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Computer simulation of polymer dynamics

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COMPUTER SIMULATION OF
POLYMER DYNAMICS

A thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
Of the requirements for the degree of
Master of Arts

by
Rebecca L. Smithson
1980
APPROVAL SHEET

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the requirements for the degree of

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ABSTRACT

The concentration dependence of the equilibrium and dynamic properties of random coil polymer chains was studied using Monte Carlo simulations. Chains of 10, 20, and 30 beads were studied at densities ranging from 0.04 to 0.80. Simulations were performed using two types of bead motions. The equilibrium properties sampled were the second and fourth moments of the end-to-end length and the diffusion constant. Relaxation behavior of the chains was studied by sampling the autocorrelation functions of end-to-end length and square end-to-end length.

The effect of concentration on the equilibrium properties agrees with previous studies and theoretical predictions. The faster relaxation modes of the chain appear to be less affected by concentration than the slower modes. The critical density, at which the onset of entangled behavior begins, was found to decrease with increasing concentration. The dependence of relaxation on polymer volume fraction agrees with the free volume theories.
COMPUTER SIMULATION
OF POLYMER DYNAMICS
CHAPTER 1

The Rouse Model

The Rouse Model has been used successfully to describe linear viscoelastic properties of random coil polymer chains in dilute solution. The polymer chain is pictured as being composed of a number of submolecules. Each submolecule is a part of the polymer chain which must be of sufficient length to approximate a gaussian distribution for the separation of end-to-end length. Hydrodynamic interactions, which are the effects of one segment on other segments caused by its motion through the viscous medium, are not included in this model. Excluded volume effects, or the obstruction of a segment by any other segments are also not included. As a result, the Rouse Model is valid only in solutions where these effects are small.
Model of the Polymer Chain

Each polymer molecule is divided up into $N$ identical submolecules. The probability that the end of one of these submolecules is located in the region $x$ to $x+dx$, $y$ to $y+dy$, and $z$ to $z+dz$ given that the other end of the molecule is fixed at the origin of this coordinate system is

$$\Psi(x,y,z)dx dy dz = \left(\frac{\beta}{\sqrt{\pi}}\right)^{3/2} \exp(-\beta(x+y+z))dx dy dz. \quad (1.1)$$

The constant $\beta$ is given by $(3/2l^2)$ where $l^2$ is the average square length of the submolecules. The number of configurations available to the chain is proportional to $\Psi(x,y,z)dx dy dz$. The relative number of configurations thus depends only on $x+y+z = r$ and is given by

$$\exp(-\beta r^2). \quad (1.2)$$

This model is equivalent to one of $N$ beads connected by $N-1$ Hookean springs. Treloar$^2$ shows this by calculating the amount of work required to move an end of the submolecule from $r$ to $r+dr$. For reversible processes it is known from thermodynamics that at constant temperature and volume

$$dE = TdS + dW \quad \text{and} \quad dA = dE - TdS.$$  

Combining these two equations gives $dA = dW$.

The Helmholtz free energy, $A$, may be found by the equation $A = E - TS$, where $E$ is the internal energy of the polymer. Therefore, at constant volume and temperature

$$\frac{dW}{dr} = \left(\frac{dE}{dr}\right) - TS/\sqrt{r}. \quad (1.3)$$

By considering a freely jointed chain, or one that is
subjected to no internal energy barriers, \( \frac{dE}{dr} = 0 \), since the internal energy will be the same for all configurations. With this, equation 1.2 becomes

\[
dW/dr = -T\left(\frac{S}{dr}\right)_{T,V}
\]

The entropy, \( S \), may be found by Boltzmann's equation, \( S = k \ln \Omega \), where \( k \) is the Boltzmann constant and \( \Omega \) is the number of possible configurations. Using equation 1.2, together with the Boltzmann equation gives

\[
S = c - k \beta r^2 \quad \text{(1.5)}
\]

The constant \( c \) includes the size of the volume element \( dx dy dz \) and is used to indicate that only differences in entropy are of interest, but not absolute values of entropy.

Substituting equation 1.5 into 1.4 gives \( dW = 2kT \, rdr \). Because work had to be done to move the end of the subchain from \( r \) to \( r + dr \), there is a restoring force acting on the chain such that \( dW = fdr = 2kT \beta rdr \), or \( f = 2kT \beta r \). The tension is proportional to the length, each submolecule may be thought of as a Hookean spring of equilibrium length zero and spring constant \( 2kT = 3kT/1^2 \) since \( \beta = (3/2)1^2 \).

In all forthcoming discussion, polymer molecules will be thought of as consisting of \( N \) beads connected by \( N-1 \) Hookean springs with these properties.

The \( 3N \) coordinates of the system will be obtained by assigning a Cartesian Coordinate system to each bead. The coordinate system assigned to the \( j \)th bead is \((x_j, y_j, z_j)\) where \( x_j \) is the displacement in the \( x \)
direction of the jth bead from its equilibrium position. The coordinates y and z describe similar displacements in the y and z directions.

**Motion of the Polymer Molecule.**

The equations of motion for the polymer molecules will be set up in a manner analogous to the method used by Zimm\(^3\), but without his inclusion of hydrodynamic interactions. The general equation used to describe the forces acting on the jth bead of the polymer chain upon application of an external force is the Langevin equation\(^4\),

\[
m \left( \frac{dv_{xj}}{dt} \right) = -\rho v_{xj} + x + A(t).
\]

(1.6)

Similar equations may be written for the y and z dimensions.

The right hand side of the Langevin equation is the sum of the forces acting on the beads. These are

1. A frictional force, \(\rho v_{xj}\), with friction constant \(\rho\) caused by motion of the bead through the solvent. The velocity of the solvent in the x-direction at the jth bead is \(v_{xj}\).

2. The term \(X\) represents the external, systematic forces exerted on bead j by the springs. The force exerted on bead j by the (j-1)st spring is \(-3kt/l^2 \left(x_j - x_{j-1}\right)\). The force exerted on this bead by the jth spring is \(-3kt/l^2 \left(x_j - x_{j+1}\right)\). The total force from the springs on the jth bead is
Because beads 1 and N are only affected by springs 1 and N - 1 the force on these beads is

\[-(3kt/l^2)(x_{i} - x_{j}) \text{ for } j = 0 \quad (1.7b)\]

and

\[-(3kt/l^2)(x_{N} - x_{N-1}) \text{ for } j = N \quad (1.7c)\]

(3) The force given by \( A(t) \) in the Langevin equation is a fluctuating force resulting from the Brownian motion of the solvent. This brownian motion causes the beads to diffuse from regions of high concentration to regions of low concentration. The driving force behind this movement may be written as the change in the Helmholtz free energy, \( \frac{\partial H}{\partial x_i} \). Expanding this gives

\( A(t) = \frac{\partial A}{\partial x} = \frac{\partial}{\partial x_i}(E - TS) = T(\frac{\partial S}{\partial x_i}). \)

The entropy may be written according to Boltzmann's relations, \( S = k \ln \Psi \) with \( k \) being Boltzmann's constant. The unknown function \( \Psi \) is a function of the coordinates \( x_1, x_2, \ldots, x_N \). It is to be interpreted as the probability of finding each bead with coordinates between \( x_i \) to \( x_i + dx_i \), \( y_i \) to \( y_i + dy_i \) and \( z_i \) to \( z_i + dz_i \), so is proportional to the number of possible configurations of the system. This leads to

\[ A(t) = -kT \frac{\partial S}{\partial x_i} \] (1.8)

The quantity \( \beta \) is a very high frequency on the order of \( 10^{13} \) sec\(^{-1}\). Since only the low frequency response of the chain is of interest and \( m (dv_{xj}/dt) << \int v_{xj} \) the left hand side of equation (1.6) may be set to zero.
Substituting equations (1.7) and (1.8) into equation (1.6) gives

\[
\dot{x}_i = \nabla x_i - D \frac{\partial \Psi}{\partial x_i} - \sigma (x_i - x_{i+1}),
\]

\[
\dot{x}_j = \nabla x_j - D \frac{\partial \Psi}{\partial x_j} - \sigma (-x_{j-1} + \partial x_j - x_{j+1}) \quad \text{for}\quad 1 \leq j \leq N,
\]

\[
\dot{x}_\nu = \nabla x_\nu - D \frac{\partial \Psi}{\partial x_\nu} - \sigma (x_\nu - x_{\nu-1}),
\]

where \( D = kT/\rho \) and \( \sigma = 3kT/l^2\rho \).

These equations may be written more compactly in matrix form

\[
\frac{\partial x}{\partial t} = \dot{x} - D \left( \frac{\partial}{\partial x} \right) \nabla \Psi - \sigma A \dot{x}. \tag{1.9}
\]

In this equation

\[
\dot{x} = \begin{pmatrix}
\dot{x}_1 \\
\dot{x}_2 \\
\vdots \\
\dot{x}_N
\end{pmatrix} \quad \nabla x = \begin{pmatrix}
\nabla x_1 \\
\nabla x_2 \\
\vdots \\
\nabla x_N
\end{pmatrix} \quad \left( \frac{\partial}{\partial x} \right) = \begin{pmatrix}
\partial/\partial x_1 \\
\partial/\partial x_2 \\
\vdots \\
\partial/\partial x_N
\end{pmatrix}
\]

and

\[
A = \begin{pmatrix}
-1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
-1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\
0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\
0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & -1 & 2 & 1 \\
0 & 0 & 0 & 0 & \cdots & -1 & 2 & 1 \\
0 & 0 & 0 & 0 & \cdots & 0 & -1 & 1
\end{pmatrix}
\]

Equations for the \( y \) and \( z \) dimensions may be written in a similar way.
These equations may now be written in terms of $\psi$ by use of the equation of continuity,

$$\frac{\partial \psi}{\partial t} = -\nabla \cdot \psi \left[ (\frac{\partial x}{\partial t}) + (\frac{\partial y}{\partial t}) + (\frac{\partial z}{\partial t}) \right]$$

with the divergence operator given by

$$\nabla \cdot \psi = \left( \frac{\partial \psi}{\partial x} \right)^T + \left( \frac{\partial \psi}{\partial y} \right)^T + \left( \frac{\partial \psi}{\partial z} \right)^T.$$

The superscript $T$ is used to indicate the transpose of a vector or matrix. This equation is a statement of the conservation of mass, that the rate at which beads enter some volume element must be equal to the rate at which they leave. Substitution into the equation of continuity for $\frac{\partial x}{\partial t}$, $\frac{\partial y}{\partial t}$, and $\frac{\partial z}{\partial t}$ as given by equation 1.9 yields

$$\frac{\partial \psi}{\partial t} = \sum_{q=1}^{\infty} \left[ -\left( \frac{\partial \psi}{\partial q} \right)^T \cdot \psi q - \psi (\frac{\partial \psi}{\partial q})^T \cdot \psi q + \delta (\frac{\partial \psi}{\partial q})^T \cdot (\frac{\partial \psi}{\partial q}) \right]$$

$$+ \sigma \left( \frac{\partial \psi}{\partial q} \right)^T \cdot A \cdot \psi q + \sigma \cdot \psi (\frac{\partial \psi}{\partial q})^T \cdot A \cdot \psi q. \quad (1.10)$$

Transformation to Normal Coordinates

Solution of equation 1.10 is simplified by a transformation to normal coordinates. These new coordinates are defined by the equations

$$\tilde{u} = R^{-1} \cdot x, \quad (1.11a)$$

$$\tilde{v} = R^{-1} \cdot y, \quad \text{and} \quad (1.11b)$$

$$\tilde{w} = R^{-1} \cdot z. \quad (1.11c)$$
The matrix $R$ in these equations is the orthogonal matrix which diagonalizes the $A$ matrix, or

$$R^{-1}AR = \Lambda = (\lambda_{\rho} \delta_{\rho \bar{\gamma}}).$$  \hfill (1.12)

The $p$th eigenvalue of $A$ is given by $\lambda_{\rho}$ and $\delta_{\rho \bar{\gamma}}$ is the Kronecker delta.

The rules for transformation of partial derivatives are found by use of the chain rule:

$$\frac{\partial \psi_j}{\partial x_j} = \frac{\partial \psi_j}{\partial x_k} \frac{\partial x_k}{\partial x_j} = \sum_k \sum_i [\frac{\partial x_k}{\partial x_j} (R_{ki}^{-1} x_i)] \frac{\partial \psi_k}{\partial x_k}$$

$$= \sum_k \sum_i [R_{ki}^{-1} x_i \frac{\partial \psi_k}{\partial \psi_k}]$$

$$= \sum_k R_{jk} \frac{\partial \psi_k}{\partial \psi_k}.$$  \hfill (1.13)

In matrix notation this becomes

$$\left( \frac{\partial \psi_j}{\partial x_j} \right) = R \left( \frac{\partial \psi_k}{\partial x_k} \right).$$  \hfill (1.14)

It may be shown in a similar manner that

$$\left( \frac{\partial \psi_j}{\partial \psi_k} \right) = R^{-1} \left( \frac{\partial \psi_j}{\partial x_j} \right).$$  \hfill (1.15)

The transformation of partial derivatives in the $y$ and $z$ dimensions are of the same form.

Before it is possible to transform the first term of equation 1.10 to normal coordinates, it is necessary to know more about the velocities $\mathbf{v}_q$. Application of a shearing
stress to the solution in the x y plane causes the velocity of the solvent to be non zero only in the x direction, as shown in Figure 1.1. Therefore,

\[ \nabla_{xj} = \alpha 2 \hat{z}, \quad \nabla_{yj} = \nabla_{zj} = 0. \]  

(1.15a)

The shear rate \( \alpha \) is

\[ \alpha = \alpha_0 \exp(i \omega t). \]  

(1.15b)

![Figure 1.1. Velocity gradient caused by a shearing motion in the x-y plane.](image)

The velocity gradient is assumed to be constant over the dimensions of a molecule. This assumption will be good except for solvents of low viscosities at high frequencies.

The first two terms of equation 1.10 now become

\[-(\partial \psi / \partial x)^T \cdot \nabla_x \psi - \psi (\partial / \partial x)^T \cdot \nabla_x = -\alpha (\partial \psi / \partial x)^T \cdot \nabla \hat{z}.

This may be written in terms of the coordinates \( u,v,w \) by multiplying by \( R^{-1} R = E \), where \( E \) is the unit matrix as follows:

\[-\alpha (\partial \psi / \partial x)^T \cdot \nabla = -\alpha (\nabla)^T \cdot (\partial \psi / \partial x) = -\alpha \nabla^T \cdot R \cdot (\partial \psi / \partial \psi). \]
Taking the transpose of both sides of equation 1.11c gives

\[(y^T) = (K^{-1} z^T)^T = z^T K^{-T} \]

Because R is an orthogonal matrix, \(R^T = R^{-1}\) giving

\[(y)^T = z^T \cdot R, \tag{1.16}\]

with similar equations for \((u)^T\) and \((v)^T\). Using equation 1.13 gives the first term as

\[-\alpha y^T \cdot (\partial \psi/\partial y) = -\alpha \sum_i w_i \partial \psi/\partial u_i. \tag{1.17}\]

The third term of equation 1.10, the Brownian motion term, may be transformed as follows:

\[\sigma \sum_i \partial \psi/\partial u_i^2 \tag{1.18}\]

Transformation of the spring terms is similar:

\[\sigma \left[ (\partial \psi/\partial x)^T \cdot A \cdot x + \psi (\partial /\partial x)^T \cdot A \cdot x \right] \]

\[= \sigma \left[ (\partial \psi/\partial x)^T \cdot R R^{-1} \cdot A \cdot R R^{-1} \cdot x + \psi (\partial /\partial x)^T \cdot R R^{-1} \cdot A \cdot R R^{-1} \cdot x \right] \]

\[= \sigma \left[ (\partial \psi/\partial y)^T \cdot \lambda_k \cdot y + \psi (\partial /\partial y)^T \lambda_k \cdot y \right] \]

\[= \sigma \left[ (\partial \psi/\partial y)^T \cdot \lambda_k \cdot y + \sigma \lambda_k \psi \right] \]

\[= \sum_i \sigma \lambda_i \left[ u_i \cdot \partial \psi/\partial u_i^2 + \psi \right]. \]
Combination of equations 1.17, 1.18, 1.19 and their counterparts for the y and z dimensions gives the diffusion equation for the polymer in the coordinates \( \tilde{u}, \tilde{v}, \) and \( \tilde{w}, \) as

\[
\frac{\partial \psi}{\partial t} = \frac{\tilde{D}}{\tilde{c}} \left\{ \sum k \left( \frac{\psi}{\partial \tilde{v}} \right)^2 + \sum \frac{\partial^2 \psi}{\partial q^2} + \lambda_k \left[ \frac{\partial \psi}{\partial q} \right] \right\}. \tag{1.20}
\]

Solution of the Differential Equation

Equation 1.20 is easily solved when no shearing motion is involved. In this case, the first term is zero, and the unnormalized solution, \( \Psi_0 \) is

\[
\Psi_0 = \exp \left( -\frac{\sigma}{\partial t} \right) \left\{ \sum_k (\nu_k^2 + \nu_k^2 + \omega_k^2) \right\}. \tag{1.21}
\]

Differentiating gives

\[
\frac{\partial \Psi_0}{\partial t} = \left( -\frac{\sigma}{\partial t} \right) \Psi_0 \quad \text{if} \quad q = \tilde{u}, \tilde{v}, \tilde{w}. \tag{1.22}
\]

The solution of 1.20 may be written as a power series in \( \sigma \)

\[
\psi = \Psi_0 \sum \psi_n \sigma^n, \tag{1.23}
\]

\( \psi_0 = 1 \) and \( \psi \) given by equation 1.15b. Substituting 1.19 into 1.16 and equating the coefficients of \( \lambda_n \) gives the recursion equations for \( \psi_n \)

\[
\frac{\partial \psi_n}{\partial t} = \sum_k \left[ (\lambda/d) \nu_k \psi_{n-1} - \nu_k \psi_{n-1} / \nu_k \right] \sum_{q=uvw} \left( \frac{\partial^2 \psi_n}{\partial q^2} - \lambda_k \frac{\partial \psi_n}{\partial q} \right) \frac{\partial q_k}{\partial q_k}. \tag{1.24}
\]

Solving this equation for \( \psi_n \) will then permit use of
equation 1.25 as a recursion relation from which \( \psi_2, \psi_3, \psi_4, \ldots \) may be found.

The equation for \( \psi_i \) is

\[
i \omega \psi = \sum_{k=1}^{\infty} \left\{ \sigma / \omega \right\}_{\sigma} \psi_k \omega_k + \sum_{k} \gamma \psi_k \omega_k \times \left( \partial^2 \psi / \partial q_k^2 - \sigma \lambda_k \psi_k \partial \psi / \partial q_k \right).
\]

A solution for \( \psi_i \) is given by

\[
\psi_i = \sum_{k=1}^{\infty} C_k \nu_k \omega_k,
\]

with

\[
C_k = \left( \frac{1}{2 \sigma} \right) \left( 1 + (i \omega / \sigma) \right).
\]

For small \( \sigma \), only this first term will be of importance and the relaxation times for the normal modes of vibration of the polymer are then given by

\[
\gamma_k = \frac{1}{2 \sigma \lambda_k} = \frac{1}{2 \sigma \lambda_k / k \pi k}.
\]

The \( \lambda_k \) are the eigenvalues of the \( A \) matrix. These are shown in Appendix A to be

\[
\lambda_k = 4 \sin^2 (\phi k / 2N) \quad \text{for } k = 0, 1, \ldots, N-1.
\]

Each of the normal coordinates represents a mode of motion of the polymer chain. These modes are independent of one another, so that superposition or combination of them gives vibrations that are not normal vibrations. All possible vibrations of the molecule can be represented by combinations of the normal vibrations.

Different types of experiments will excite certain modes of motion. For example, mechanical measurements will
predominantly excite the lower modes of motion, whereas dielectric type experiments will excite higher frequencies $^{10}$. 
CHAPTER 2

Monte Carlo Studies of Random Coil Polymer Chains.

A second approach used in investigating both the equilibrium and dynamic properties of polymers is the computer simulation of lattice model polymer chains based on Monte Carlo techniques. This approach makes it possible to study the effects of excluded volume conflicts which are not easily treated analytically.

The Model

A polymer chain is represented in this model as a series of points or beads on a cubic lattice. Each bead lies on one of the cube's vertices and they are connected along the cube sides. Each connection, called a bond, is of unit length. The initial chain configurations are generated randomly. Movement of the chain due to Brownian motion is
then simulated by picking either a bead or a bond at random and moving it according to the rules to be given later. Each movement of a bead or a bond is called a bead cycle. Without excluded volume more than one bead may occupy a lattice site at a given time. The excluded volume condition is realized by allowing only one bead per lattice site at any one time.

The beads of a chain are indexed from 1 to N. Let \( \mathbf{r}_j \) be the vector pointing from bead \( j \) to bead \( j + 1 \). The movement of a bead that is not an endbead is accomplished by an interchange of vectors. This interchange for bead \( j \) is

\[
\mathbf{r}_j' = \mathbf{r}_{j-1} \quad \text{and} \quad \mathbf{r}_{j-1}' = \mathbf{r}_j \quad \text{for } 2 \leq j \leq N-1, \tag{2.1}
\]

where the prime denotes the vector after the move. This type of vector exchange, which involves the movement of only one bead is pictured in Figure 2.1. It is called a single bead movement. The endbeads, numbered 1 and N are moved by replacing \( \mathbf{r}_1 \) and \( \mathbf{r}_{N-1} \) by a vector chosen at random from one of the six vectors originating at beads 2 or N-1, respectively.

The second type of bead movement, pictured in Figure 2.2, is called a crankshaft bead movement. It results in the movement of two beads instead of just one. The bond connecting bead \( j \) and bead \( j + 1 \) is moved by the following
Figure 2.1

The possible Single Bead Moves for Midbeads in the Presence of Excluded Volume.

a) no move possible if the angle between beads is 180°.

b) move across the diagonal if angle is 90° between beads.
Figure 2.2
The Possible Crankshaft bead moves for midbonds in the Presence of Excluded Volume.
rules:
\[ \mathcal{F}_{j-1} = \mathcal{F}_{j+1}, \]
\[ \mathcal{F}_j = \mathcal{F}_i, \]
\[ \mathcal{F}_{j+1} = \mathcal{F}_{i-j} \quad \text{for } 1 \leq j \leq N-1. \quad (2.2) \]

The subscripts 0, 1, N and N - 1 label vectors that are chosen at random from the six possible vectors.

The time interval, in bead cycles, over which the dynamics of the chains are observed is called a frame. Each frame is further divided into samples. The number of bead cycles in each sample varies, and is controlled by input to the program.

At the start of each frame the initial end-to-end length, \( l_0 \), of each chain is calculated, as well as \( l^2 \) and the position of the center of mass. For each subsequent sample, \( l_t, l^2_t, l^4_t \), and the position of the center of mass are again sampled. The products \( l_0 \cdot l_t \) and \( l_0 \cdot l^2_t \) are calculated. This procedure is repeated for some number of frames that is defined by input to the program. This group of frames is called a run.

The products \( l_0 \cdot l_t \) and \( l_0 \cdot l^2_t \) are summed over all the frames for each time, \( t \). The values of \( l, l^2, l^4 \) and the change in the position of the center of mass from the proceeding sample, \( d \), are added into running sums at the end of each sample. At the end of a run the sums are averaged to the quantities
From this the correlation functions for each chain as a function of time may be computed as:

\[ p(1,1,t) = \frac{\langle 1_o \cdot 1_e \rangle}{\langle 1^2 \rangle}, \]

\[ p(1^2,1^2,t) = \frac{\langle 1^2 \cdot 1^2 \rangle - \langle 1^2 \rangle^2}{\langle 1^4 \rangle - \langle 1^2 \rangle^2}. \quad (2.3) \]

This procedure is repeated for a number of runs, again defined by input. The final configurations of each run are used as the initial configuration of the next. Final averages are obtained over all runs for each chain, and then over all the chains. The standard deviation of the final averages is used as a measure of the uncertainty in the results.

It is evident that this model emphasizes the chain connectivity properties of a real polymer chain. It is not possible to look at effects due to short range forces within the polymer. Its utility comes, however, in looking at the long range, longtime cooperative motions of the chain.
CHAPTER 3

Comparison of Monte Carlo Techniques with the Rouse Model

model polymer chains without excluded volume have shown
remarkable agreement with the Rouse statistical bead
model\textsuperscript{12,13}. In particular, a lattice model chain of \( N \) beads
behave very much like a Rouse chain of \( N \) statistical
segments. Theoretical explanations for this have been given
by various authors\textsuperscript{14,15,16}. The method used by Verdier\textsuperscript{16} will
be used here to show the similarities in the relaxation
times and correlation functions for the two models.
Although only single bead moves are considered here, this
method may be extended to include either pure crankshaft or
a mixture of crankshaft and single moves\textsuperscript{17}.

The Relaxation Times

For single bead moves there are two types of bond
exchanges which result in bead moves. The first is given by
equation 2.1 which is a simple exchange of vectors. The second is one in which an end bond is lost and replaced by one created at random. Calculation of the relaxation of quantities linear in the bond vectors may be accomplished by finding the expectation \( \langle \sigma_j(t) \rangle \). This is just the expectation that the ith vector in the initial set of vectors \( \{ \sigma, \sigma \sigma, \cdots, \sigma_n \} \) will migrate in \( t \) moves to the jth position. The angular brackets are used to denote the average over all possible motions of the chain for \( t \) steps. Any vector that is absorbed by being replaced at the end, or any vector created at the end will not contribute to this expectation. It can be written then as

\[
\langle \sigma_j(t) \rangle = \sum_{i=1}^{n-1} \sigma(i) \rho_{ij}^{(t)}
\]

(3.1)
The \( \rho_{ij}^{(t)} \) are the probabilities of a vector moving from position \( i \) to position \( j \) in \( t \) bead cycles.

Calculation of the \( \rho_{ij}^{(t)} \) for this case is very similar to that of the \( t \)-step transition probabilities for a random walk on a line with two absorbing barriers. These \( t \)-step probabilities may be calculated with only the knowledge of the one step transition probabilities, \( \rho_{ij}^{(1)} = \rho_{ij} \).

The probability that an interior bond will move one step to the right or one step to the left is given by \( \rho_{j,j+1} = 1/N \) or \( \rho_{j,j-1} = 1/N \). The probability that the bond will not move is \( \rho_{ij} = (N-2)/N \). The matrix of these transition probabilities then looks like
Here the constant $K$ is used to denote $(N-2)/N$, and $\Pi$ is a matrix of order $N-1$.

Diagonalization of this matrix yields the $t$ step transition probabilities. Then, by expressing the bond vectors as normal coordinates which are similar to the Rouse normal coordinates, Verdier \textsuperscript{16} shows that the relaxation of these normal coordinates is simple exponential and independent of initial configuration.

The relaxation times are therefore of the form $\exp\left(-1/\tau_{NK}\right)$ where

$$\tau_{NK} = -\ln(1 - (4/N)\sin^2(k\eta/2N)).$$  

(3.2)

Comparison of the relaxation times for the two models requires rewriting equations 1.23 and 3.2 so that they can be expressed in terms of the same unit of time. This is done by computing the translational diffusion constant, $D_c$, for both models. For the lattice model, Einstein's relation gives $D_c = 1/6 \cdot \bar{\nu} \sigma^2$, where $\bar{\nu}$ is the number of times a bead is moved per unit time and $\sigma$ is the rms magnitude of each displacement \textsuperscript{19}. Only one bead is moved each bead cycle, so $\bar{\nu} = 1$ and $\sigma = 2/N$. The diffusion constant is then $D_c = (2/N^2 \cdot 1/6) = 1/3N^2$. 

$$\Pi = \begin{pmatrix} K & 1/N & 0 & \cdots & 0 & 0 & 0 \\ 1/N & K & 1/N & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \ddots \\ 0 & 0 & 0 & \cdots & 1/N & K & 1/N \\ 0 & 0 & 0 & \cdots & 0 & 1/N & K \end{pmatrix}$$
For the Rouse Model, the diffusion constant of a single bead, \( D \), in equation 1.5 is equal to \( kT/\ell^2 \). This is related to the diffusion of the center of mass by \( D = D_{cm} N \).

The relaxation times for the two models may now be written as

\[
\tau_{nk} = (3N^2 D_{cm} \ln(1 - (4/N) \sin^2(k\pi/2N))) \quad (3.3)
\]

for the lattice model, and

\[
\tau_{nk} = \left( \frac{2\mu N D_{cm} \sin^2(k\pi/2N)}{K} \right)^{-1} \quad K = 0, 1, \ldots, N-1 \quad (3.4)
\]

for the Rouse Model. In writing 3.4 the mean square extension of a submolecule, \( l^2 \), is taken as unity.

Both expressions exhibit the same general behavior. The longest relaxation time is for \( k = 1 \). Spacing between relaxation times is large for small values of \( k \), but decreases as \( k \) increases. The relaxation times for both models approach the same value for large \( N \). Even for \( N = 8 \) the difference in the longest relaxation times for the two models is less than 3%.

The Correlation Functions

Direct comparison between the Rouse model and computer simulations may be made by calculating the correlation functions of equations 2.3 for the Rouse model. In particular, \( \ell(t) = \langle l_0 \cdot l(t)/\langle l^2 \rangle \) may be calculated as follows.

The vector end-to-end length, \( l \), may be written as \( \vec{l} = \vec{r}_N - \vec{r}_1 \) where \( \vec{r} = (x_i, y_i, z_i) \) for bead \( i \). Also, let \( \vec{u}_m \) be
the normal coordinates of the Rouse Model. Then by a simple
extension of equation 1.11 the \( \bar{r}_k \) may be written as
\[
\bar{r}_k = \sum_{m=0}^{N} R_{jm} \bar{u}_m.
\]
Since \( R \) is an orthogonal matrix, its inverse is
equal to its transpose and \( R^{-1} = R^T = \frac{(2/N)^{1/2} \cos(n\pi(j - 1/2))/N)}{\sqrt{n}} \). Let \( B_m = R_{jm} - R_{om} = \frac{(2/N)^{1/2} \cos(n\pi(N - 1/2))/N)}{\sqrt{n}} - \frac{(2/N)^{1/2} \cos(-1/2n\pi)/N)}{\sqrt{n}} \). The correlation functions for vector
1 may now be written as
\[
\rho(1,1,t) = \frac{\langle 1(t) \cdot 1(0) \rangle}{\langle 1^2 \rangle} = \frac{\sum_{k=0}^{N-1} \langle B_k^2 \bar{u}_k(t) \bar{u}_k(0) \rangle}{\sum_{k=0}^{N-1} \langle B_k^2 \bar{u}_k(0) \rangle}.
\]
The normal coordinates, \( \bar{u}_k \), may be written as
\[
\bar{u}_k = \langle u_k^2 \rangle \exp(-t/\tau_k) \] where \( \tau_k \) is the relaxation time of the kth
normal mode of vibration and \( \langle u_k^2 \rangle_c \) is the mean square of the
coordinate at equilibrium. Verdier shows that \( \langle u_k^2 \rangle_c = \frac{1}{4} \left( \frac{1}{4} \right) \sin^2 \left( \frac{1}{2N} \right) = 1/\tau_c \). This gives
\[
\rho(1,1,t) = \frac{\sum_{k=0}^{N-1} (B_k^2 / \tau_k^2) \exp(-t/\tau_k)}{\sum_{k=0}^{N-1} (B_k^2 / \tau_k)}.
\] These correlation
functions were calculated by computer. The graphical
results of these calculations for \( N = 9 \) and 15 are shown in
figures 3.1a and b. Also shown are the results for Monte
Carlo simulations for the same chain lengths.
Figure 3.1a

Autocorrelation functions, \( \rho(l, l, t) \) for the Rouse Model and for Monte Carlo Simulation.

\[ N = 9 \]
Figure 3.1 b

Autocorrelation functions, $P(l,l,t)$ for the Rouse Model and for Monte Carlo Simulation.

$N = 15$
CHAPTER 4

Computer Simulation of the Equilibrium and Dynamic Properties of Random Coil Polymer Chains.

The concentration dependence of both the equilibrium and dynamic properties of polymer chains was studied. Computer experiments for chain lengths of 10, 20 and 30 were performed with concentrations ranging up to 0.8. Both single bead movement rules and mixed rules were used. In order to minimize box edge effects, boxes the size of the chains were used in as many simulations as possible. Smaller boxes were used in some of the runs at higher concentrations because of limitations imposed by computer time. Previous experiments have been performed by Bellemans for equilibrium properties only, and for chains of the same lengths. Kranbuehl and Schardt studied the concentration dependence for both the equilibrium and dynamic properties for chain lengths of 10 and 20 for concentrations of up to 0.6 using single bead movement rules and smaller boxes than were used in this study.
Equilibrium Properties

The equilibrium data sampled in each simulation are \( \langle l^2 \rangle \), \( \langle 1^4 \rangle \) and \( \langle d^2 / \text{frame} \rangle \). Also of interest is the expansion factor, \( \alpha \). This quantity may be defined by the equation

\[
\langle l^2 \rangle = \alpha^2 \langle l_o^2 \rangle.
\]

The average end-to-end length squared of the unperturbed chain is given by \( l_o^2 \). By unperturbed is meant the dimensions of the random flight or Gaussian chain, in which the end-to-end length is affected only by bond angles and bond lengths. A polymer molecule will assume unperturbed dimensions at the theta temperature, where deviations from ideality vanish. However, in a good solvent at non-theta conditions the attraction of the polymer to the solvent is greater than the attraction of the polymer segments for each other. The polymer will tend to expand so as to minimize these less favorable contacts. Similarly, in a poor solvent at non-theta conditions polymer-polymer contacts are favored over polymer-segment contacts and the chain will contract.

An expression for \( \langle l_o^2 \rangle \) may be obtained from equation 1.1 by performing the integration as described by Flory. The result is \( \langle l_o^2 \rangle = x \), where \( x \) is the number of bonds in the chain, and \( \langle l_o^2 \rangle \) is expressed in units of the bond length. This gives \( \alpha = \langle l^2 \rangle / (N - 1) \), where \( N \) is the number of beads in the chain. The expansion factor is expected to be unity under ideal conditions. Fixman and Peterson have
derived an analytical expression which describes the concentration dependence of in a good solvent. Initially, will be greater than one. As the concentration increases in dilute solutions, decreases rapidly. This decrease slows at higher concentrations, and approaches unity as where is the concentration of the solution.

Studies by Bishop et al\textsuperscript{22}, Wall et al\textsuperscript{23}, Okamoto\textsuperscript{24}, Kranbuehl and Schardt\textsuperscript{25}, De Vos and Bellemans\textsuperscript{26,27}, and Curro\textsuperscript{28,29,30}, have shown that for chains in dilute solution \[ \langle 1^2 \rangle \propto (N - 1)^\alpha . \] As the solution becomes more concentrated the chains contract and the polymer sizes approach a proportionality of \((N - 1)^\alpha\) in the bulk phase. This implies that \(\alpha > 1\) for dilute solution and becomes one in bulk. This is in line with Flory's reasoning that in the bulk phase the inter-chain repulsions are exactly balanced by the intra-chain repulsions. Therefore the chain will not contract or expand, and \(\langle 1^2 \rangle\) will be proportional to \((N - 1)^\alpha\). An \((N - 1)^\alpha\) dependence in the bulk phase has been observed by Cotton et al\textsuperscript{31} by neutron scattering experiments on bulk polystyrene.

The average squared distance traveled per frame, \(\langle D^2 \rangle /\text{frame}\), is another property sampled by the program. This is used to calculate the translational diffusion constant, \(D_t\), given by \(D_t = (1/6)\langle D^2 \rangle /t\). The time \(t\) is the number of bead cycles in a frame divided by the total number of beads cubed. This time was chosen because a frame
length, whenever possible was one relaxation time. It is not known if this time interval is of sufficient length for the longest range motions of the chain to occur. Data for diffusion over longer time intervals would help to answer this question.

The actual calculation of the chains diffusion became complex because the chain was allowed to penetrate the box walls. This means that when a bead hit a box wall it was moved to the other side of the box. The continuity of the chain was always preserved. Each such hit had to be recorded and used to calculate the diffusion for each chain. Details of this procedure are discussed in Appendix B.

Two factors were found to affect the diffusion of the chains. The first of these is the frame length, the diffusion being greater for greater frame lengths. The second is concentration. Figures 4.1a and 4.1b show the effect of concentration on diffusion for 20 and 30 bead chains. These are graphs of the probability distribution of the average square diffusion of the center of mass of the chain with diffusion measured in the number of lattice sites traveled. As can be seen in these plots, increasing concentration causes the distribution to become sharper and the chains to travel less distance.

Exact calculation of diffusion was not possible using our algorithm if the number of beads in the chain was greater than the box length. However, because of computer
time restrictions it became necessary to go to smaller boxes for the higher concentrations of the 20 and 30 bead chains. The diffusion of chains in these smaller boxes was calculated by assuming that the chain would travel no more than half the box length. Selection of a box size for which this condition would be met was made using Figures 4.1a and 4.1b.

The approach used in calculating the box size and frame length for these smaller boxes is exemplified by the method used in calculating these quantities for concentrations of 0.5 and greater for the 20 bead chains. Analysis of Figure 4.1a indicates that by choosing a box size of 10 and not increasing the frame length no chain should travel more than 5 lattice sites when the density is increased to 0.5.

This box size of 10 was used for all concentrations of 0.5 and higher. The frame length for the density of $\rho = 0.6$ was chosen by multiplying the frame length used at $\rho = 0.5$ by the quantity $D(\rho = 0.4)/D(\rho = 0.5)$. This allows the frame length to increase within safe limits by taking into account the fact that as density increases the diffusion will be less. Frame lengths for densities of 0.7 and 0.8 were chosen in the same way. A similar analysis of Fig. 4.1b led to the use of a box size of 14 for 30 bead chains.
Dynamic Properties

As a measure of the dynamics of the system, the autocorrelation function,

\[ \rho(1,1,t) = \langle l_0 \cdot l_z \rangle / \langle l^2 \rangle, \]

and

\[ \rho(1^2,1^2,t) = (\langle l_0^2 \cdot l_z^2 \rangle - \langle l^2 \rangle^2) / (\langle l^2 \rangle - \langle l_z^2 \rangle) \]

were obtained from the program. The time, t, is measured in N bead cycles, where N is the total number of beads. These autocorrelation functions are normalized so that they have a value of one at t=0 and decrease to zero as time increases. This relaxation behavior of the autocorrelation functions is characteristic of the overall relaxation behavior of the chain. It is not simple exponential. However, for times after which the autocorrelation function has dropped to about 1/2, it is nearly simple exponential and may be fitted to a function of the form \( \rho(t) = \exp(-t/\tau) \). This part of the graph is fitted to a function of the form \( \ln \rho(1,1,t) = \ln A - t/\tau_z \). The relaxation time, \( \tau_z \), may then be calculated from the limiting slope. This relaxation time should be representative of the longest relaxation time found in the Rouse Model. It will therefore involve the long range motions of the chain.

A second relaxation time, \( \tau_{1/e} \), is defined as the time it takes \( \rho(1,1,t) \) to relax to a value of 1/e. This
relaxation time is characteristic of the overall relaxation of the chain.

Results and Discussion

The results for the equilibrium properties are shown in tables 4.1 and 4.2. Previous studies of the concentration effects on the equilibrium dimensions were made by De Vos and Bellemans\textsuperscript{26,27}. For low concentration Bellemans used the same model as in the present study, with crankshaft bead movement rules. Samples of $\langle l^2 \rangle$ were made about every 200 bead moves. Because this model has a large number of excluded volume conflicts at high concentrations resulting in large amounts of computer time needed, a different approach was taken. Bellemans approach was to use single bead rules but to pick an empty lattice site at random. If an adjacent bead could move to this site it was moved. Bellemans data is summarized in Table 4.3. Figure 4.2 shows a graphical comparison of our model to Bellemans. Mixed bead movement results are shown, the results of the single bead movements are very similar. All points are within one standard deviation of Bellemans results. This data shows that $\langle l^2 \rangle$ decreases with increasing density. The last four points fit better to $\rho^{-32}$ than $\rho^{-1}$.

The dependence of end-to-end length on chain length may be found by taking the slope of lines generated by a log-log plot of $N - 1$ vs $\langle l^2 \rangle$. The results are shown in Table 4.4.
The parameter \( a \) is the exponent in the equation \( \langle l^2 \rangle \propto (N - 1)^a \). It is simply the slope of the plot of \( \log \langle l^2 \rangle \) vs \( \log (N - 1) \). Results compare with those of Bishop et al.\textsuperscript{2,2} and Bellemans\textsuperscript{2,7}. They show a decrease in the exponent \( a \) from 1.2 for a single chain to a value approaching 1 in bulk.

That chains in concentrated solutions show the behavior of \( \langle l^2 \rangle \propto (N - 1)^{1.6} \) means that they behave as Gaussian or ideal chains. This does not mean that the complete distribution of chain segments is gaussian, since the distribution is uniquely determined by all even moments, not just the second.

The average end-to-end length squared vs density is plotted in Fig 4.3. The results have been extrapolated to a density of 1. The theoretical results for \( \langle l^2 \rangle \) from second order (5 choice) random walk calculations on a cubic lattice at this density are given by Curro\textsuperscript{30} as

\[
\langle r^2 \rangle = \frac{(1 + S)/(1 - S)n - 2}{(1 - S^m)/(1 - S^n)}
\]

where \( S = 1/(q - 1) \) and \( q \) is the coordination number of the lattice (6 for a cubic lattice). The extrapolated results are close for all three chain lengths, as expected. No exact expression was readily available for \( \langle l^4 \rangle \), but the theoretical values for \( \langle l^4 \rangle/\langle l^2 \rangle^2 \) were obtained from Curro as 1.47, 1.51 and 1.55 for chain lengths of 10, 20 and 30 respectively. Plots of \( \langle l^4 \rangle/\langle l^2 \rangle^4 \) for all three chain lengths vs density are given in Fig 4.4. They are again
extrapolated to a density of 1, and the agreement is good with the results for a gaussian chain.

The distribution function $W(r)$ is completely determined by the even moments. It is a slowly converging series, however, so it can only be written in terms of just the second and fourth moments as a rough approximation. Curro gives this as

$$W(r) \sim n^{3/2} \exp(-r^2)((1 + 15g_{\rho}) - 20g_{\rho}r^2 + 4g_{\rho}^2)$$

where $r^2 = 3r^2 / 2\langle r^2 \rangle$ and $g = 0.125((3/5)\langle r^2 \rangle / \langle r^2 \rangle^2 - 1)$.

The concentration dependence of $\langle 1^2 \rangle$ and $\langle 1^4 \rangle / \langle 1^2 \rangle^2$ with the ideal chain values suggests that this approximate distribution is the same for all chain lengths for the bulk system and the gaussian chain. Data for the higher even moments would be necessary to show with a higher certainty that the two distributions are the same.

The concentration dependence of $\langle 1^2 \rangle$ is predicted by theory to be $\langle 1^2 \rangle \sim \rho^{-\gamma}$ with $\gamma = 0.25$ in three dimensions. Least squares fits of the plots of $\log \langle 1^2 \rangle$ vs $\log \rho$, shown in Figure 4.5, gave values of $\gamma$ to be $0.07 \pm 0.005$, $0.12 \pm 0.05$ and $0.13 \pm 0.04$ for chain lengths of 10, 20, and 30. Table 4.4b shows a comparison of those of Curro and Bishop et al. Our results are within one standard deviation of both sets of data. The exponents for
the small chain lengths are less than predicted by theory. For the longer chain lengths used by Bishop et al., the exponents did approach the expected result of 0.25.

Plots of $D_\xi$ vs. bead density are shown in Fig. 4.6a for mixed bead movements and in Fig. 4.6b for single bead movements. The diffusion constant appears to be independent of chain length. $D_\xi$ decreases linearly with increasing concentration. This decrease might be expected to be less pronounced because frame lengths of less than one relaxation time were used for the higher concentrations of the 20 and 30 bead chains. This length of time is most likely not sufficient for the long range motions of the chain to have occurred, with the result that $D_\xi$ is too small.

Plots of $\ln \rho(1,1,t)$ vs. time are shown in Figures 4.7a through 4.7h. The time is measured in $N^3$ bead cycles, with $N$ being the total number of beads in the box. The error bars correspond to one standard deviation of the mean.

The Dynamic results are shown in tables 4.5 and 4.6. Figure 4.8 is a plot of $\tau_5$ vs. bead density. The behavior of $\tau_5$ is different for the mixed and single bead movement rules. It is the same, however, for the three chain lengths using a given rule. $\tau_5$ varies much more slowly at low concentrations for the mixed plots than for the single ones. Behavior is similar for the two bead movement rules for concentrations above about 0.5.

For the mixed moves, $\tau_5$ changes very little at the low
densities, but increases very rapidly at the high densities. This effect is much less pronounced for the single moves. A behavior was seen by Kranbuehl and Verdier in the study of the effect of bead movement rules on isolated chains of various lengths. They found that $\tau$ increased much more slowly for mixed moves at small chain lengths (10 to 20 beads) than for either pure single or pure crankshaft moves. They also found that the increase in $\tau$ with chain length was similar for all bead movement rules at longer chain lengths.

The smaller dependence of $\tau$ on density at low densities than at high densities may be explained as follows. At low densities each chain is isolated from the others, each chain forming a cluster. As chains are added this situation does not change until some critical density, $\rho^*$, is reached. At this point the chains become entangled and the relaxation is slowed by these interchain excluded volume effects. At this density $\tau$ begins to rise sharply with increasing density.

Figures 4.9a and b are log-log plots of $\tau$ vs density. The concentration, $\rho^*$, at which entanglement begins is the concentration at which the two lines intersect. These concentrations are given in Table 4.7. Schaefer, Joanny and Pincus have predicted that $\rho^*$ is proportional to $1/(N-1)^{1/3}$. As expected, the critical density decreases with increasing chain length. It does not decrease as
rapidly as expected, however. Little can be seen from the runs using single bead moves because runs were not taken to high enough densities.

Figures 4.10a and 4.10b are plots of \( \ln \tau_3 \) vs. \( \ln(N) \) for the various densities. Table 4.8 shows the slopes for each of these lines. For both types of bead movement rule the dependence on chain length increases with increasing density. This dependence is much larger in the single bead movement rules than for the mixed ones.

Figures 4.10c and 4.10d are similar plots of \( \ln \tau_{fc} \) vs. \( \ln(N) \). The overall relaxation of the chain shows little change in its \( N \)-dependence with increasing densities until a density of \( \rho = 0.6 \), at which point it also begins to increase.

The dimensionless quantity \( \tau_3 D_t \langle \gamma^2 \rangle \) has been found to be nearly linear, as shown in Table 4.5. This gives

\[
D_t \propto \frac{\tau_3}{\langle \gamma^2 \rangle}.
\]

(4.1)

Einstein's equation relates \( D \) to the viscosity, \( \eta \), by the equation

\[
D_t \propto \frac{1}{\eta}.
\]

(4.2)

Combining equations 4.1 and 4.2 gives

\[
\eta \propto \frac{\langle \gamma^2 \rangle}{\tau_3}.
\]

(4.3)

Cohen and Turnbull derived a relation between the diffusion and free volume by considering transport in a liquid of hard spheres. The molecules are pictured as traveling in a cage consisting of their nearest neighbors.
Diffusion occurs when a hole large enough for the molecule to move through opens up in the cage and another molecule occupies its original position before it is able to return. Using this approach they found that

\[
D = D(v^*) \exp(-\gamma v^*/v_f^*). \tag{4.4}
\]

In this equation \(v^*\) is a critical volume just large enough to allow another molecule to jump in after the displacement. The average free volume per molecule, \(v_f^*\), is the volume within the cage minus the volume of the molecule. The contribution of the molecule to the diffusion coefficient is \(D(v^*)\), as \(D(v)\) is zero if \(v < v^*\). \(D(v^*)\) is equal to \(ga^*u\) with \(a^*\) being the molecular diameter, \(u\) the velocity of the molecule and \(g\) is a geometrical factor. The final quantity, \(\gamma\) is a numerical factor introduced to include the overlap of free volume between molecules and should lie between \(1/2\) and 1.

An empirical relation of the same form, \(\gamma = A \exp(Bv_f^*/v_o)\) was found by Doolittle for simple hydrocarbons\(^{36}\). Here \(v_f^*\) is the free volume of the molecular unit or bead and \(v_o\) is the volume of the bead.

Combining equations 4.2, 4.3, and 4.4 gives

\[
\langle 1^2 \rangle / \tau_\gamma \propto D(v^*) \exp(\gamma v^*/v_f^*). \tag{4.5}
\]

The quantity \(\gamma v^*\) must be nearly equal to the molecular volume, giving

\[
\langle 1^2 \rangle / \tau_\gamma \propto \exp(1/v_f^*),
\]
The free volume, $v_f$, is the total free volume divided by the number of beads, $N$. Letting $V$ be the total volume, $v_f = (V - N)/N = (1 - \rho)/\rho$. Therefore $\langle l^2 \rangle / \tau_s \propto (\rho/(1 - \rho))$. A plot of $\ln(\langle l^2 \rangle / \tau_s)$ vs. $\rho/(1 - \rho)$ is given in Figure 4.11. As predicted it is a linear graph. Also $\langle l^2 \rangle / \tau_s$, which is proportional to $D_f$, is independent of chain length.

Table 4.9 shows the values for $\tau_{\text{eq}}(l^2)$ and $\tau_s(l^2)$ for the correlation functions $\rho(l^2, l^2, t)$. Plots of $\rho(l^2, l^2, t)$ vs time are shown in Figures 4.12a and b. The dependence of $\tau_s(l^2)$ on concentration is shown in figure 4.13. There appears to be no difference based on chain lengths. Figure 4.14 shows that a break point occurs at a density of 0.46. This is comparable to the density at which the break point occurred in $\tau_s$ for the longest chain length studied.

The effect of concentration on equilibrium properties agrees with previous studies. $\langle l^2 \rangle$ is proportional to $(N - 1)^\alpha$ where the exponent $\alpha$ is near 1.2 for the single chain and approaches an extrapolated value of 1.0 in bulk. Agreement of $\langle l^2 \rangle$ and $\langle l^4 \rangle / \langle l^2 \rangle^2$ at high concentrations with random walk calculations in bulk is good. This suggests that the distribution of end-to-end length for the bulk system is consistent with that of the gaussian chain. The exponent in the equation $\langle l^2 \rangle \propto (N - 1)^\alpha$ was found to be lower than predicted by theory. The exponent agrees with previous simulations, which show that the theoretical value
is approached as chain length is increased. Diffusion decreases linearly with concentration and is not dependent on chain length.

The behavior of the longtime relaxation, $\tau_j$, is different for mixed and single bead movement rules at low concentration. Behavior is similar at high concentrations. The critical density was found to decrease with increasing chain length, but at a much slower rate than predicted by theory. The $N$ dependence of $\tau_j$ increases with increasing density. This increase appears to be stronger for the single bead movement rules than for the mixed ones. The slope of $\ln(\tau_j)$ vs. $N$ increases by a factor of 1.33 for the mixed moves vs. 1.73 for the single moves in the concentration range 0.04 to 0.5. The $N$ dependence of $\tau_{j/c}$ is less pronounced for low concentrations than high ones. Again this increase is larger for single moves. For single moves the slope of $\ln(\tau_{j/c})$ vs. $N$ increases by a factor of 1.45 vs. an increase of 1.08 for the mixed moves in the concentration range 0.04 to 0.5. The overall increase in the $N$ dependence of the long-time relaxation is less than that of the overall relaxation. This suggests that the short range, faster relaxation modes are less affected by concentration changes than the long range cooperative relaxation modes.

The quantity $\ln \left( \frac{1^2}{\tau_j} \right)$ vs $\left( \rho/\rho_c \right)$ is linear as predicted by the free volume theories of Doolittle and
Williams, Landel, and Ferry. The free volume theory provides a good description of the dependence of the relaxation time on polymer volume fraction.
Table 4.1

Mixed Bead Movements. Equilibrium Data.

<table>
<thead>
<tr>
<th>Length</th>
<th>#Runs</th>
<th>#Frames</th>
<th>Box Dens</th>
<th>\langle D^2 \rangle Std</th>
<th>\langle D_1 \rangle Std</th>
<th>\langle L^2 \rangle Std</th>
<th>\langle I^4 \rangle Std</th>
<th>\langle L^2 \rangle Std</th>
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Table 4.2

Single Bead Movements. Equilibrium Data.

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<th>$\langle L^2 \rangle$ Std</th>
<th>$\langle L^4 \rangle$ Std</th>
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<td>1.613 0.09</td>
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Table 4.3
Concentration dependence of the end to end length. Data from A. Bellemans and E. De Vos

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<td>$\alpha^2$</td>
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<td>14.587 ± 0.027</td>
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<td>0.2015</td>
<td>14.312 ± 0.020</td>
<td>1.590</td>
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<td>0.2933</td>
<td>14.111 ± 0.023</td>
<td>1.568</td>
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<td>0.3608</td>
<td>13.988 ± 0.018</td>
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<td>13.786 ± 0.034</td>
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<td>1.502</td>
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<td>0.9497</td>
<td>12.924 ± 0.088</td>
<td>1.436</td>
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- The first set of data at each chain length (up to the first blank line) was obtained using a computer model the same as in the present studies.
- The second set of data was obtained by use of a model in which empty lattice sites are moved instead of beads.
- The data given for polymer volume fraction of one was obtained by extrapolation of the computer results.
Table 4.4

a. The dependence of $\langle 1^2 \rangle$ on chain length

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$\langle 1^2 \rangle \propto (N-1)^a$

b. The dependence of $\langle 1^2 \rangle$ on density

<table>
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<tr>
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<th>$\gamma$ (Curro)</th>
<th>$\gamma$ (Bishop)</th>
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<td>$0.06 \pm 0.01$</td>
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$\langle 1^2 \rangle \propto \rho^{-\gamma}$
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Table 4.7

Densities at which chain entanglements begin
Mixed Moves

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Table 4.8

The dependence of relaxation times on chain length

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Table 4.9

Relaxation of $\rho(L^2, L^2, T)$

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Figure 4.1a
The effect of concentration on Diffusion for 20 bead chains

20X20X20 Box

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<tr>
<td>○</td>
<td>0.40</td>
<td>0.33</td>
</tr>
</tbody>
</table>

$P(D^2)$

$D$ (number of Lattice Sites)
Figure 4.1 b

The effect of concentration on Diffusion for 30 bead chains

30 X 30 X 30 Box

<table>
<thead>
<tr>
<th>Symbol</th>
<th>$\rho$</th>
<th>Frame Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.04</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$P(D^2)$

D (number of Lattice Sites)
Figure 4.2

The concentration dependence of the linear expansion factor.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>.</td>
<td>10</td>
</tr>
<tr>
<td>▲</td>
<td>20</td>
</tr>
<tr>
<td>□</td>
<td>30</td>
</tr>
</tbody>
</table>

closed symbols: Bellemans data
open symbols: data from current study

- - - : $p^{-1}$
Figure 4.3

$\langle l^2 \rangle$ as a function of density.

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>12.87</td>
</tr>
<tr>
<td>20</td>
<td>27.87</td>
</tr>
<tr>
<td>30</td>
<td>42.87</td>
</tr>
</tbody>
</table>

$\times$ indicates ideal chain obtained from second order random walk calculations.
Figure 4.4

\[ \langle r^4 \rangle / \langle r^2 \rangle^2 \] as a function of density.

- \( x \) - ideal chain value, obtained from second order random walk calculations.
Figure 4.6a

The Concentration dependence of the translational diffusion constant: mixed bead movements.

<table>
<thead>
<tr>
<th>symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>◦</td>
<td>10</td>
</tr>
<tr>
<td>○</td>
<td>20</td>
</tr>
<tr>
<td>□</td>
<td>30</td>
</tr>
</tbody>
</table>

Symbol Key:
- ◦: Chain Length 10
- ○: Chain Length 20
- □: Chain Length 30

Bead Density vs. $D_t$ relationship.
Figure 6.6b

The concentration dependence of the translational diffusion constant single bead movements

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>◯</td>
<td>10</td>
</tr>
<tr>
<td>○</td>
<td>20</td>
</tr>
<tr>
<td>□</td>
<td>30</td>
</tr>
</tbody>
</table>

Bead Density

$D_t$
Figure 4.7a: ln(\(l_1(1, t)\)) vs time for mixed bead movements
multiple 10 bead chains

Time (N. bead cycles)
Figure 4.7 b

$\ln f(1,1,t)$ vs time for mixed bead movements multiple 10 bead chains.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>□</td>
<td>0.5</td>
</tr>
<tr>
<td>△</td>
<td>0.6</td>
</tr>
<tr>
<td>.</td>
<td>0.7</td>
</tr>
<tr>
<td>○</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Time ($N^3$ bead cycles)
Figure 4.7 c

\[ \ln(P_{(1,1,t)}) \] vs time for mixed bead movements, multiple 20 bead chains.

Legend:
- \[ \circ \]: Density 0.04
- \[ \square \]: Density 0.20
- \[ \triangle \]: Density 0.40

Time (N bead cycles)
Figure 4.7 d

$\ln \rho(1,1,t)$ vs time for mixed bead movements
multiple 20 bead chains
Figure 4.7 e

$\ln \beta(1,1,t)$ vs time for mixed bead movements multiple 30 bead chains.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>□</td>
<td>0.04</td>
</tr>
<tr>
<td>△</td>
<td>0.20</td>
</tr>
<tr>
<td>○</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Time ($N^3$ Bead Cycles)
Figure 4.7f

$\ln \rho(1,1,t)$ vs time for multiple 30 bead chains. Mixed bead movements.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>□</td>
<td>0.5</td>
</tr>
<tr>
<td>△</td>
<td>0.6</td>
</tr>
<tr>
<td>○</td>
<td>0.7</td>
</tr>
<tr>
<td>●</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Time ($N^3$ bead cycles)
Figure 4.7 g

$\ln \rho(1,1,t)$ vs time for single bead movements

Multiple 20 bead chains.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>□</td>
<td>0.04</td>
</tr>
<tr>
<td>△</td>
<td>0.20</td>
</tr>
<tr>
<td>○</td>
<td>0.40</td>
</tr>
<tr>
<td>○</td>
<td>0.50</td>
</tr>
<tr>
<td>○</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 4.7 h

\[ \ln(\overline{p}(1,1,t)) \text{ vs time for single bead movements} \]

multiple 30 bead chains.
Figure 4.8
$\gamma_5$ vs Bead Density

<table>
<thead>
<tr>
<th>symbol</th>
<th>chain length</th>
<th>type move</th>
</tr>
</thead>
<tbody>
<tr>
<td>•</td>
<td>10</td>
<td>mixed</td>
</tr>
<tr>
<td>▲</td>
<td>20</td>
<td>mixed</td>
</tr>
<tr>
<td>■</td>
<td>30</td>
<td>mixed</td>
</tr>
<tr>
<td>○</td>
<td>10</td>
<td>single, Schardt's Data</td>
</tr>
<tr>
<td>◊</td>
<td>10</td>
<td>single</td>
</tr>
<tr>
<td>△</td>
<td>20</td>
<td>single, Schardt's Data</td>
</tr>
<tr>
<td>□</td>
<td>20</td>
<td>single</td>
</tr>
<tr>
<td>□</td>
<td>30</td>
<td>single</td>
</tr>
</tbody>
</table>

Bead Density

$\gamma_5$
Figure 4.9 a

Log-Log plot of $\tau_5$ vs Density

mixed bead movement rules

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
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<tr>
<td>▲</td>
<td>20</td>
</tr>
<tr>
<td>■</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 4.9 b

Log-Log plot of $\tau_s$ vs Density

Single bead movement rules.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>▲</td>
<td>20</td>
</tr>
<tr>
<td>□</td>
<td>30</td>
</tr>
</tbody>
</table>

$\log(\tau_s)$ vs Log(density)
Figure 4.10 a
\( \ln \tau_b \) vs \( \ln(N) \) for Mixed bead movements.

Figure 4.10 b
\( \ln \tau_b \) vs \( \ln(N) \) for Single bead movements.

\( \rho = .9 \)
\( \rho = .7 \)
\( \rho = .6 \)
\( \rho = .5 \)
\( \rho = .4 \)
\( \rho = .2 \)
\( \rho = .04 \)

\( \bigcirc \) Single Chain values

\( \times \) Schardt's Data
\( \bigcirc \) Single Chain values
Figure 4.10 c

$\ln \tau_{\text{fe}}$ vs $\ln(N)$ for

Mixed bead movements.

$\ln(\tau_{\text{fe}})$

$\rho = .8$

$\rho = .7$

$\rho = .6$

$\rho = .5$

$\rho = .4$

$\rho = .3$

$\rho = .2$

$\rho = .1$

$\rho = .04$

○ Single Chain values

× Schardt's Data

Figure 4.10 d

$\ln \tau_{\text{fe}}$ vs $\ln(N)$ for

Single bead movements.

$\ln(N)$
Figure 4.11

The dependence of $\ln(1^2/\tau_s)$ on Free Volume

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>*, o</td>
<td>10</td>
</tr>
<tr>
<td>△, △</td>
<td>20</td>
</tr>
<tr>
<td>■, □</td>
<td>30</td>
</tr>
</tbody>
</table>

Closed symbols: single bead movements.

Open symbols: mixed bead movements.
Figure 4.12b

\[ \ln \rho(l^2, l^2, t) \] vs time for mixed bead movements
Multiple 20 bead chains.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>□</td>
<td>0.5</td>
</tr>
<tr>
<td>○</td>
<td>0.6</td>
</tr>
<tr>
<td>・</td>
<td>0.7</td>
</tr>
<tr>
<td>△</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Time (N bead cycles)
Figure 4.12 a

\[ \ln \rho(l^2, l^2, t) \] vs time for mixed bead movements

Multiple 20 bead chains.
Figure 4.13

$\tau_s (l^2)$ vs Density

for mixed bead movements.
Figure 4.14

Log-Log plot of $\tau_s(l^2)$ vs Density for Mixed bead movements.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>10</td>
</tr>
<tr>
<td>□</td>
<td>20</td>
</tr>
<tr>
<td>△</td>
<td>30</td>
</tr>
</tbody>
</table>

$\log \tau_s(l^2)$ vs Log(Density)
APPENDIX A

A Solution of the Eigenvalue Problem.

The matrix $A$ derived in Chapter 1 may be written as

$$
A = \begin{pmatrix}
2 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
-1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\
0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\
0 & 0 & 0 & 0 & \cdots & 0 & -1 & 2
\end{pmatrix}
$$

by preforming a series of row and column additions on the original matrix. This matrix may be diagonalized by an orthogonal transformation,

$$
R^{-1} AR = \Lambda = \lambda_i \delta_{i,j}
$$

where $\lambda_p$ is the $p$th eigenvalue of $A$, and $\delta_{i,j}$ is the Kronecker delta.

Writing $A$ as the sum of two matrices, $C$ and $D$ gives
The orthogonal matrix, \( R \), which diagonalizes \( C \) also diagonalizes \( D \). The eigenvalues of \( A \) are related to the eigenvalues, \( \lambda_i \), of \( C \) by
\[
\lambda_i = 2 + \xi_i. \tag{A1}
\]
The eigenvalues of \( C \) are easily found by considering a more general matrix, \( \overline{\tau} \), which is of the same form as \( C \),
\[
\overline{\tau} = \begin{pmatrix}
  0 & p & 0 & \cdots & 0 & 0 & 0 \\
p & 0 & p & \cdots & 0 & 0 & 0 \\
0 & q & 0 & p & \cdots & 0 & 0 \\
0 & 0 & q & p & \cdots & 0 & 0 \\
0 & 0 & 0 & 0 & \cdots & q & p \\
0 & 0 & 0 & 0 & \cdots & 0 & p \\
0 & 0 & 0 & 0 & \cdots & 0 & 0
\end{pmatrix}
\]
Using the orthogonal transformation \( B \overline{\tau} B^{-1} = \lambda_i \delta_{ij} \), or \( B \overline{\tau} = \lambda B \) with \( B = (\beta_1, \beta_2, \ldots, \beta_{\omega-1}) \), yields upon multiplication the following set of second order difference equations:
\[
p \beta_{k-1} + q \beta_{k+1} = \lambda_k \beta_k \quad (k = 0, 1, 2, \ldots, N-1). \tag{A2}
\]
The quantities \( \beta_c \) and \( \beta_\omega \) are set to zero. \( ^{15} \)
This set of equations may be solved by assuming a solution of the form
\[
\beta_k = \alpha r^k. \tag{A3}
\]
Substituting A3 into A2 shows that this can be a solution only if \( r \) is a root of the quadratic
\[
p - \lambda r + qr^2 = 0. \tag{A4}
\]
There will, in general, be two distinct, independent roots to this quadratic, \( r_1 \) and \( r_2 \). Therefore a solution to the difference equation \( (A2) \) will be in the form of a geometric progression

\[ \rho^K = \alpha_1 r_1^K + \alpha_2 r_2^K. \] (A5)

Because \( \rho_0 = \rho_N = 0 \), it is easy to show that \( \alpha_1 + \alpha_2 = 0 \) and that \( r_1^* = r_2^* \). Rewriting this last equation gives

\[ r_i^* = r_2^* \exp(2\pi ij), \text{ or} \]

\[ r_i = r_2 \exp(2\pi ij/N) \text{ for } j = 0, 1, 2, \ldots, N-1. \] (A6)

where \( i = \sqrt{-1} \) and \( \exp(2\pi ij) = \cos 2j\pi + i\sin 2j\pi = 1 + i \cdot 0 = 1 \).

By equation A6, \( r_1 \) and \( r_2 \) must be complex conjugates of each other. The absolute values of \( r_1 \) and \( r_2 \) may be found by using this fact as follows, \( r^2 - \lambda/q + p/q = (r - r_1)(r - r_2) = 0 \). Equating the coefficients of the two equations gives \( \lambda = q(r_1 + r_2) \) and \( r_1 r_2 = p/q \). The roots of \( A4 \) are

\[ r = p/q \exp(\pi ij/N) \text{ and} \]

\[ r_\pm = \sqrt{p/q} \exp(-\pi ij/N) \text{ (j = 0, 1, 2, \ldots, N-1).} \] (A7)

The eigenvalues of \( \Pi \) are \( \lambda_i = q(r_1 + r_2) = -2\sqrt{pq} \cos(\pi i/N) \text{ j = (1, 2, \ldots, N-1)}. \) Substituting \( p = q = -1 \) gives \( c_i = 2\cos(\pi i/N) \text{ (i = 1, \ldots, N-1)}, \) and from equation A1

\[ \lambda_i = 2 + 2\cos(\pi i/N) = 4\sin^2(\pi i/2N) \text{ (i = 1, \ldots, N-1)} \] (A8)
The corresponding eigenvectors are given by the columns of the matrix \( R \). The elements of \( R \) are given by Verdier's formula

\[
R_{nj} = \cos\left(\frac{n - \frac{1}{2} \pi j}{N}\right).
\]
APPENDIX B

Procedure used for the calculation of Diffusion Data

The exact number of lattice sites each chain moved during some time interval was calculated by the following method. This method is valid only if the chain length is less than or equal to the box size.

The subroutine performing the bead movements needed two arrays. These are IMOVE(I,J) and IWALL(I,J). The subscript I is 1, 2, or 3 if the chain moved in the x, y, or z dimension, respectively. The J subscript is used to denote the chain of interest.

Each time an end bead moves out of the box a one is added to or subtracted from IMOVE(I,J). If the new coordinates of the bead in the I dimension is greater than the box size then a one is added. Otherwise a one is subtracted from IMOVE(I,J). The wall through which the bead moved is also recorded. The walls are defined as:
Initially, \( IMOVE(I,J) \) is set to zero if the chain is connected. If it is broken then \( IMOVE(I,J) \) is set to -1 if \( 0 < \text{the center of the chain} < \text{Box Size}/2 \). If \( \text{Box Size}/2 \leq \text{the Center of mass of the chain} \) then \( IMOVE(I,J) \) is set to +1. If the chain is broken more than once then the diffusion of the chain is not calculated for that frame. This initialization procedure also occurs before each call to the subroutine which performs bead movements. The center of mass of each chain is calculated by summing over the \( x \), \( y \), or \( z \) coordinates and dividing by the number of beads in the chain. These sums always start with the first bead of the chain. If the difference in coordinates between two beads is greater than one then the chain is split and a box dimension is added or subtracted to the bead coordinate before the center of mass is calculated. This is to say that the center of mass is always calculated from a fully connected chain. If the center of mass lies outside the box then a box dimension is added to or subtracted from it to put it inside the box.
The diffusion is then calculated by the procedure outlined in Figure B1. The variables in this flowchart are defined as

- \( \text{CMO}(I,J) \) = the position of the center of mass of the chain the last time its properties were sampled.
- \( \text{CM}(I,J) \) = the current position of the center of mass of the chain.
- Box = the box dimension and
- DCM = the distance the chain has moved in one of the three dimensions since the last time its properties were sampled.

The function \( \text{INT}(A) \) where \( A \) is a floating point number is defined as \( \text{INT}(A) = \text{largest integer} \leq |A| \).

There is one exception to this procedure which had to be accounted for. This case is outlined in Figure B2. Diffusion is considered in the \( x \) dimension only. The bead represented by the open circle is bead number 1. The arrows mean that some number of bead movements have occurred to cause the chain to reach the new configuration pictured. It was reached in such a way that the variables \( \text{MOVE}(I,J) \) and \( \text{IWALL}(I,J) \) set according to the above rules are as shown.

To calculate DCM by the procedure of Figure B1 the following choices would be made:

1. The chain is not connected
2. A wall was hit
3. The center of mass, \( \text{CM}(I) \) is nearest wall 1
(4) Wall 1 waw hit.

The formula used to calculate DCM is, then

\[ DCM = CM(1) - CMO(1,1) + \text{INT}(\text{IMOVE}(1,1)) + \text{INT}(\text{IMOVE}(1,1)/2) \]
* BOX. Substituting for these variables from Fig B2 gives

\[ DCM = 2.2 - 7.3 + 0 = -5.10. \]

This is clearly wrong. The chain did not move 5.10 lattice sites to the left but 10.2 - 7.3 = 2.9 lattice sites to the right.

The correction was made to the program by the addition of the subroutine CHAIN. This subroutine checks to see if an end bead moves through a wall, and then through the opposite wall. If this type of movement is detected the IWALL(I,J) is set to zero. In the above example, the choices made in B1 are

(1) The chain is not connected
(2) no wall was hit.

Therefore, \( DCM = CM(I) - CMO(1,1) = 2.2 - 7.3 = -5.10 \)

and

(3) \(-5.10 < \text{BOX}/2\), so

\[ DCM = 8.0 - 5.10 = 2.90, \]

which is correct.
FIGURE B1
Algorithm for calculation of diffusion

START

is the chain connected

yes

DCM = CH(I) - CNO(I,J)
+ INTH(I,J)/2
* BOX

no

was a wall hit

no

DCM = CH(I,J) - CNO(I,J)

no

DCM = DCM
+ BOX

yes

DCM = DCM - BOX

DCM = BOX/2

no

DCM = CH(I,J) - CNO(I,J)

no

DCM = DCM
+ BOX

yes

DCM = DCM - BOX

DCM = BOX/2


Is CH(I) near TMALL(I,J)

yes

DCM = CH(I,J) - CNO(I,J)
+ INTH(I,J)/2
* BOX

no

DCH = CH(I,J) - BOX + INTH(I,J)/2
* BOX

Is TMALL(I,J) = 1, 2, or 3

yes

DCM = CH(I,J) - CNO(I,J) + BOX + INTH(I,J)/2
* BOX

no
Figure B2
Example of diffusion in the x dimension for a 1 chain system

CM0(1,1) = 7.3
IMOVE(1,1) = 1
IWALL(1,1) = 0

CM(1) = 10.2 - 8 = 2.2
IMOVE(1,1) = 1
IWALL(1,1) = 1
## APPENDIX C

*The Simulation Program*

<table>
<thead>
<tr>
<th>Main Program</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subroutines</td>
<td></td>
</tr>
<tr>
<td>Ncyc</td>
<td>94</td>
</tr>
<tr>
<td>Prime</td>
<td>95</td>
</tr>
<tr>
<td>Sample</td>
<td>98</td>
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<td>Ctmmap</td>
<td>121</td>
</tr>
<tr>
<td>Pack</td>
<td>122</td>
</tr>
</tbody>
</table>
MEMBER NAME MAIN

THIS PROGRAM HANDLES ONLY CHAINS THAT ARE ALL
THE SAME LENGTH, GREATER THAN A READS LONG
IT IS FOR EXCLUDED VOLUME CONDITIONS ONLY
DIFFUSION CALCULATIONS ARE EXACT, BUT THE BOX
SIZE MUST BE AT LEAST AS LARGE AS THE CHAIN
LENGTH FOR THE DIFFUSION TO BE CORRECT.

************* MAXIMUM DIMENSIONS *************
NO. CHAINS TO BE SAMPLED = 50
NO. READS = 15000
NO. RENS = 30
NO. FRAMES = 50
NO. SAMPLES = 30
MAXIMUM BOX SIZE = 32X32X32

*************** LOGICAL #1 HEADER (30), SPACE

COMMON N,IJ,RN,N,IS,IYS,IZS,NCH,ISUM(3),IS(3),ISEP(3),
           IFRAME,NFAMS,NCHAIN,NCHAIN,NJNUN
           ISUN,NCYCLE,NEWTV,IKYS,IP_FILE,KNUM,TABLE(32),IMOVE(3,50),
           NSTART(15000),NEND(15000)

COMMON/CROSS/LF(4,50,500),CROSS(5,2,50),START(3,50),START2(50),
           ACROSS(5,2,50),ACROSS2(5,2,50),ACROSS3(2,2),ACROSS3(2,50),
           AVG(4,30),AVG30(4,50)

DATA SPACE/IH /
DIMENSION AVG(4),CROSS(4)

INTEGER LTAB(3)

READ THE RANDOM NUMBER SEED
READ 10,1,44
10 FORMAT(110)
   READ 12,11N,1OUT
11 FORMAT(310)
C IF IFIN READ IN LTAB
C IF IFIN=1 READ IN NTAB
C IF IFOUT=0 WRITE FINAL READ CONFIGURATION
C IF IFOUT=1 WRITE FINAL READ CONFIGURATION TO DISK FILE
C AS SPECIFIED ON DTGDP001 ON JCL
DD 20 1=1,40
20 HEAD=1 SPACE
READ (5,30) HEADER
30 FORMAT (114,30A1)
PRINT 40,HEADER
40 FORMAT (114,30A1)
READ 10,NUN
MEMBER NAME: MAIN

READ (5,50) NFRAMES,KCHAIN
50 FORMAT (1111,911,11)

WRITE (6,60) NFRAMES,KCHAIN
60 FORMAT (1010,1010)

READ (70,IXS,ISYS,IZS)
70 FORMAT (3110)

PRINT (70,IXS,ISYS,IZS)
80 FORMAT (910)

PRINT (70,IXS,ISYS,IZS)
90 FORMAT (910)

C WHEN MORE THAN ONE CHAIN IS USED, TREAT THEM AS ONE CHAIN
C WITH MORE THAN TWO END READS
NCF=0

READ (5,100) NCHAIN,NSTART(I),NEND(I),I=1,NCHAIN
100 FORMAT (1111)

IF (NCHAIN.GT.0) NCF=1
IF (NSTART(NCHAIN).GT.9000) GO TO 130

NCF=NEND(NCHAIN)-NCHAIN
NCHAIN=NCHAIN*2

DO 120 I=NCHAIN,NCF+1
120 CONTINUE

NCF=0

IF (I.IN.2,I,10) GO TO 515

DO 510 J=1,N
510 FORMAT (910)

READ (500,LTAB(J),I=1,N)
500 CONTINUE

CALL PACK(LTAB(J))

CONTINUE

GO TO 515
515 FORMAT (910)

READ (515,NTAB(I),I=1,N)
515 CONTINUE

PRINT (520,IRAN=10)
520 FORMAT ('** INITIAL CONFIGURATION FINAME',5X,'IRAN= ',9(111,5X,'**','i,13))

DO 540 E=0,J=1,NCHAIN

I=NSTART(J)
J=NEND(J)
PRINT (540,E,J,NTAB(I),I=1,J,10)
540 FORMAT ('** FINAME',5X,'CHAIN= ',9(111,5X,'**','i,13))
MEMBER NAMM MAIN
550 CONTINUE
IF (NCHAIN.LE.50) ISAMP=NCHAIN
IF (NCHAIN.LE.50) IINC=1
IF (NCHAIN.LE.50) GC TO 560
INC=NCHAIN/50
ISAMP=NCHAIN/INC
IF (INC.EQ.0) IINC=1
IF (ISAMP.GT.20) ISAMP=50
560 DT=70 J=1 ISAMP
INC(J)=0
DO 570 J=1,2
AVGL(I,J)=0.0
AVGL(I,J)=0.0
D4(J)=0.0
D2(J)=D2(J)
IF (NFRAME.LE.5) NTIME=NFRAME
IF (NFRAME.GT.5) NTIME=5
DO 570 KMM=1,NTIME
ECROSS(KMM,I,J)=0.0
570 RCROSS(KMM,I,J)=0.0
IFrame=1
CALL LDAMP
FRAME=NFRAME
CALL CHMAP
CALL CTMAP
NCYCLE=0
NTEV=0
DO 590 J=1,N
DC 590 J=1,ISAMP
DO 590 K=1,KYS
DO 590 K=1,KYS
DO 590 K=1,KYS
DO 590 K=1,KYS
590 CONFIN(I,J,K)=0.0
CALL PRM
C COMPUTE THE FRACTION OF EXCLUDED VOLUME CONFLICTS
PEVC=FLOAT(NTEV)/FLOAT(NCYCLE)
C COMPUTE THE BEAD DENSITY
BDEN=FLOAT(N)/BOX(1)*BOX(2)*BOX(3))
C IF (IBOUT.EQ.0) GO TO 595
WRITE (*,595) (NTAB(J),J=1,N)
595 FORMAT (8(Z8,4X))
C COMPUTE AND PRINT DATA FOR EACH CHAIN
585 DO 600 J=1,ISAMP
PRINT 400,HEA2
PRINT 590,NCYCLE,NFRAME,NCYCLE,PEVC
590 FORMAT (*14,'NFRAME=',I3,'NFRAME=',I4,'TOTAL BEAD CYCLES=',I3,
*12,'BDEN=1.0000',F6.4)
C COMPUTE THE NUMBER OF BEADS IN JTH CHAIN
NFRAME(N-J-1)-NTAB(J)+1
PRINT 600,HEA15
600 FORMAT (*12,'CHAIN #=',I3,' BOX=',I3,' TOTB # READS=',I3,
*12,'BDEN=',F6.4)
**MEMBER NAME MAIN**  

**COMPUTE <L2>,<L4>, AND THEIR STD OVER THE N RUNS**

```plaintext
AVGL(2,1:J)+AVGL(4,1:J) = AVGL(2,1:J) + AVGL(4,1:J) / NRUN
```

**COMPUTE <D> AND ITS STD OVER THE RUNS**

```plaintext
DF = 0.0, DF = SUM((XJ=I,J) – XJ=J,J) / NRUN
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <P(L2,L2,T)> THIER STD AND NATURAL LCS**

```plaintext
DO 670 K = 1, KOUNT
```

**COMPUTE <KJ> AND KJ>**

```plaintext
DO 670 K = 1, KOUNT
```
MEMBER NAME MAIN

IF (ISAMP.LE.2) GO TO 915
PRINT 40, NREAD
PRINT 600, XCH1A, NRUN, NFRAME
690 FERMAT('AVERAGES OF '12,'CHAINS FOR '13,'RUNS OF '14,'FRAMES EACH')
PRINT 700, CYCLE, PEVC, RDEN
700 FERMAT('1H,'TOTAL BEAD CYCLES','18,'XMOV/100','FC',"
*BEAD DENSITY ','FC',"
PRINT 710, INSYS, ISSN, ISAMP
710 FERMAT('1H,'BOX','12,2('X','12'),'TOTAL' # OF BEADS','13"
*14,'TOTAL # OF CHAINS','13'
D1=0 4
D3=0 .
PCH=0
DO 720 J=1,4
720 AVG(1)=0.0
DC 730 J=1,ISAMP
AVG(1)=AVGL2(1,J)+AVG(1)
AVG(2)=AVGL2(1,J)+AVG(2)
AVG(3)=AVGL4(1,J)+AVG(3)
AVG(4)=AVGL4(1,J)+AVG(4)
IF(D(J),NE.0) MCH=MCH+1
D1=D(J)+1
D3=D(J)+3
AVG(2)=SORT((AVG(2)-AVG(1)**2/ISAMP)/(ISAMP-1))
AVG(1)=AVGL1/ISAMP
AVG(4)=SORT((AVG(4)-AVG(3)**2/ISAMP)/(ISAMP-1))
AVG(3)=AVGL3/ISAMP
PRINT 610,'(AVG(1),J=1,4)
IF ((MCH.GT.0).AND.(MCH.EQ.1)) GO TO 731
731 D555hh='(D3-DO**2/MCH)/(MCH-1))
D1=D1/MCH
PRINT 620,D1,D3
DC 750 K=1,NCOUNT
DO 760 I=1,4
760 COEFC(1)=0.0
DC 770 J=1,ISAMP
COEFC(1)=COEFC(1)+COEFC(1)
COEFC(2)=COEFC(2)+2+COEFC(2)
COEFC(3)=COEFC(3)+COEFC(3)
COEFC(4)=COEFC(4)+2+COEFC(4)
750 CONTINUE
COEFC(2)=SORT((COEFC(2)-COEFC(1)**2/ISAMP)/(ISAMP-1))
COEFC(1)=COEFC(1)/ISAMP
COEFC(4)=SORT((COEFC(4)-COEFC(3)**2/ISAMP)/(ISAMP-1))
TENP=COEFC(1)
IF (TENP.LE.2.0) TENP=.0001
ALNL=LOG(TENP)
TENP=COEFC(3)
IF (TENP.LE.2.0) TENP=.0001
ALNL=LOG(TENP)
IF (K.NE.1) GO TO 765
PRINT 40,1,(COEFC(1),I=1,4),ALNL,(COEFC(1),I=3,4),ALNL2
IP=0
WRITE(8,240) IP,COEFC(1)
MEMBER NAM MAIN
CT 2 760
760 IF(NFRAME>LE5,5)NTIME=NFRAME
1F(NFRAME<GT5)NTIME=5
DO 450 KM=1,NTIME
DO 770 L=1,ISAMP
CCROSS(KMM,1)=0.0
DO 770 KM=1,NTIME
CCROSS(KMM,1)=CCROSS(KMM,1,1))**2+CCROSS(KMM,1,1)
CCROSS(KMM,2)=CCROSS(KMM,2,1)**2+CCROSS(KMM,2,1)**2/ISAMP)
CCROSS(KMM,1)=CCROSS(KMM,1,1))**2+CCROSS(KMM,1,1)**2/ISAMP)
CCROSS(KMM,2)=CCROSS(KMM,2,1)**2+CCROSS(KMM,2,1)**2/ISAMP)
810 PRINT 310
820 FORMAT(' C C O R R E L A T I O N T A B L E ')
830 PRINT 300
840 PRINT 300
900 PRINT 900
910 FORMAT(' D**2 F(D**2')
915 DD 920 I=1,ISAMP
920 L=1**2
930 FORMAT(' END
COMMON HRF,13N,IXS,IYS,12S,11CHAIN,ISUM(3),15(S),1SEP(3),
1 IFRAME,NFX,IX,JCHAIN,NCHAIN,NRUN,
2 NICYC,NCYC,LNV,LKYS,NPRINT,KOUNT,NTABLE(32),MOVE(3,50),
3 CNM1(15000),MAP(4096),NSTART(15000),
4 NCHAIN(15000)
C
1 COMMON/CORRFN/FLSOR(50),FLFIGHT(50),NCYC(35),TCYC(35),TCINC(35),
2 SIN0(2,50,35),CORPFN(4,50,35),ISAMP,INCR,HCV(3),SOCM(3,50),
3 AVGX(2),AVG(2,50),
4 READ 10, FACTOR, FCUBE, FADD
C
MEMBER NAME = MAIN

10 FORMAT (3F10.4)
IN = IEND(1)-NSTART(1)+1
TOTAL = AINT(FCUBE*FLCAT(IN*IN/N))
TOLD = T
KYS = 0
KUFI = 0
ISY = 0
C IF MORE THAN 50 SAMPLES ARE DESIRED, COUNTER MUST BE INCREASED.
IF(FCUBE*FLCAT(IN*IN/N)) .GT. 50
KYS = KYS + 1
TNEW = INT(TOLD*FACTC) + FADD
IF(TNEW = TOTAL) 40, 30, 20
20 TNEW = TOTAL
30 NCYCS(1) = TNEW - TOLD
TNC(1) = TNEW
NCYC = NCYC + 1
TCYC(1) = TCYC + 1
30 CONTINUE
50 TOTAL = TNEW
60 PRINT 70
70 FORMAT (1H, 'NCYCS RESPONSED')
71 KYS
80 FORMAT (1H, NUMBER OF SAMPLES PER FRAME = '13.5X,
* NUMBER OF BEADS = ', 15)
PRINT 90, FACTC, FCUBE, FADD
90 FORMAT (1H, 'FACTOR = ', F10.3, 'FCUBE = ', F10.3, 'FADD = ', F10.3)
PRINT 200, TOTAL
200 FORMAT (1H, TOTAL NUMBER OF BEAD CYCLES PER FRAME = ', F7.0)
PRINT 210, TOLD
210 FORMAT (1H, 'TNEW = INT(TOLD*FACTC) + FADD')
PRINT 220
220 FORMAT (1H, 'NO. OF SAMPLE NCYC , TCYC , TCYC/N**3')
PRINT 230, TN, TCYC(1), TCYC(1), TCYC(1), TCYC(1), TCYC(1)
230 RETURN
END
SUBROUTINE PRINT

COMMON N, IR, IPAM, IXS, IYX, I2Z, I2S, I2N, ICHAIN, ISUM(3), IS(3), ISEP(3)
1 IPAM**NAME,NCHAIN,NCAYL,NCHAIN,NSEP,
2 ICHAIN, NCYCL, KYS, PRINT, KCOUNT, TABLE(32), IMOVE(3,50),
3 INULL(3,50), NTAE(15000), MMPI(4050), NSTART(15000),
4 KFAM(15000)

COMMON JREF, FLHSG, FLHSG(50), FLHSG(50), NCYCS(35), TCYC(35), TCYC(35),
1 CPFGN(4,50,30), ISAMP,1KCF, JPX(3), JDCM(3,50),
2 SVDCM(50), KSR(50), JFRAME(50), D2(50), D4(50), AVGJ(2,50),
3 AVGJ(2,50)

INTEGER*4 T, NSFR
MEMBER NAME MAIN

220  FORMAT( 11, 13, 15, 16, 17) TCYCS( -1), NCYCS( -1)

230  CONTINUE

DO 240 I = 1, KUNIT

240  CONTINUE

260  CONTINUE

280  CONTINUE

300  CONTINUE

320  CONTINUE

340  CONTINUE

360  CONTINUE

380  CONTINUE

1006  CONTINUE

COMMON H, L, IRAN, IXS, IYX, IZS, IN, IRCHAIN; ISUM(3), IS(3), ISEP(3),

I FRAMES; CHAIN, INCHAIN, KNPUT;

L; IMOVE(3, 50), IMPULS(3500), MAP(4095).

PAGE 0034
DIMENSION S(3), E(3), B(3)

J = 0

DO 140, I = 1, NCHAIN, NCR
    J = J + 1

140 CONTINUE

CALL UNPACK(N1, N2)

LGF = 0

DO 20, I = 1, J

20 CMNI = CMN(I) / FLOAT(I + N2 - N1)

C PUT CENTER IF X<0 INSIDE OF THE BOX

DC 30, I = 1, J

30 IF (CMNI(I, 1, 0)) CMNI = CMNI + BOX(I)

IF (KPMNI(N, 1)) GO TO 50

LSOP(J) = LSOP

DO 40, J = 1, J

40 SL(I, J) = SL(I)

IF (I(EF(J - 1, 1))) GO TO 45

50 CONTINUE

GO TO 100

CALCULATE DIFFUSION

C
MEMBER NAME MAIN

COMMON/COREFH/FLSOFR(50),FLFOUR(50),NCYCS(35),TCYCS(35),TCNCR(35),
1 CCSTR(2,50,35),CCDFH4(4,50,35),FAMP,FACR,DFX(3),SDCM(3,50),
2 CCDFH(50),CDFH(50),DFRAME(50),DZ(50),D4(50),AVGL2(2,50),
3 AVGL4(4,50)

DO 10 J=1,NCHAIN,INCR
    IF (ICHAIN.EQ.IJ) IM=1
    IF (ICHAIN.EQ.IJ) ICHAIN=IJ
    IF (IJ.EQ.50) IJ=NCHAIN
    CONTINUE
    RETURN
10 END

PAGE 003B
MEMB NAME: LDMAP

LDMAP CSECT

SAVE (14,12) INITIAL LOADING OF MAP FROM NTAB

* LDMP: INITIALIZES MAP TO ZERO AND THEN LOADS MAP ACCORDING TO LTAE

* EVERY POSSIBLE READ LOCATION CORRESPONDS TO A BIT IN MAP.

* A BIT IN MAP IS ONE IF THE CORRESPONDING READ LOCATION CONTAINS A READ AND ZERO OTHERWISE.

* EACH WORD IN MAP CORRESPONDS TO A SET OF READ LOCATIONS WITH A

* PARTICULAR PAIR OF X AND Y COORDINATES AND VARYING VALUES OF Z.

* THE 32 BITS IN EACH WORD CORRESPOND TO EITHER THE 32 LOCATIONS WHERE X IS LESS THAN OR EQUAL TO 31 OR THE 32 LOCATIONS WHERE X IS GREATER THAN OR EQUAL TO 32. TO DIFFERENTIATE BETWEEN THESE TWO CASES, A

* BIT IN THE ADDRESS OF MAP IS EITHER 1 OR 0.

* HENCE THE CORRESPONDENCE BETWEEN WORDS IN MAP AND READ LOCATIONS IS:

* (X,Y,Z) => MAP(Y*(Z**7) + Z + C*(2**6))

* WHERE C = 0 IF X<32 AND C=1 IF X>31.

* FOR ANY PARTICULAR WORD IN MAP, IF THE NTH BIT IS 1, THEN THERE IS A

* READ AT (N-1,Y,Z) OR (N-1+32,Y,Z).

* FOR EXAMPLE, IF MAP(1)=1000000000000000000000000000000001, THEN THERE IS A READ AT (1-1,0,0) OR (1-1+32,0,0).

* IF MAP(1000000000000000000000000000000001) =

* THEN THERE ARE READS AT (X,Y,Z) = (12,4,3), (12,4,3), (24,4,3), (36,4,3).

* THEN THERE ARE READS AT (X,Y,Z) = (44,4,3), (45,4,3), (56,4,3).

* TABLE(32) IS INITIALIZED. TABLE(1)=Z**1(1-1)

* LA 3,1

* TABLE(32) IS INITIALIZED. TABLE(1)=Z**1(1-1)

* LA 5,31

* L1 4,1

* ST 4,1

* TABLE(32)

* A 3=F4

* BCT 5,1

* ZERO OUT ALL OF MAP

* LA 15,ACMC4

* LA 1,0

* LA 5,4

* L 5,F'1638'6

* LA 6,0

* AGAIN ST 5,5(4,15)

* HLX 1,2 AGAIN

* LOAD MAP

* NOTE: VALUES FOR X, Y, AND Z OCCupy 6 BITS

* SLP 1,1

* REG 1 - INDEX OF NTAB

* SLP 11

* HERE

* SLP 5,5

* SRL 5,4

* SRL 5,4

* SRL 5,4

* SRL 5,4

* CR 4,10

* COMPARE X WITH 31
<table>
<thead>
<tr>
<th>MEMBER NAME</th>
<th>LOAD MAP</th>
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<tr>
<td>MNH</td>
<td>DON'</td>
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<tr>
<td>PUT 1 IN UNUSED BIT BETWEEN X AND Z</td>
<td>00030590</td>
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<td>DONT</td>
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<td>2,=F'14*</td>
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<td>4,=H4*</td>
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<td>7,0(3,15)</td>
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<td>ST</td>
<td>0(3,15)</td>
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<td>INCREMENT NTAB POINTER</td>
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<td>PCT</td>
<td>11,HERE</td>
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<td>13,SAVI+4</td>
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<td>12(13),X'FF'</td>
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</table>
MEMBER NAME: CHAIN

CHAIN SECTION

* THIS SUBROUTINE DETERMINES IF A WALL HIT SHOULD BE COUNTED
* AS A HIT. FOR EXAMPLE IF A LOW X WALL WAS HIT FOLLOWED BY
* A HIGH X WALL HIT THEN THE NET EFFECT IS THAT NO WALL WAS
* HIT AND IWALL MUST BE SET TO EITHER 0 OR TO THE NUMBER OF
* THE WALL HIT PREVIOUS TO THESE TWO HITS.

SAVE (14,12)
HELP 11
USING 9,11
L 12,ACOM F12 = ADDRESS OF BLANK COMMON
USING N,12
ST 13,SAV+4
LA 13,SAV

* IT CONTAINS THE NUMBER OF WALL HIT. THIS IS PASSED IN P7 FROM CYCLE.

* IWALL = 1 IF THE LOW X WALL WAS PENETRATED
* IWALL = 2 IF THE HIGH X WALL WAS PENETRATED
* IWALL = 3 IF THE LOW Y WALL WAS PENETRATED
* IWALL = 4 IF THE HIGH Y WALL WAS PENETRATED
* IWALL = 5 IF THE LOW Z WALL WAS PENETRATED
* IWALL = 6 IF THE HIGH Z WALL WAS PENETRATED

* IF THIS IS THE FIRST TIME THROUGH CYCLE THEN
* ZERO THE ARRAYS END,BEGIN, AND BOTH OTHERWISE DON'T

ST 3,PLACE P4 = ADDRESS OF PASSED ARGUMENT
L 4.0(1) P4 = TIME
C 4,=F101 IF TIME > 0 THEN
BNE NO DON'T ZERO ARRAYS
ZERO ARRAYS

XU 3,3
LA 9,530
XU 9,3
ST 5,TBL1(3)
ST 5,COUNT(3)
ST 5,TBL(3)

SB 3,4(3)
BCT 5.5
LA 3,PLACE TEST TO SEE IF A WALL IN THIS
C 5,=F101 DIMENSION WAS HIT BEFORE BY THIS
ST 5,PLACE CHAIN
BE 12 IF NOT GO TO ONE
C 5,=F11 IF THIS WALL HAS BEEN HIT BY THIS
BE 10 TO CHAIN ONE BEFORE TO TWO

* SAME WALL HAS BEEN HIT TWO TIMES BEFORE THIS HIT BY THE SAME CHAIN
ST 5,TBL(3) FS = LAST WALL HIT
ST 5,TBL3(3) FS = LAST WALL HIT
ST 5,TBL(3) FS = LAST WALL HIT
ST 5,TBL3(3) FS = LAST WALL HIT
C 5,=F120 IF SAME WALL WAS HIT
RE ZIP THIS TIME GO TO ZIP
LA 6.1 CANCEL LAST HIT
ST 5,COUNT(3) COUNT = 1
L 5,TBL1(3)
ST 5,IWALL(3) IWALL IS THE WALL HIT 2 TIMES AGO
ST 5,TBL(3) TBL = 0

ZIP LA 5.5 WALL HIT THIRD TIME
ST 5,COUNT(3) SAME AS IF WALL HAS BEEN HIT ONCE
XR 5.5
MEMBER NAME : CHAIN

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<th>Variable</th>
<th>Address</th>
<th>Description</th>
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<td>ST</td>
<td>7</td>
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<td>7</td>
<td>TBL(1)</td>
</tr>
<tr>
<td>B</td>
<td>RETURN</td>
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<tr>
<td>L</td>
<td>5</td>
<td>TBL(1)</td>
</tr>
<tr>
<td>CP</td>
<td>5,7</td>
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</tr>
</tbody>
</table>

* WALL HAS BEEN HIT BY CHAIN 2 TIMES IN A ROW

<table>
<thead>
<tr>
<th>Variable</th>
<th>Address</th>
<th>Description</th>
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<tr>
<td>ST</td>
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<td>Iwall(3)</td>
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<tr>
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<td>7</td>
<td>TBL(3)</td>
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<td>ST</td>
<td>6</td>
<td>COUNT(3)</td>
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<tr>
<td>R</td>
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</tr>
<tr>
<td>ONE</td>
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<td></td>
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<tr>
<td>ST</td>
<td>7</td>
<td>Iwall(3)</td>
</tr>
<tr>
<td>LA</td>
<td>5,1(5)</td>
<td></td>
</tr>
<tr>
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<td>COUNT(3)</td>
</tr>
<tr>
<td>R</td>
<td>RETURN</td>
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<tr>
<td>ONE2</td>
<td></td>
<td></td>
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<tr>
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<tr>
<td>L</td>
<td>14,15,12(13)</td>
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<tr>
<td>SAV</td>
<td>DS 19F</td>
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<tr>
<td>TBL1</td>
<td>DS 150F</td>
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</tbody>
</table>

THE WALL HIT 2 TIMES BEFORE BY GIVEN CHAIN

THE WALL HIT BY GIVEN CHAIN

NUMBER OF TIMES A CHAIN HAS HIT A GIVEN WALL FROM 0 TO 2

TIME = 0 FIRST TIME BRANCH FROM CYCLE OCCURS

INDEX FOR VARIABLES IN ALL ARRAYS IN THIS SUBPROGRAM

A(GO) DC A(N)

N DC F

Iwall DS 203F

MEMBER NAME CHAIN
MEMBER NAME CYCLE

CYCLE CSCT

- SUBROUTINE TO PERFORM READ MOVEMENTS
- CYCLE
- CSCT
- COUNTER AND TIMING
- MEMBER
- NAME
- CYCLE
- CSCT
- INITIALIZATION
- LENGTH OF ENTRY NAME
- 12(15)
- ENTRY
- NAME
- CLTV CYCLE
- ENTRY POINT NAME
- SAVE
- ENTRY POINT NAME
- 14(12)
- SAVE ALL REGISTERS EXCEPT 13
- L
- 2,0(1)
- F2 = ADDRESS OF THE PASSED ARGUMENT
- USING
- 1,12
- LOAD BASE ADDRESS
- USING
- N
- 11
- ACOM
- ST
- 13,SAV+4
- SET UP SUBROUTINE SAVE AREA
- LA
- 13,SAX
- TIME = 0
- START
- 4,TIME
- FIRST TIME THROUGH CHAIN
- XG
- 3,3
- ICHAIN = 0
- L
- 5,CHAIN
- ****************************************************
- M
- 4,MULT
- GENERATE A RANDOM NUMBER OF
- N
- 5,00
- IF IT IS 0 DO A CRANKSHAFT
- ST
- 5,CHAIN
- IF IT IS 1 DO A SINGLE
- LA
- 3,2
- READ MOVEMENT
- SLN
- 3,1
- MVNE
- HN
- 4,3
- ******************************************************
- FN
- 4,FQ0
- SINGLE READ MOVEMENT SELECTED
- ******************************************************
- L
- 5,ICHAIN
- ****************************************************
- M
- 4,MULT
- GENERATE A RANDOM NUMBER FROM 0 TO N-1
- N
- 5,00
- P3 = P3 * 2
- ST
- 3,1
- ******************************************************
- HN
- 4,3
- ****************************************************
- ST
- 4,IR
- THIS IS NEEDED FOR ADDRESSING
- ******************************************************
- XG
- 7,7
- F3 = 1 INCREMENT BY 1 EACH TIME
- LA
- 3,1
- THROUGH THE LOOP
- XG
- 6,6
- USE TO INDEX NEND
- LA
- 9,ICHAIN
- F3 = 0
- LA
- 4,IR
- L
- 9,KCHAIN
- F9 = NO OF CHAIN TO BE SAMPLED
- LA
- 4,IR
- LOOP
- L
- 10,ACOM
- F10 = ADDRESS OF NEND
- LA
- 9,0L
- P3 = P3 + 1
- CP
- 4,0
- COMPARE IF+1 TO NEND
- PH
- 4,0
- IF+1 IS NOT LE NEND, SO CHAIN
- ST
- 3,ICHAIN
- NUMBER IS NOT ICHAIN
- B
- FOUNH
- JUMP OUT OF LOOP
- ROM
- 3,13
- ICHAIN = ICHAIN + 1
- LA
- 6,AFC
- IF CHAIN IS ICHAIN
- HCT
- 3,LOOPC
- CHAIN NO IS BETWEEN 0 AND N-1
- FOUND
- 3,EE
- ICHAIN = ICHAIN + 4
- SLL
- 3,2
- 00000010
- 00000020
- 00000330
- 00000340
- 00000350
- 00000360
- 00000370
- 00000380
- 00000390
- 00000400
- 00000410
- 00000420
- 00000430
- 00000440
- 00000450
- 00000460
- 00000470
- 00000480
- 00000490
- 00000500
- 00000510
- 00000520
- 00000530
- 00000540
- 00000550
- 00000560
- 00000570
- 00000580
MEMBER NAME: CYCLE

LA 5,3
ST 5,READ          BEAD = 3
B STPLACE

* BEADIC L 4,1R
ELL 4,2
LL 6,NTAB(4)
LA 5,0
ST 5,READ
H STPLACE
  FIRST BEAD IN A CHAIN SELECTED
  RA = 4*(IR - 1)  INDEX REGISTER

* BEADNC L 4,1R
ELL 4,2
LL 6,NTAB(4)
LA 5,0
ST 5,READ
H STPLACE
  THE LAST BEAD IN A CHAIN SELECTED

STPLACEC ST 4,PLACE
  PLACE=ADDRESS IN NTAB OF MOVING BEAD

RANENDC L 5,1RAN
  ***************

ST 4,ICE
C 4,IF '1'
  IF ICE = 0 OR 1 THEN MOVE IN

CNH 4,IF '2'
  IF ICE = 2 OR 3 THEN MOVE IN

CTOC 4,IF '3'
  IF ICE = 0 ADD 1 TO X DIMENSION

CTOC 4,IF '4'
  IF ICE = 0 ADD 1 TO X DIMENSION

TRIVC L 4,PLACE
  PLACE = ADDRESS IN NTAB OF MOVING BEAD

ST 4,ICE
C 4,IF '1'
  IF ICE = 0 OR 1 THEN MOVE IN

CNH 4,IF '2'
  IF ICE = 2 OR 3 THEN MOVE IN

CTOC 4,IF '3'
  IF ICE = 0 ADD 1 TO X DIMENSION

CTOC 4,IF '4'
  IF ICE = 0 ADD 1 TO X DIMENSION

ADD 4,ADD
  IF ICE = 3 THEN ADD 1 TO Y POSITION

SUBT 4,SUBT
  IF ICE = 3 THEN SUBTRACT 1 FROM Y

ADD 4,ADD
  IF ICE = 3 THEN ADD 1 TO Z POSITION

SUBT 4,SUBT
  IF ICE = 3 THEN SUBTRACT 1 FROM Z

MOVE AN END BEAD

SUBTC ER 8,10
  STSTAVC

ADD 8,ADD
  STAB = MOVED BEAD COORDINATES

STSTAVC ST 2,STAR
  STAB = MOVED BEAD COORDINATES

ST 8,STAR
  R8 = 0

L 4,PLACE
  R4 = ADDRESS IN NTAB OF MOVING BEAD

L 5,READ
  R5 = ADDRESS IN NTAB OF MOVING BEAD

PL TESTCC
  NO_MORE MOVES NECESSARY

RE 5,STAR

L 4,PLACE
  RB = STAB + NTAB(IR)
<table>
<thead>
<tr>
<th>MEMBER NAME</th>
<th>CYCLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 NTAB - 4(4)</td>
</tr>
<tr>
<td></td>
<td>4 STAB</td>
</tr>
<tr>
<td></td>
<td>4 PLACE</td>
</tr>
<tr>
<td></td>
<td>4 STAB1</td>
</tr>
<tr>
<td></td>
<td>5 STAB</td>
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<tr>
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<td>5 STAB4</td>
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<td>4 STAB1</td>
</tr>
<tr>
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<td>3128</td>
</tr>
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<td>5 ef '129Val</td>
</tr>
<tr>
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<td>5 ef '129Val</td>
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<td>5 ef '129Val</td>
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<td>5 ef '129Val</td>
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<tr>
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<td>4 STAB1</td>
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<td>3128</td>
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<td>4 STAB1</td>
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<td>5 ef '129Val</td>
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<tr>
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<td>5 ef '129Val</td>
</tr>
</tbody>
</table>

PAGE 0018
MEMBER NAME  CYCLE
ST 5,MAP181  MAP181=INDEX IN MAP FOR STAB1 00004670
L 4,MAP181  R4 = TABLE181 00004680
L 5,MAP181  R5 = MAP181 00004690
* NO EXCLUDED VOLUME CONFLICT FOR STAB OR STAB1 SO CHANGE MAP AND
* UPDATE NTAB FOR NEW LOCATION OF STAB
PUT L 7,MAP181  00004700
L 10,ACM+12  R10 = ADDRESS OF MAP 00004710
ST 7,05,10  MAP(5) = 1 00004720
* REMOVE IF IN MAP FOR OLD LOCATION FOR STAB
L 10,ACM+12  R10 = ADDRESS OF MAP 00004730
C 10,IF*3' 00004740
ONE  H,PLACE IF LAST BOND MOVED 00004750
L 3,PLACE  THEN PLACE=PLACE*4 00004760
L 4,NTAB(2)  DLDC=NTAB OF LAST READ ON CHAIN 00004770
L 3,PLACE  RA = NTAB OF LAST READ IN CHAIN 00004780
L 0,HL8  END BOND DID NOT MOVE 00004790
ST 3,PLACE  RA = NTAB OF MOVING READ 00004800
L 4,NTAB(3)  OLDC=NTAB(PLACE) 00004810
MEMBER NAME  CYCLE
ST 5,MAP181  MAP181=INDEX IN MAP FOR STAB1 00004820
L 4,MAP181  R4 = TABLE181 00004830
L 5,MAP181  R5 = MAP181 00004840
* NO EXCLUDED VOLUME CONFLICT FOR STAB OR STAB1 SO CHANGE MAP AND
* UPDATE NTAB FOR NEW LOCATION OF STAB
PUT L 7,MAP181  00004850
L 10,ACM+12  R10 = ADDRESS OF MAP 00004860
ST 7,05,10  MAP(5) = 1 00004870
* REMOVE IF IN MAP FOR OLD LOCATION FOR STAB
L 10,ACM+12  R10 = ADDRESS OF MAP 00004880
C 10,IF*3' 00004890
ONE  H,PLACE IF LAST BOND MOVED 00004900
L 3,PLACE  THEN PLACE=PLACE*4 00004910
L 4,NTAB(2)  DLDC=NTAB OF LAST READ ON CHAIN 00004920
L 3,PLACE  RA = NTAB OF LAST READ IN CHAIN 00004930
L 0,HL8  END BOND DID NOT MOVE 00004940
ST 3,PLACE  RA = NTAB OF MOVING READ 00004950
L 4,NTAB(3)  OLDC=NTAB(PLACE) 00004960
MEMBRANE NAME CYCLE
BAGGINSC BUF DL 5,8
SCL 5,24
NTAB(X) IN R0
SCL 2,6
SPL 7,24
STAB(X) IN R7
SF 7,7
NTAB(X)-STAB(X) IN R5
C 9,=F*2
HIGH WALL HIT
FH X1 9,=F*2
LOW WALL HIT
PL 5,3
ALL 3 DIMENSIONS HAVE BEEN CHECKED.
* THE FOLLOWING LINES UP TO FINISH ARE BRANCHED TO IF A WALL
* HAS BEEN PENETRATED. OTHERWISE THEY ARE NOT EXECUTED.
X0 3,5
L 7,IMOVE(3)
LOW X WALL HIT
S 7,=F*1
ST 7,IMOVE(3)
MOVE=MOVE+1
LA 7,1
R7 = 1, PASS TO CHAIN
RALP 14,15
ADD SUB
F15 = ADDRESS OF CHAIN
ST 14,TIME
R14 > 0
NEW CYC
L 3,5
MOVE NEXT BEAD
ST 14,TIME
TIME > 0
NEW CYC
L 3,5
MOVE NEXT BEAD
X1 3,5
L 7,IMOVE(3)
HIGH X WALL HIT
S 7,=F*1
ST 7,IMOVE(3)
MOVE=MOVE+1
LA 7,4
PASS F7=4 TO CHAIN
RALR 14,15
ADD SUB
F15 = ADDRESS OF CHAIN
ST 14,TIME
TIME > 0
NEW CYC
L 3,5
MOVE NEXT BEAD
Y0 3,5
LA 3,4(3)
LOW Y WALL HIT
ST 7,IMOVE(3)
MOVE = MOVE+1
LA 7,2
R7 = 2 PASS TO CHAIN
RAL 14,15
ADD SUB
F15 = ADDRESS OF CHAIN
ST 14,TIME
TIME > 0
NEW CYC
L 3,5
MOVE NEXT BEAD
Y1 3,5
LA 3,4(3)
HIGH Y WALL HIT
ST 7,IMOVE(3)
MOVE = MOVE+1
LA 7,5
P7 = P7+1
ST 7,IMOVE(3)
MOVE = MOVE+1
LA 7,5
ST 14,TIME
TIME > 0
NEW CYC
L 3,5
SAMP
PL 15,ADDRSUB
R15 = ADDRESS OF CHAIN
AR 14,15
BRANCH TO CHAIN
ST 14,TIME
TIME > 0
NEW CYC
L 3,5
H BAGGINSC
NEW CYC
L 3,5
SAMP
LA 3,4(3)
HIGH Z WALL HIT
ST 7,IMOVE(3)
MOVE = MOVE +1
LA 7,3
P7 = P7+1
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,3
ST 14,TIME
TIME > 0
NEW CYC
L 3,5
SAMP
LA 3,9(3)
LOW Z WALL HIT
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,9
P7 = P7+1
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,3
ST 14,15
BRANCH TO CHAIN
NEW CYC
L 3,5
SAMP
LA 3,9(3)
LOW Z WALL HIT
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,9
P7 = P7+1
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,3
ST 14,15
BRANCH TO CHAIN
NEW CYC
L 3,5
SAMP
LA 3,9(3)
LOW Z WALL HIT
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,9
P7 = P7+1
ST 7,IMOVE(3)
MOVE = MOVE -1
LA 7,3
ST 14,15
BRANCH TO CHAIN
MEMBER NAME PACK
PACK CSECT
* THIS SUBPROGRAM PACKS THE X, Y, AND Z COORDINATES OF ONE BEAD INTO NTAB.
* NTAB(1) = (LTAB(3,1)+2*16)+(LTAB(2,K)+2*8)+(LTAB(3,1))
* 
SAVE (1+12)
RAE 3,0
USING 12 ACOM
F12 = ADDRESS OF BLANK COMMON
L 12, ACOM
* 
L 3,0(1)
S 3 =F'1'
SLL 2,2
L 2,0(1)
* 
L 4,0(2)
L 5,4(2)
L 6,4(3)
L 6,5
SPL 6,6
SPL 6,7
SPL 7,8
ST 7, NTAB(3)
LM 1,16,12(13)
LM 1,12,24(13)
XVI 12(13), X'FF'
* 
ENTRY UNPACK
* UNPACK CALCULATES THE SUM OF X, Y, AND Z COORDINATES AS WELL AS VECTOR EN TO END LENGTH AND THE NUMBER OF TIMES THE CHAIN IS SPLIT. THESE ARE USED IN SUBROUTINE SAMPLE
* 
UNPACK SAVE (1+12)
USING UNPACK,15
L 12, ACOM
USING 12, ACOM
* 
L 3,0(2)
S 3 =F'1'
SLL 3,2
L 2,0(1)
* 
L 2,0(2)
L 3,2
SLL 2,2
ST 2, N1
* 
F2 = ADDRESS OF N2
F3 = ADDRESS OF N3
F2 = ADDRESS OF NTAB OF NTAB OF
THE LAST BEAD IN THE CHAIN
R2 = N1
R1 = (N1-1) * 4
N1 IS THE ADDRESS IN NTAB OF THE FIRST HEAD IN THE CHAIN
FIND OUT HOW MANY TIMES THE CHAIN IS SPLIT
*
MEMBER NAME: BACK

* TO FIND OUT HOW MANY TIMES THE CHAIN IS SPLIT LOOK AT SUCCESSIVE PAIRS OF READS TO SEE IF THEY ARE MORE
* THEN ONE LATTICE SITE APART, THESE PAIRS ARE LABELED X1Y1Z1 AND X2Y2Z2 IN THE COMMENTS.

LOOP

C
LA 10,8
R10 = 8

L 3,1
F3 = 3

L 4,NTAB(2)
F4 = NTAB OF FIRST READ = X1Y1Z1

L 6,NTAB+4(2)
F6 = NTAB OF SECOND READ = X2Y2Z2

C
SPLDL 4,8
R4 = - X1Y1Z5

SPLDL 6,4
R6 = - X2Y2Z4

SPL 7,2a
R7 = - Z2 - Z1

ST 7,2a
F5 = Z2 - Z1

C
7,SF+1
IF Z2 = Z1 = 1 THEN

BE WHOLE
THE CHAIN IS NOT SPLIT

C
7,SP-1
IF Z2 = Z1 = -1 THEN

BE WHOLE
THE CHAIN IS NOT SPLIT

C
7,SF+0
IF Z2 = Z1 = 0 THEN

BE WHOLE
THE CHAIN IS NOT SPLIT

L 9,ISEP(10)
FIND X,Y, OR Z SET

ST 9,ISEP(10)
ISEP = ISF + 1

WHOLE

RCT 3,6
CHECK Y, THEN X

LA 3,4(2)

ST 2,12
IF ALL READS HAVE BEEN
CHECKED LEAVE LOOP

* CALCULATE CENTER OF MASS OF CHAIN

* FIRST READ IN CHAIN DOESN'T NEED RECONNECTION

L 2,4:1
F2 = X1

L 4,NTAB(2)
F4 = _X1Y1Z1, NTAB OF FIRST READ

SPLDL 4,8
F4 = - X1Y1R5 = Z1

SPL 5,2a
R5 = Z1

ST 5,LAST+3
LAST+3 = Z1

ST 5,ISUM+3
ISUM+3 = Z1

SPLDL 5,4
F5 = _X1

SPL 6,2a
R6 = 0 P5 = X1

ST 5,FIRST+4
FIRST+4 = Y1

ST 5,ISUM+4
ISUM+4 = Y1

SPLDL 5,4
F5 = _X1

SPL 6,2a
R6 = 0 P5 = X1

ST 5,LAST
LAST = X1

ST 5,ISUM
ISUM = X1

ST 5,FIRST
FIRST = X1

* NOW DO REST OF CHAIN. ADD Coord INTO ISUM FOR CENTER OF MASS CALCULATIONS

* BEFORE ADDING X,Y, OR Z COORDINATES OF CURRENT READ,
* GIVEN BY X2Y2Z2, CHECK TO SEE IF IT IS MORE THAN ONE LATTICE SITE AWAY FROM THE LAST READ (AFTER
* THE LAST READ WAS RECONNECTED IF CHAIN WAS SPLIT).
* THE RECONNECTED COORDINATES OF THE PREVIOUS READ
* ARE GIVEN BY _X1Y1Z1 IN THE COMMENTS.

PAGE 0006
MEMBER NAME: PACK

* SUBTRACT A BOX DIMENSION (RECONNECT THE CHAIN)
A 5, IX(11)
R \# WHOLE1

* ADD A BOX DIMENSION

WHOLE1 ST 5, LAST(11)
A 5, ISUM(11)

* COMPUTE VECTOR END TO END LENGTH

LA 3, 3
XR 1, 100

LOOP2 LL 5, FIRST(10)
R4 = XLYLZL OF LAST HEAD
RG 4, 5, 120
ST 4, IS(10)
CT 3, LOOP2
LM 10, 12(13)
HVI 12(13), X*FF'

N1 DS F
ADRESS IN NTAB OF LAST HEAD IN CHAIN
N2 DS F
ADRESS IN NTAB OF LAST HEAD IN CHAIN
LAST DS 3F
BEAD COORD OF HEAD AFTER RECONNECTION
FIRST DS 2F
BEAD COORD. OF FIRST BEAD IN CHAIN
ACOM DC 4,4

N DS F

IXS DS 2F

ISUM DS 3F
SUM OF RECONNECTED BEAD COORDINATES
ISEP DS 3F
END TO END LENGTH
References


Vita

Rebecca Louise Moss Smithson

Born in Frederick, Maryland on December 31, 1953. Graduated from Governor Thomas Johnson High School in that city in June, 1971. Entered Hood College in Frederick, Maryland in September of 1971 and in May of 1975 received a B.A. in Chemistry and Mathematics. In September of 1975 the author entered a Post-Baccalaureate program in engineering at the University of Virginia in Charlottesville and continued in this program until December of 1975. She then worked in the Polymer Section of the NASA Langley Research Center in Hampton Virginia from January of 1976 until August of that year.

In September of 1976 the author entered the graduate program in Chemistry at the College of William and Mary. In September of 1978 she entered the program in Applied Science at William and Mary. She is currently a research assistant in the Programming Techniques Branch of the NASA Langley Research Center.