Molecular-dynamics simulations of polymers in a solvent

Anthony Jon Zukaitis
University of Nevada, Las Vegas

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UMI
MOLECULAR-DYNAMICS SIMULATIONS

OF POLYMERS IN

A SOLVENT

by

Anthony J. Zukaitis

Bachelor of Science
University of Wyoming, Laramie
1996

A thesis submitted in partial fulfillment
of the requirements for the degree of

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ABSTRACT

Molecular-Dynamics Simulations
of Polymers in
a Solvent

by

Anthony J. Zukaitis

Dr. Tao Pang, Examination Committee Chair
Professor of Physics
University of Nevada, Las Vegas

Molecular-dynamics simulations were carried out for linear, flexible polymers in a solvent environment. Both static and dynamic properties were calculated for polymer chains of 8, 16, 24, 32, and 40 monomers in length. The effects of solvent density on the diffusion coefficient, the average radius of gyration, and the average magnitude of the end-to-end distance vector of the polymer are studied. The same properties of loops or 'ring' polymers were studied by connecting the ends of the polymers together. We observed that the calculated properties scale with the number of monomers in a power-law form. The exponents of each quantity are sampled in our simulations. For long polymers, the diffusion coefficient for the open and ring polymers is found to be inversely proportional to the average radius of gyration. For shorter polymers, the ring structure plays a more prominent role in the diffusion process.
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CHAPTER 1

INTRODUCTION

The focus of this thesis is on understanding the dynamical and statistical behavior of polymers. For the purposes of this study, polymers are long, chain-like molecules, which are present in many common materials. It is helpful in understanding the properties of these materials if they can be studied from a molecular scale. The detailed knowledge of the molecules may lead to a fundamental understanding of bulk properties and aid in the development of new, polymer-based materials.

A polymer is made of two kinds of elements: monomers and links [1, 2]. A monomer is a distinct chemical unit along the chain which is linked to neighboring monomer(s) by chemical bonds. These links can be very soft or very stiff, depending on the specifics of the system. For example, polyethylene is a common polymer made up of carbon and hydrogen. The monomers in this polymer are the ethylene groups CH₂ and the links are the carbon to carbon covalent bonds. These bonds are stiff, but allow much rotational freedom. In describing long, complicated molecules, the generic monomer-and-link model can be used. From the study of this generic model, we can gain qualitative, and sometimes quantitative knowledge of the structural and dynamical properties of polymer systems.
In this work, we study a generic polymer-solvent system with molecular-dynamics simulations. The molecular-dynamics scheme is devised to sample the dynamics of complicated systems [3]. Many-body problems are very complicated and the exact solutions to these problems are rare. In a simulation, a simplified model for the microscopic system is specified and an exact solution for specified model parameters is possible. After the simulation, one can study some of the general properties of the solution and try to apply the results to real systems. Therefore, a computer simulation of a generic model is valuable in obtaining some general information on real materials.
CHAPTER 2

BASIC THEORY OF POLYMER DYNAMICS

The model adopted in this study begins with a set of $N$ beads linked in a chain or a Kramer's chain. We will use this model to describe a single polymer whose ends are not connected. Each bead represents a monomer which is joined to its neighbor(s) with a bond. The bonds will be approximated by stiff, massless rods of length $b$ whose direction is unrestricted. With such a simple model we can study many properties of polymer systems. Two of them that we will start with are the average square of the magnitude of the end to end distance vector $\langle R^2 \rangle$, and the average square of the radius of gyration $\langle S^2 \rangle$. A schematic diagram showing what these properties represent is shown in Fig 2.1. The average square of the magnitude of the end-to-end distance vector $\langle R^2 \rangle$ provides a measure of the average length squared of the polymer. $\langle R^2 \rangle$ is defined as

$$\langle R^2 \rangle = \langle |r_1 - r_N|^2 \rangle. \quad (2.1)$$
where \( \mathbf{r}_1 \) and \( \mathbf{r}_N \) are the position vectors of the first and last beads, respectively.

The average square of the radius of gyration is defined as

\[
\langle S^2 \rangle = \langle \frac{1}{N} \sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{Z}|^2 \rangle.
\]  

(2.2)

This value defines the average distance that each bead is away from

\[
\mathbf{Z} = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i.
\]  

(2.3)

where \( \mathbf{Z} \) is the position vector of the center of mass of the polymer and \( \mathbf{r}_i \) is the position vector of the \( i \)th bead. From this value, we can define a sphere of radius \( \sqrt{\langle S^2 \rangle} \) that the polymer occupies on average. Under the ideal chain model [2], the polymer can be imagined as a random walk stepping from the first monomer to the \( N \)th monomer. Each of these \( N - 1 \) steps, or bonds, is associated a vector \( \mathbf{x} \), whose direction is unrestricted and magnitude is \( b \). Averaging over all possible orientations for the bonds, one finds that

\[
\langle R^2 \rangle = \sum_{i,j=1}^{N-1} \langle \mathbf{x}_i \cdot \mathbf{x}_j \rangle = (N - 1)b^2.
\]  

(2.4)

and

\[
\langle S^2 \rangle = \frac{\langle R^2 \rangle}{6}.
\]  

(2.5)

when \( N \) is large.
In deriving these expressions, it is assumed that the monomers can occupy the same space with

$$\langle x_i \cdot x_j \rangle_{i \neq j} = 0. \quad (2.6)$$

Of course this is an unphysical approximation, but for some systems this could be a good approximation. In general, $$\langle x_i \cdot x_j \rangle_{i \neq j}$$ is nonzero and decays exponentially in the limit of $$|i - j| \gg 1$$. The characteristics of this quantity are primarily dependent on the system. If the effective interaction distance between two non-bonded monomers is much less than the bond length $$b$$, the approximation in Eq. (2.6) is usually valid. The fixed bond-length approximation can be under scrutiny if the stiffness of the bonds is low; that is, the bonds are soft and can be stretched or
compressed easily. If this is the case, one can use the average bond length in place of $b$.

Under the ideal chain model, the distribution function for magnitude of the end-to-end distance vector can also be approximated for large $N$ as

$$P(R) = \left( \frac{3}{2 \langle R^2 \rangle \pi} \right)^{3/2} \exp \left( \frac{-3R^2}{2 \langle R^2 \rangle} \right).$$

where $R$ is the magnitude of the end-to-end distance vector. The spatial distribution function is just $4\pi R^2 P(R)$ which has a maximum at $R = \sqrt{\frac{2}{3} \langle R^2 \rangle}$. From Eq. (2.7) one can see that the probability for the polymer to be fully extended is small. For this distribution function one finds that the entropy of an ideal chain

$$S(R) = S(0) - \frac{3R^2}{2 \langle R^2 \rangle}.$$  

(2.8)

decreases as the length increases [1].

The interactions among monomers is taken into account by the excluded volume model. Excluded volume here refers to the fact that monomers do interact repulsively at short distances and cannot occupy the same space. The effect is most prominent in $(\mathbf{x}_i \cdot \mathbf{x}_{i+1})$ which describes the interactions between two directly neighboring monomers. These terms are also dependent on the allowed angle between the directly neighboring bonds. As a quick example, for hard-sphere monomers of radius $\sigma < b/2$, the minimum angle between three monomers is shown in Fig. 2.2.
Figure 2.2: A diagram representing the minimum angle $\theta$ between the bonds of length $b$ of three neighboring hard-spheres along the chain with radius $\sigma$.

The minimum angle $\theta_{\text{min}}$ that can be made between these two bonds is given by

$$\theta_{\text{min}} = \cos^{-1} \left( 1 - \frac{2\sigma^2}{b^2} \right). \quad (2.9)$$

with the limit $0 < \theta_{\text{min}} < \pi/3$. One can then show that

$$\langle x_i \cdot x_{i-1} \rangle = \frac{b^2 \cos^2(\theta_{\text{min}})}{4}. \quad (2.10)$$

Including this term in Eq. (2.4) gives

$$\langle R^2 \rangle = \sum_{i,j=1}^{N-1} \langle r_i \cdot r_j \rangle = (N - 1)b^2 + (N - 2) \frac{b^2 \cos^2(\theta_{\text{min}})}{2}. \quad (2.11)$$

For the next order of corrections, the terms are more difficult to compute, but the end result can be shown to be proportional to $N$. Many theoretical and numerical calculations including excluded volume effects have demonstrated that for an
excluded volume polymer with large \( \mathcal{V} \). \( \langle R^2 \rangle \) and \( \langle S^2 \rangle \) go as

\[
\langle R^2 \rangle \propto \langle S^2 \rangle \propto (\mathcal{V} - 1)^{2\nu}.
\] (2.12)

where the exponent \( \nu \) is primarily dependent on the dimensionality of the system. For three-dimensional systems, \( \nu \approx 3/5 \) \[4\]. This same value of exponent has also been attained in the study of self-avoiding walks \[1\]. A typical value of \( \nu \) obtained in numerical studies is slightly higher than 1/2, which is the value of \( \nu \) for the ideal chain model. Even when one considers a polymer in a solvent, the exponent range in Eq. (2.12) is still about \( \nu = 1/2 - 3/5 \) depending on the solvent quality. For a good solvent, an exponent of \( \nu \approx 3/5 \) is expected while and exponent of \( \nu \approx 1/2 \) is obtained for a poor solvent. For ring polymers, one expects the same power law behavior for the average square of the radius of gyration \[5\].

Another property we can calculate using molecular-dynamics simulations is the sphericity \( \alpha \) of the polymer.

\[
\alpha = \frac{1}{2} \frac{\langle \sum_{i>j} (\lambda_i - \lambda_j)^2 \rangle}{\langle \sum_{i=1}^3 \lambda_i^2 \rangle}.
\] (2.13)

Here \( \lambda_i \) are the eigenvalues of the moment of inertia tensor of the polymer. A value of \( \alpha \approx 1 \) defines a rodlike structure and a value of \( \alpha \approx 0 \) defines a spherical structure.

Under the solvent conditions, the diffusion coefficient of a polymer can be analyzed in the simulations as well. The diffusion coefficient \( D \) of the polymer is related
to the mean square displacement of the position vector of the center of mass of the polymer by

$$\langle |Z(t) - Z(0)|^2 \rangle = 6Dt. \quad (2.14)$$

The diffusion coefficient is a measure of how well the polymer moves in the solvent which can also be obtained by integrating the velocity autocorrelation function of the polymer.

$$D = \frac{1}{3} \int_0^\infty \langle V(t) \cdot V(0) \rangle dt. \quad (2.15)$$

where $V(t)$ is the velocity of the center of mass of the polymer at time $t$.

For a simple sphere of radius $R_p$ in a solvent, the diffusion coefficient $D$ for a single sphere can be approximated with the help of the Einstein-Stokes relationship to be

$$D = \frac{k_B T}{6\pi \eta R_p}. \quad (2.16)$$

where $\eta$ is the viscosity of the solvent. $T$ is the absolute temperature, and $k_B$ is Boltzmann’s constant. For a polymer, a simple radius cannot be defined as in the particle case because the size of the polymer changes dynamically in time. When measuring the diffusion of a polymer, one can replace $R_p$ in Eq. (2.16) with the hydrodynamic radius $R_h$, which is defined as

$$\langle \frac{1}{R_h} \rangle = \left( \frac{1}{N^2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} \right). \quad (2.17)$$
$R_h$ is a property that can be used in addition to $\langle S^2 \rangle$ to characterize the size of the polymer. Experimentally, $R_h$ cannot be measured directly and one often obtains the hydrodynamic radius from diffusion coefficient measurements [6]. Because the average radius of gyration also describes the size of the polymer, i.e. $R_h \approx \sqrt{\langle S^2 \rangle}$, and it can be proposed that the average radius of gyration also satisfies the relation [7]

$$D \propto \frac{1}{\sqrt{\langle S^2 \rangle}}.$$  \hspace{1cm} (2.18)
CHAPTER 3

THE POLYMER-IN-SOLVENT SYSTEMS

The system we wish to simulate is a generic polymer in a solvent under infinite dilution. The potentials in the model studied are the same as those of Rapaport and Smith [7]. It was our intention to use their system to generate a working molecular-dynamics program for our studies and their study appeared to be a good choice. In their model, every monomer and solvent particle is represented by the shifted Leonard Jones (LJ) potential cut off at $r = 2^{1/6}$.

\[
V'(r) = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] & r \leq 2^{1/6} \sigma, \\
0 & r > 2^{1/6} \sigma.
\end{cases}
\] (3.1)

where $\epsilon$ and $\sigma$ set the energy scale and interaction range, respectively. All particles (solvent and monomers) were treated as having the same mass $m$ and interaction range $\sigma$. For bonded monomers, a second potential $V_b(r)$ is added to the nearest neighbor interaction to create the bonds

\[
V_b(r) = V'(d - r)
\] (3.2)
Figure 3.1: The two potentials used for the simulation with $d = 2.1$. The solid line is $V(r)$ and the dashed line is $V(r) + V_b(d - r)$.

and $d$ is the distance shifted. For the ring polymers an additional bond is applied between the first and $N$th beads of the polymer. The value of $d$ is critical in designating the average bond length of the polymer. The combination of the two potentials, shown in Fig. 3.1, gives a nonharmonic bond with a minimum at $r = d/2$ with $d = 2.1$. All units used in the simulation are based on the energy unit $\epsilon$, the mass $m$, and the interaction length $\sigma$. Because of this choice, the simulation can be done dimensionlessly with the parameters of the system given in the following unit convention. For example, $\sqrt{\frac{\epsilon}{m}}$ is the unit for velocity, $\sigma\sqrt{\frac{m}{\epsilon}}$ is the unit for time, and $\frac{\epsilon}{k_B}$ is the unit for temperature under this choice. In order to compare our data to that of Rapaport and Smith [7], all of the parameters for our system were chosen to match theirs. Five different lengths of chains (8, 16, 24, 32, and 40 monomers)
in two different solvent densities of 0.625 (density A) and 0.417 (density B) were studied. The units for the solvent density based on the previously mentioned units are \( \frac{M}{\sigma^3} \). A temperature of \( T = 2.0 \) and a time step of \( \delta t = 0.005 \) were used. One value that could not be matched was the value for \( d \). This value was not stated in Ref. [7]. The value we decided on, \( d = 2.1 \), came from a book by Rapaport [8]. The choice for this value will be explained later in Chapter 4. Ring polymers with the same numbers of monomers were studied under the same conditions.

In order to simulate the system, boundary conditions have to be properly chosen. Our system was a box containing a number of solvent particles and an embedded polymer. The box size was determined by the length of the polymer and the number of solvent particles needed to attain the higher solvent density of 0.625. The number of solvent particles was chosen such that at this density, the polymer would never extend outside of the box during the simulation. This condition is chosen to exclude polymer entanglements from our simulation which could arise from the periodic boundary conditions that will be explained shortly. For example, for a length of \( V = 8 \) monomers, the side length of the box would be 8 times the average bond length, which is estimated to be 1.05. In a molecular dynamics simulation, the computing time of the program increases with the number of particles. For our box, the number of solvent particles increases as the cube of the side length \( L \). Therefore, it is helpful if the size of the box is selected at its allowed minimum.

As a matter of fact, the probability for a polymer to become fully stretched in
Table 3.1: Particle numbers and corresponding box dimensions used for the simulations. \( N \) is the number of monomers. \( N_s \) is the number of solvent particles, and \( L_A \) and \( L_B \) are the side lengths of the box at a solvent density of 0.625 and 0.417, respectively.

<table>
<thead>
<tr>
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<th>( N_s )</th>
<th>( L_A )</th>
<th>( L_B )</th>
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</tr>
<tr>
<td>40</td>
<td>12000</td>
<td>26.7</td>
<td>30.6</td>
</tr>
</tbody>
</table>

A solvent is very small as seen in Eq. (2.7). Not only does the polymer have to be fully extended, it has to lie in the direction of the edges of the box. So it is plausible that the size of the box could be reduced. In Table 3.1, the numbers of solvent particles \( N_s \) used for different lengths of polymers are given. Using these numbers, the polymers never crossed over the boundaries of the box. The number of solvent particles was calculated by a trial and error correction method: if the polymer ever crossed the boundary, the simulation was restarted with a larger box. Note that for the 8-monomer system, the side length of the box exceeded the maximum length of the polymer. Fewer solvent particles could have been used for this short polymer, but this was what Rapaport and Smith [7] used and we attempted to match their conditions in order to test our program.

Periodic boundary conditions were applied to the box in order to get a representation of the bulk of the solvent [3]. Surrounding the box are exact copies of itself on each side. A two dimensional picture of the periodic boundary conditions can be seen in Fig. 3.2. Although we are simulating a three dimensional system, a
two dimensional picture is shown to illustrate the idea. This means that if there is a particle at \( \mathbf{r} \), there are also image particles at \( \mathbf{r} + \mathbf{R}_n \), where \( \mathbf{R}_n \) is the vector pointing to the center of the \( n \)th box. Every time a particle exits one side of the box, its image will enter the box from the opposite side, keeping the number of solvent particles inside the box constant. The interactions applied across the sides of the box only involved the hard-core potentials of the solvent particles and monomers. \( V(r) \). The shifted bond potential was never needed because that would mean that our polymer had crossed the boundary of the box, violating our previous condition. When the monomers interact across the boundary, they interact as if they were solvent particles. This would eliminate the possibility of the polymer moving into a hole seen at the edge of the box. Also, since the polymer never crossed the boundary of the box, the effects of the polymer becoming entangled with its own image were avoided.

In order to incorporate all of these conditions in the simulation, the polymer had to be kept from diffusing outside of the box. This is done by keeping the origin of the coordinate system at the center of mass of the polymer. Each time the polymer moved in a certain direction, the coordinates of the solvent were adjusted respectively and the motion of the polymer was recorded for the calculation of the displacement of the polymer. After each shift, the periodic boundary conditions were enacted again. Thus, at every time step of the simulation, the polymer is at the center of the box even though our 'viewing box' had been moved accordingly.
Figure 3.2: A schematic view of the periodic boundary conditions for the simulation box. The main box and particles use the solid lines while the image boxes and image particles are drawn with dashed lines.
CHAPTER 4

THE MOLECULAR-DYНАМICS SCHEME AND TESTING

The molecular-dynamics simulations performed are based on the leap-frog algorithm of Verlet [9, 10]. From Newton’s equation, the acceleration \( \mathbf{a}_i \) of the \( i \)th particle at time \( t \) is given by

\[
\mathbf{a}_i(t) = \frac{1}{m} \sum_{j \neq i}^{N} \mathbf{F}_{ij}(t).
\]

(4.1)

where \( \mathbf{F}_{ij}(t) \) is the force on particle \( i \) by particle \( j \). The particles with an index of \( i \leq N \) are the monomers and the particles with an index of \( i > N \) are the solvent particles. The forces are obtained from the gradient of the potential.

\[
\mathbf{F}_{ij} = -\nabla_i V(r_{ij}).
\]

(4.2)

where \( V(r_{ij}) \) is the interaction potential between particles \( i \) and \( j \) and \( r_{ij} \) is the separation distance between the particles. For the nearest neighbor monomers, \( V_b(r_{ij}) \) from Eq. (3.2) should be added to \( V(r_{ij}) \) in Eq. (4.2). After a small time step \( \delta t \), the next positions can be approximated by

\[
\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t) + \frac{\delta t^2}{2} \mathbf{a}_i(t) + O(\delta t^3).
\]

(4.3)
where \( \mathbf{r}_i(t) \) is the position vector of the \( i \)th particle at time \( t \) and \( \mathbf{v}_i(t) \) is the velocity of the \( i \)th particle at the same time. If we assume linear acceleration in the time interval \([t, t + \delta t]\), we have

\[
\mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{\delta t}{2} (\mathbf{a}_i(t + \delta t) + \mathbf{a}_i(t)) + O(\delta t^2).
\] (4.4)

Eqs. (4.1)-(4.4) make up the velocity version of the Verlet algorithm, which is unique in the sense that the velocity at time \( t + \delta t \) comes from the average of the forces at \( t \) and \( t + \delta t \). This procedure is repeated for many time steps to find the dynamics of the particles to a desired accuracy. This was checked by computing the total energy for the system. An overall increase or decrease in the total energy would indicate that the time step was too large. In our simulation, the total energy fluctuated about 1% of the mean value, indicating that a proper time step was selected.

An even shorter time step could have been used, but to sample the system for the same time length, more time steps must be used. By choosing a reasonably large time step, a long time duration could be sampled in order to gain more accurate statistics. Different simulations for \( \delta t = 0.004 \) were carried out and no differences were observed in the data. As expected, the fluctuations of the total energy were reduced with a smaller step.

The cell-list scheme [3] was also used in the simulations. The cell-list method enhances the efficiency of the program by sorting the particles into numbered cells whose dimensions match the cut-off interaction distance \( 2^{1/6} \sigma \) of the potentials.
For example, if a particle is in a particular cell, we know that it will only interact with particles in directly neighboring cells and the particles within the same cell. Particles in other cells can be neglected because they are separated by at least one cell length, that is, away from the cut off distance. Most implementations of the algorithm rely on arrays whose complexity grows as the number of cells. With the cell number growing to the number on the order of $10^3$, these arrays become enormously complex to compute. So instead, a list was generated that recorded the pairs of cells that would be close enough to have particles within the interaction range. The total number of interacting cells, including periodic boundary conditions, is equal to $13M$, where $M$ is the total number of cells. The only deficiency of this method is the memory required for storing the list. This method proved to increase the efficiency of the program dramatically because of the large number of particles required for the simulations as well as the short interaction ranges of the model adopted.

The program was written in Fortran 90 and run on various computer architectures: DEC Alpha, SGI O2, and SGI Power Challenge. No differences in results were observed among them. Different parallelization techniques with MPI (Message Passing Interface [12]) were also looked into. Only at very large numbers of particles (exceeding the numbers we used) the advantage of the parallelization was realized.

On initialization, the program would place a randomly oriented polymer into the box. Next, random positions for the solvent particles were attempted. The random
positions were only accepted if the distance to the closest neighbor was greater than some preselected distance. Velocities were also assigned randomly from a Gaussian distribution [3]. In order to assure that our system was not moving as a whole, the velocity of the center of mass of the whole system was subtracted from each particle.

Once the initial conditions were set, we started integrating the equations of motion. For the first 2000 steps, the velocities were rescaled every 50th step in order to attain the correct temperature given by

$$T = \frac{1}{3(N_s + N - 1)} \sum_{i=1}^{N_s + N} |v_i|^2. \quad (4.5)$$

The rescaling was implemented by computing the temperature of the system. If the temperature was too high, the velocities of the the particles were scaled uniformly to give the correct temperature. After the first 2000 steps, the system was allowed to evolve without any rescaling of the temperature. We did try to see if any center of mass motion of the system as a whole developed during the integration. Any motion calculated turned out to be insignificant and was neglected. We found that the temperature and the total energy were relatively stable with the selected time step of $\delta t = 0.005$. Although the temperature and energy did fluctuate, the averages stayed the same. After $2.0 \times 10^4$ steps, data were recorded at every time step for another $2.0 \times 10^6$ steps. For subsequent runs, we used positions and velocities saved from the end of the previous runs. When starting with the previously saved configurations, there was no need to rescale the temperature because it remained
constant after the very first rescaling.

At the end of every run, we calculated the velocity autocorrelation function as well as \(|\mathbf{Z}(t) - \mathbf{Z}(0)|^2\) for the specific run to find the diffusion coefficient from two different methods, that is, via Eq. (2.14) and Eq. (2.15). For the Einstein-Stokes relation Eq. (2.14), an approximated slope was fitted for large \(t\) to obtain \(6D\). For the velocity autocorrelation function in Eq. (2.15), the integration to infinity was extrapolated to avoid the numerical noise in the large \(t\) limit. The typical difference between the two diffusion coefficient values obtained from the two different methods was about 5%.

Once the program was written, it was put through months of rigorous testing because of problems in reproducing the results of others. The first problem arose when we could not reproduce Rapaport and Smith's [7] results for the same systems. We used all of the parameters published in their work except for the value of \(d\). As stated before in Chapter 3, \(d\) determines the shift of the L.J potential that makes up the bond. This would directly influence the average bond length and indirectly affect the allowed bond angles. A value of \(d \approx 2.0 - 2.4\) was suggested as the range to be studied [13]. After further tests, a value of \(d = 2.13\) was chosen to fit one of their data points. With other parameters fixed, the density was changed to test another data point of Rapaport and Smith [7], which could not be reproduced in our simulations.

A second system was chosen [14] to help in testing and debugging the program.
The system in Ref. [14] was similar to the one we were studying, except the bonding part of the potential, $V_b(R)$, was different. The results obtained with our program were in good agreement with those of Ref. [14]. One might question the validity of changing systems. For example, the testing of the system of Ref. [14] was done by changing only two lines in the program: one for the potential and another for the force of the bond. The rest of the parameters were represented by variables in the computer program that could easily be changed.

After the test against the result of Ref. [14], we then analyzed some other work done by Rapport [8]. In Ref. [8], some examples for almost the same systems studied in Ref. [7] were given. Two densities, 0.417 and 0.625, were used in Ref. [7] whereas a density of 0.5 was used in Ref. [8]. The value for $d = 2.1$ was stated in Ref. [8] and we were also able to reproduce those results as well. We then decided to produce independent results for the systems studied in Ref. [7]. It was observed that for some of the configurations and time durations, the polymer would extend outside of the box, even after recentering the coordinate system on the center of mass of the polymer. Since this was a violation of our boundary conditions, we were required to use a larger box size (more solvent particles) for the systems in Ref. [7].

One might question what effects the size of the box would have on the dynamics of the polymer. For example, when a polymer extends outside of the box, the ends of a polymer could get entangled and one might see a melt effect under the periodic boundary conditions. In a polymer melt, many polymers are present and
entanglements between polymers changes the properties of the system. This is a system we are not studying and therefore need to avoid. Other studies have studied the effects of a smaller box and the effects of the periodic boundary conditions [15]. No statement was given as to whether they kept their box centered on the center of mass of the polymer, but the results showed that the size of the box did affect some of the calculations. As to whether to use fewer or more solvent particles, common sense says that more would be better if the computing resources are available.
CHAPTER 5

RESULTS AND OBSERVATIONS

For reference, we simulated both open and ring polymers in a vacuum, that is, without a solvent environment. No dependence of the average bond length on the number of monomers \( V \) was observed for the open polymers in either the vacuum or the solvent environment. For the open polymer in a vacuum, an average bond length of 1.0572 ± 0.0004 was obtained. For the solvent systems of densities 0.625 and 0.417, we obtained average bond lengths of 1.0482 ± 0.0004 and 1.0534 ± 0.0004, respectively. The average bond lengths calculated are in good agreement with the position of the minimum of the potential at \( r = 1.05 \) in Fig. 3.1. Comparing our results to those of Rapaport and Smith [7], we observed smaller values for the average bond lengths in general, but found the same change in the average bond lengths between the two solvent densities. The importance of this data is that the bonds are being compressed by the solvent. As the solvent density is increased the polymer sees more solvent particles which compresses the bonds.

For the sphericity of the open polymer, no dependence on polymer length or solvent density was observed. A value of \( \alpha = 0.55 \pm 0.03 \) was obtained which is in good agreement with the work of Rapaport and Smith [7]. This value of \( \alpha \) indicates
that on average the polymers take on a stretched ellipsoidal shape.

For the $\langle R^2 \rangle$ and $\langle S^2 \rangle$ in the open polymer systems, a fit to $a(N-1)^{2v}$ is proposed as expected from Eq. (2.12). In subsequent fitting, all but the $N = 8$ data was used because the rest of the data seemed to agree well with a power-law behavior in the limit of large $N$. In Fig. 5.1 and Fig. 5.2, one can see how well both $\langle R^2 \rangle$ and $\langle S^2 \rangle$ follow the power-law behavior. In Table 5.1 and Table 5.2 the exponents and proportionality constants obtained in the fits are listed.

The exponents agree well with theory for excluded volume chains, $v \approx 3/5$. It is observed that both the fitted parameters, $a$ and $v$, for both $\langle R^2 \rangle$ and $\langle S^2 \rangle$ decreased
Table 5.1: Fitted values to $a(N - 1)^{2v}$ for the average square of the end-to-end distance vector $\langle R^2 \rangle$ of the open polymers.

| Solvent Density | $a$  | $v$  | error (|Δv|) |
|-----------------|------|------|-----------|
| 0.625 (A)       | 1.25 | 0.60 | 0.08      |
| 0.417 (B)       | 1.05 | 0.63 | 0.05      |
| 0.0 (Free)      | 1.18 | 0.61 | 0.04      |

Figure 5.2: The average square of the radius of gyration versus the number of monomers for the open polymers. The diamonds are the data points for a solvent density of 0.625, the crosses are for a solvent density of 0.417, and the boxes are for the polymers without the presence of a solvent. The parameters for fit to $a(N - 1)^{2v}$ are listed in Table 5.2.

Table 5.2: Fitted values to $a(N - 1)^{2v}$ for the average radius of gyration $\langle S^2 \rangle$ of a chain polymer.

| Solvent Density | $a$  | $v$  | error (|Δv|) |
|-----------------|------|------|-----------|
| 0.625 (A)       | 0.23 | 0.57 | 0.03      |
| 0.417 (B)       | 0.18 | 0.62 | 0.02      |
| 0.0 (Free)      | 0.20 | 0.60 | 0.01      |

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as the solvent density increased. The strange result is that the values of the fitted parameters for the free polymers lie right in between those of the two systems where a solvent was present. This is due to the large amount of error for the open polymer systems which will be explained later. The error in fitting an exponent to our data was estimated by the maximum deviation of the slope within the calculated error bars.

One more point that should be made is that the data for \( \langle S^2 \rangle \) are much more accurate than the data for \( \langle R^2 \rangle \) because of the fact that at each time step we are averaging over all of the monomers instead of just the end ones which were used to calculate the average magnitude of the end-to-end distance vector. It is also pointed out that the ratio of the proportionality constants \( a \) from Table 5.1 and Table 5.2 for \( \langle R^2 \rangle \) and \( \langle S^2 \rangle \) is about 5.6, slightly less than 6.0 which is the value that is predicted for the ideal chain model given in Eq. (2.5).

Eq. (2.18) states that the diffusion coefficient is inversely proportional to the average radius of gyration. So we use a fit that represents the expected exponential behavior, \( D = a(N - 1)^{-\alpha} \). In Fig. 5.3 we see relatively good agreement between the fit and our data. The values for the fitting parameters are listed in Table 5.3. There is good agreement between the exponents for the diffusion coefficient and the average radius of gyration for the low solvent density of 0.417. For the higher density of 0.625, the slope is not well resolved and therefore it is hard to make a comparison between the exponent obtained for the diffusion coefficient and the average radius.
Figure 5.3: The diffusion coefficient versus the number of monomers for the open polymers. The diamonds are the data points for a solvent density of 0.625 and the crosses are for a solvent density of 0.417. The parameters for the fit to $a(N - 1)^{-v}$ are listed in Table 5.3.

It was observed that the rings had the same average bond lengths as the open polymer systems in each solvent density. The sphericity was found to be $\alpha = 0.258 \pm 0.02$, which is about 1/2 of the value obtained for the open polymers. This is reasonable because the polymer ring is more spherical than the open ended polymer.

Table 5.3: Fitted values to $a(N - 1)^{-v}$ for the diffusion coefficient $D$ for the open polymers.

| Solvent Density | $a$  | $v$  | error ($|\Delta v|$) |
|-----------------|------|------|----------------------|
| 0.625 (A)       | 13.2 | 0.39 | 0.20                 |
| 0.417 (B)       | 0.18 | 0.60 | 0.10                 |
Table 5.4: Fitted values to $a N^{2\nu}$ for the average radius of gyration $\langle S^2 \rangle$ of a ring polymer.

| Solvent Density | $a$    | $\nu$ | error ($|\Delta \nu|$) |
|-----------------|--------|-------|-----------------------|
| 0.625 (A)       | 0.095  | 0.607 | 0.005                 |
| 0.417 (B)       | 0.105  | 0.602 | 0.005                 |
| 0.0 (free)      | 0.076  | 0.667 | 0.005                 |

As stated in Chapter 2, we expect the power-law behavior for $\langle S^2 \rangle$. The fit is similar to the same expression $\langle S^2 \rangle = a N^{2\nu}$ as before except we now have $N$ bonds instead of $N - 1$. From Fig. 5.4 almost no difference in the slope can be resolved between the two solvent densities. The exponents in Table 5.4 for the polymer rings in both solvent densities are much closer to the analytical value of $\nu = 3/5$, expected for excluded volume open polymers [1, 2]. These values are in good agreement with the results of Bishop and Michels who studied ring polymers by Brownian dynamics [5].

The exponent of the average square of the radius of gyration for the free ring polymer is $\nu \approx 2/3$, much higher than the exponents that were obtained when the solvent was present.

We also calculated the diffusion coefficient for the ring polymers in the solvent. We still expect that the diffusion coefficient is inversely proportional to the average radius of gyration. Again we use a fit that represents the expected power-law behavior, $D = a N^{-\nu}$. The values obtained for the fit are given in Table 5.5 and the graph is in Fig. 5.5. The exponents for the diffusion coefficient are smaller overall than those calculated for the average radius of gyration. In general, the diffusion
Figure 5.4: The average square of the radius of gyration versus the number of monomers for a ring polymer. The diamonds are the data points for a solvent density of 0.625, the crosses are for a solvent density of 0.417, and the boxes are for the polymers without the presence of a solvent. The parameters for the fit to $aN^{2r}$ are listed in Table 5.4.
Figure 5.5: The diffusion coefficient for a ring polymer as a function of the number of monomers. The diamonds are the data points for a solvent density of 0.625, the plus signs are for a solvent density of 0.417. The parameters for the fit to $a N^{-\nu}$ are listed in Table 5.5.

Coefficients are slightly higher than those of the open chain due to the fact that the overall size of the polymer is decreased.

In Eq. (2.18), we assumed that the diffusion coefficient is inversely proportional to the average radius of gyration. In Fig. 5.6 this dependence is plotted explicitly for all the diffusion coefficients obtained. For the shorter chains with a small $\sqrt{\langle S^2 \rangle}$.

Table 5.5: Fitted values to $a N^{-\nu}$ for the diffusion coefficient $D$ of a ring polymer.

| Solvent Density | $a$     | $\nu$ | error ($|\Delta \nu|$) |
|-----------------|---------|-------|------------------------|
| 0.625 (A)       | 19.45   | 0.46  | 0.05                   |
| 0.417 (B)       | 47.58   | 0.53  | 0.05                   |

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we can see a difference between the diffusion of an open chain and a ring. For the longer chains in the large $\sqrt{\langle S^2 \rangle}$ regime, the points start to overlap, indicating that the average radius of gyration is dominant in the diffusion process.
Figure 5.6: The diffusion coefficient of all of our polymers in both densities versus the average radius of gyration. In the lower solvent density of 0.417, the ring polymers are represented by boxes and the open polymers are represented by crosses. In the higher solvent density of 0.625, the ring polymers are represented by circles and the open polymers are represented by diamonds.
CHAPTER 6

CONCLUSIONS AND DISCUSSIONS

Many computer simulations have been done on polymer/solvent systems systems, looking at the effect the solvent has on the conformation and dynamics of a polymer. For example, Smit et al. observed the effect by using a variable to change the strength of the monomer/solvent interactions directly [16]. We have also observed the effect of the solvent on the polymer for both the ring and open polymer configurations. The trend is that as the solvent density increases, the size of the polymer decreases. This was observed in both the open and ring polymer systems. Strangely enough, the exponents and proportionality coefficients in Table 5.1 and Table 5.2 of the free open polymers are in between those of the two solvent systems. One must remember that the simulation error in those systems is quite large as compared to the ring polymers. This is because the number of conformations available to the open polymer is much more that the number of conformations available to the ring polymer. Thus our statistical error is much lower in the ring systems. It is also believed that the vacuum systems should have been studied using a Brownian Motion model to accurately calculate appropriate quantities.

This solvent effect was observed with higher accuracy in the ring systems for
the two solvent densities as well. Clearly the data show that as the solvent density increases, \( \langle S^2 \rangle \) gets smaller. The data are also in excellent agreement with the power-law fit. The exponents in Table 5.4 of \( \langle S^2 \rangle \) could not be distinguished between the two densities. The agreement with the expected exponent \( \nu = 3/5 \) of the excluded volume model was observed in the solvent system, but an exponent of \( \nu = 2/3 \) was observed for the ring polymers in a vacuum. This may seem odd that such a large exponent is present for the vacuum system, yet Bishop and Michels found a large exponent of \( \nu = 0.65 \) for a similar ring system in which no solvent was present [5].

For the diffusion coefficients of our system, the solvent density was very important. When the solvent density is high, it is harder for the polymer to move around and thus we see a smaller diffusion coefficient overall for all of the polymers. It could be that for our system the viscosity of the solvent is increases with solvent density. Although this relationship was not investigated, it would correlate well with Eq. (2.16).

It was also observed that the average radius of gyration plays an important role in the diffusion of the polymers as well. Keeping the solvent density constant, one can see that the diffusion constants for the ring and open polymers in the large \( N \) regime are more dependent on the size of the polymer. For the small \( N \) regime a larger difference can be seen between the diffusion constant of a ring polymer and an open polymer of the same size. It could also be speculated that in the large \( N \) regime, the effects of the ring conformation are overwhelmed by the motion of the
polymer as a whole and therefore could not be resolved in our simulation.

As far as the future work is concerned, it would be interesting to resolve the data for the open chain systems, which would require much longer computer runs because simulation errors for the large systems is significant. The data obtained for the open polymers in two solvent densities had much more error than that of the ring polymers. The data for the ring systems is very good because the number of conformations accessible to a ring is much smaller than the number of conformations of an open chain of the same length. Another question one might ask is how charged monomers would affect the properties of the dynamics of polymer systems in general. With such long range forces, it is hard to say how the systems would behave.
BIBLIOGRAPHY


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