX(K5)=90
      NXTY(K5)=DELY(K4)+UY(K5)
      IF(NXTY(K5).EQ.91)NXTY(K5)=1
      IF(NXTY(K5).EQ.0)NXTY(K5)=90
      NXTZ(K5)=DELZ(K4)+UZ(K5)
      IF(NXTZ(K5).EQ.91)NXTZ(K5)=1
      IF(NXTZ(K5).EQ.0)NXTZ(K5)=90

```

```

        IF (HOME(NXTX(K5),NXTY(K5),NXTZ(K5))) NO=NO+1
3050  CONTINUE
        PR(K4)=OP(NO)
        TOT=TOT+PR(K4)
        ENDIF
3040  CONTINUE
        A=A*TOT
C PICK A POSITION TO MOVE TO
        DO 3080 K8=1,3
            SM=SM+PR(K8)
            IF (SM.GE.A) THEN
                CORX(J)=DETX(K8)
                RCORX(J)=RCORX(J)+MOVEX(K8)
                CORY(J)=DELY(K8)
                RCORY(J)=RCORY(J)+MOVEY(K8)
                CORZ(J)=DELZ(K8)
                RCORZ(J)=RCORZ(J)+MOVEZ(K8)
                GO TO 2700
            ENDIF
3080  CONTINUE
2700  HOME(CORX(J),CORY(J),CORZ(J))=.TRUE.
C*****
C RECORD COR TO TAPE
C
        I9=I9+1
        IF (I9.EQ.65) THEN
            CALL EXEC(2,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
            DBLOCK=DBLOCK+3
            CALL EXEC(2,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
            DBLOCK=DBLOCK+3
            CALL EXEC(2,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
            DBLOCK=DBLOCK+3
            I9=1
        ENDIF
        DO 2753 I8=1,LENGTH
            TPX(I8,I9)=RCORX(I8)
            TPY(I8,I9)=RCORY(I8)
            TPZ(I8,I9)=RCORZ(I8)
2753  CONTINUE
C SINGLE CHAIN WORKUP
        SUM=SUM+(TPX(1,I9)-TPX(LENGTH,I9))**2
        *      +(TPY(1,I9)-TPY(LENGTH,I9))**2
        *      +(TPZ(1,I9)-TPZ(LENGTH,I9))**2
        X(I1)=TPX(1,I9)-TPX(LENGTH,I9)
        Y(I1)=TPY(1,I9)-TPY(LENGTH,I9)
        Z(I1)=TPZ(1,I9)-TPZ(LENGTH,I9)
2800  CONTINUE
        CALL EXEC(2,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
        DBLOCK=DBLOCK+3
        CALL EXEC(2,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))

```

```

        DBLOCK=DBLOCK+3
        OPTION=1000008
        CALL LURQ(OPTION)
        WRITE(1,10)DBLOCK
10  FORMAT(' NEXT AVAILABLE BLOCK IS ',1110)
C*****
C      RECORD DATA
        R2=SUM/30000.
        RSQ=R2/3.
        JTIME=0
        OPEN(UNIT=8,FILE='BD24')
        WRITE(8,50)LENGTH,NUM,RSQ,POT
C CALCULATE THE AUTOCORRELATION FUNCTION OF THE
C END-TO-END VECTOR
        DO 1301 I2=1,200
            SUM=0
            MAXI=30000-I2
            DO 1401 I3=1,MAXI
                J=I2+I3
                SUM=SUM+X(I3)*X(J)+Y(I3)*Y(J)+Z(I3)*Z(J)
1401  CONTINUE
            TAU=DBLE(SUM)/DBLE(MAXI)/R2
            JTIME=JTIME+4
            WRITE(8,1402)JTIME,TAU
1402  FORMAT(' TIME=',F7.3,5X,'TAU=',PE13.6)
1301  CONTINUE
        CLOSE(8)
C*****
C WRITE THE COORDINATES TO TAPE
C
125  OPEN(UNIT=6,FILE='BODY241')
        REWIND(6)
        WRITE(6,50)LENGTH,NUM,RSQ,POT,ITIME(1)
        WRITE(6,129)(CORX(J),RCORX(J),CORY(J),RCORY(J),
*      CORZ(J),RCORZ(J),J=1,LENGTH)
        WRITE(6,50)LENGTH,NUM,RSQ,POT,ITIME(1)
        CLOSE(6)
129  FORMAT(20I4)
        CALL FMPRUNPROGRAM(STRING,0,0,0,0,0,NAME)
        STOP
        END
C
C ARAN SEEDS THE RANDOM NUMBER GENERATOR THROUGH THE
C SUBROUTINE INIT. ARAN USES THE HP CLOCK AS A SEED.
        FUNCTION ARAN(I)
            SAVE
            REAL*8 IRAND,MULT,LARGE
            INTEGER ITIME(5)
            DATA IRAND/14532.,MULT/65539./
            DATA LARGE/2147483648./
            IF(I.EQ.0)GOTO 1
            CALL EXEC(11,ITIME)

```

```

      IRAND=IRAND*DBLE(ITIME(1)+ITIME(2)+ITIME(3)
      *      +ITIME(4))
      WRITE(1,393)IRAND
393    FORMAT(F10.2)
      GOTO 2
C
1      IRAND=IRAND*MULT
2      IRAND=DMOD(IRAND,LARGE)+1
      ARAN=(IRAND)/(LARGE+1)
      K=ARAN*30000
      ARAN=FLOAT(K)/30000.
      IF(ARAN.GE.1)ARAN=.999999
      IF(ARAN.LE.0)ARAN=.000001
      RETURN
      END

```

```

C THIS IS THE SHIFT RANDOM NUMBER GENERATOR
      FUNCTION R250(IPOINT)
      INTEGER*4 IRND(5000),MASK,I
      DIMENSION RND(5000)
      EQUIVALENCE (IRND(1),RND(1))
      COMMON IRND
      DATA MASK/1073742082/
      IPOINT=IPOINT+1
      IF(IPOINT.GT.5000)CALL REINT(IPOINT)
      I=IEOR(IRND(IPOINT-250),IRND(IPOINT-103))
      IRND(IPOINT)=IOR(I,MASK)
      R250=RND(IPOINT)-1.0
      RETURN
      END

```

```

C REINT REINITIALIZES R250
      SUBROUTINE REINT(IPOINT)
      INTEGER*4 IRND(5000),IRND2(250)
      EQUIVALENCE (IRND(4751),IRND2(1))
      COMMON IRND
      DO 1 I=1,250
        IRND(I)=IRND2(I)
1      CONTINUE
      IPOINT=251
      RETURN
      END

```

```

C INITIALIZES R250
      SUBROUTINE INIT(IPOINT)
      DIMENSION RND(5000)
      INTEGER*4 IRND(5000),MASK
      EQUIVALENCE (RND(1),IRND(1))
      COMMON RND
      DATA MASK/1073741568/
      A=ARAN(1)
      DO 1 I=1,250

```

```
      RND(I)=ARAN(0)  
      IRND(I)=IAND(IRND(I),MASK)  
1     CONTINUE  
      IPOINT=250  
      RETURN  
      END
```

APPENDIX VI

FORTRAN CODE FOR THE CALCULATION OF NORMAL MODES

This code reads in the sampled coordinates from the tape using the arrays TPX, TPY, and TPZ. The details of the arrays function is the same as was described on page 163, but now the arrays will be used to read from the tape instead of to write to the tape. The sampled coordinates are Cartesian. This program converts them to normal coordinates and then calculates the autocorrelation functions of the first three normal modes.

```

$FILES 1,3
$CDS ON
C THIS PROGRAM CALCULATES THE NORMAL COORDINATES FROM
C CARTESIAN COORDINATES AND THEN CALCULATES AND PRINTS OUT
C THE AUTOCORRELATION FUNCTIONS OF THE FIRST 3 MODES.
C UK 1, UK 2, AND UK 3 ARE THE FIRST THREE
C NORMAL COORDINATES, TP (24,64) IS THE BUFFER ARRAY
C THAT READS IN THE CARTESIAN COORDINATES FROM THE TAPE
PROGRAM N24
EMA UKX1,UKY1,UKZ1,UKX2,UKY2,UKZ2,UKX3,UKY3,UKZ3
REAL UKX1(30000),UKY1(30000),UKZ1(30000),RN1(24)
REAL UKX2(30000),UKY2(30000),UKZ2(30000),RN2(24)
REAL UKX3(30000),UKY3(30000),UKZ3(30000),RN3(24)
INTEGER TPX(24,64),TPY(24,64),TPZ(24,64)
INTEGER BLOCK(2),BUFLEN,NAME(3)
INTEGER*4 DBLOCK
EQUIVALENCE (BLOCK(1),DBLOCK)
LU=24
OPTION=000001B
CALL LURQ(OPTION,LU)
PI=3.1416
I9=64
AUTO1=0.0
AUTO2=0.0
AUTO3=0.0
BUFLEN=1536
DBLOCK=0
DO 35 K=1,24
RN1(K)=COS((K-.5)*PI/24)
RN2(K)=COS((K-.5)*PI*2/24)
RN3(K)=COS((K-.5)*PI*3/24)
35 CONTINUE
C THIS LOOP READS IN THE CARTESIAN COORDINATES AND
C CONVERTS THEM TO FIND THE FIRST THREE NORMAL COORDINATES
DO 10 I=1,30000
I9=I9+1
IF (I9.EQ.65) THEN
CALL EXEC(1,24+100B,TPX,BUFLEN,BLOCK(1),BLOCK(2))
BLOCK(2)=BLOCK(2)+3
CALL EXEC(1,24+100B,TPY,BUFLEN,BLOCK(1),BLOCK(2))
BLOCK(2)=BLOCK(2)+3
CALL EXEC(1,24+100B,TPZ,BUFLEN,BLOCK(1),BLOCK(2))
BLOCK(2)=BLOCK(2)+3
I9=1
ENDIF
SUMX1=0
SUMY1=0
SUMZ1=0
SUMX2=0
SUMY2=0
SUMZ2=0
SUMX3=0
SUMY3=0

```

```

SUMZ3=0
DO 20 I8=1,24
  X1=RN1(I8)*TPX(I8,I9)
  Y1=RN1(I8)*TPY(I8,I9)
  Z1=RN1(I8)*TPZ(I8,I9)
  X2=RN2(I8)*TPX(I8,I9)
  Y2=RN2(I8)*TPY(I8,I9)
  Z2=RN2(I8)*TPZ(I8,I9)
  X3=RN3(I8)*TPX(I8,I9)
  Y3=RN3(I8)*TPY(I8,I9)
  Z3=RN3(I8)*TPZ(I8,I9)
  SUMX1=SUMX1+X1
  SUMY1=SUMY1+Y1
  SUMZ1=SUMZ1+Z1
  SUMX2=SUMX2+X2
  SUMY2=SUMY2+Y2
  SUMZ2=SUMZ2+Z2
  SUMX3=SUMX3+X3
  SUMY3=SUMY3+Y3
  SUMZ3=SUMZ3+Z3
20 CONTINUE
UKX1(I)=.2886751*SUMX1
UKY1(I)=.2886751*SUMY1
UKZ1(I)=.2886751*SUMZ1
UKX2(I)=.2886751*SUMX2
UKY2(I)=.2886751*SUMY2
UKZ2(I)=.2886751*SUMZ2
UKX3(I)=.2886751*SUMX3
UKY3(I)=.2886751*SUMY3
UKZ3(I)=.2886751*SUMZ3
TMX1=UKX1(I)
TMY1=UKY1(I)
TMZ1=UKZ1(I)
TMX2=UKX2(I)
TMY2=UKY2(I)
TMZ2=UKZ2(I)
TMX3=UKX3(I)
TMY3=UKY3(I)
TMZ3=UKZ3(I)
C AVE IS THE DENOMINATOR OF THE FORMULA FOR THE
C AUTOCORRELATION FUNCTIONS.
C THE NUMBER AT THE END GIVES THE RESPECTIVE FUNCTION
C TWO NUMBERS ARE FOR CROSS-CORRELATIONS
  AUTO1=AUTO1+TMX1**2+TMY1**2+TMZ1**2
  AUTO2=AUTO2+TMX2**2+TMY2**2+TMZ2**2
  AUTO3=AUTO3+TMX3**2+TMY3**2+TMZ3**2
  AUTO12=AUTO12+TMX1*TMX2+TMY1*TMY2+TMZ1*TMZ2
  AUTO23=AUTO23+TMX2*TMX3+TMY2*TMY3+TMZ2*TMZ3
10 CONTINUE
OPTION=100000B
CALL LURQ(OPTION)

```

```

      AVE1=AUTO1/30000.0
      AVE2=AUTO2/30000.0
      AVE3=AUTO3/30000.0
C AVE12 AND AVE23 GIVE THE ZERO TIME AVERAGE OF THE
C CROSS-CORRELATIONS
      AVE12=AUTO12/30000.0
      AVE23=AUTO23/30000.0
      OPEN(UNIT=6,FILE='U241')
      OPEN(UNIT=7,FILE='U242')
      OPEN(UNIT=8,FILE='U243')
      WRITE(6,50)AVE1,AVE12,AVE23
      WRITE(7,50)AVE2
      WRITE(8,50)AVE3
50  FORMAT(1X,1PE13.6,1X,1PE13.6,1X,1PE13.6)
      I5=0
C THIS LOOP CALCULATES THE AUTOCORRELATION FUNCTIONS
DO 30 I1=1,200
      I2=30000-I1
      R1=0
      R2=0
      R3=0
      I5=I5+4
      DO 40 I3=1,I2
        J=I3+I1
        R1=R1+UKX1(I3)*UKX1(J)+UKY1(I3)*UKY1(J)
        *      +UKZ1(I3)*UKZ1(J)
        R2=R2+UKX2(I3)*UKX2(J)+UKY2(I3)*UKY2(J)
        *      +UKZ2(I3)*UKZ2(J)
        R3=R3+UKX3(I3)*UKX3(J)+UKY3(I3)*UKY3(J)
        *      +UKZ3(I3)*UKZ3(J)
40  CONTINUE
      AUT1=R1/(AVE1*I2)
      AUT2=R2/(AVE2*I2)
      AUT3=R3/(AVE3*I2)
      WRITE(6,60) I5,AUT1
      WRITE(7,60) I5,AUT2
      WRITE(8,60) I5,AUT3
60  FORMAT(' TIME=',F7.2,5X,'AUT=',PE13.6)
30  CONTINUE
      CLOSE(6)
      CLOSE(7)
      CLOSE(8)
      CALL FMPRUNPROGRAM(STRING,0,0,0,0,0,NAME)
      STOP
      END

```

VITA

James Patton Downey was born in Huntsville, Al. on October 4, 1960. He graduated Huntsville High School in May 1979. He attended the University of Alabama in Huntsville from August 1979 to August 1984, graduating with a BS in Chemistry, Physics, and Mathematics. In September 1984, he enrolled in the University of Tennessee in Knoxville, and began work on a PhD in Chemistry with a specialization in chemical physics.