MONTE CARLO SIMULATIONS TO STUDY THE EFFECT OF CHAIN STIFFNESS ON STATIC, DYNAMIC, AND EQUATION-OF-STATE PROPERTIES OF POLYMER MELTS

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Kiran Khanal

August, 2009
MONTE CARLO SIMULATIONS TO STUDY THE EFFECT OF CHAIN STIFFNESS ON STATIC, DYNAMIC, AND EQUATION-OF-STATE PROPERTIES OF POLYMER MELTS

Kiran Khanal

Thesis

Approved:  

Advisor  
Dr. Jutta Luettmer-Strathmann

Accepted:  

Dean of the College  
Dr. Chand Midha

Committee Member  
Dr. Alper Buldum

Dean of the Graduate School  
Dr. George R. Newkome

Committee Member  
Dr. Ben Yu-Kuang Hu

Date

Department Chair  
Dr. Robert R. Mallik
ABSTRACT

Static and dynamic properties of polymers are affected by the stiffness of the chain molecules. In this work, we investigate static and dynamic properties of a lattice model for semiflexible polymer chains. The model is an extension of Shaffer’s bond-fluctuation model and includes attractive interactions between monomers and an adjustable bending energy that determines the Kuhn segment length. For this work, we performed Monte Carlo simulations for polymer melts with a range of values of the bending energy, density, and temperature. We find that the Kuhn segment length increases monotonically with the bending energy for a wide range of bending energies. This allows us to model melts of flexible and semiflexible chains. Results for self diffusion coefficients show that the translational mobility is strongly reduced by increasing chain stiffness. We implemented a bead insertion method and a chain insertion method to calculate the pressure of the melts. While chain insertion is a reliable method to determine the pressure at low filling fractions of the lattice, it becomes very inefficient at higher densities. Bead insertion, on the other hand, yields good statistics, even at high densities, but the evaluation depends on an assumption that breaks down for semiflexible chains. We find that bead and chain insertion give comparable results for the pressure of melts of flexible chains at sufficiently high densities.
ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Dr. Jutta Luettmer-Strathmann, for her constant encouragement, support and guidance throughout this work.

I would also like to express my gratitude to my committee members: Dr. Alper Buldum and Dr. Ben Yu-Kuang Hu for being on the committee and for their cooperation. Special thanks also go to my friends Michael Avon, Vincent, and Charles Barr for their valuable assistance. I am always thankful to the faculty and staff in the Department of Physics for their direct or indirect help during my study and research.

Finally, I would like to express my deep appreciation to my husband, Laxmi P Subedi, for his support during this work.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THEORY</td>
<td>4</td>
</tr>
<tr>
<td>2.1 Chain Conformation</td>
<td>4</td>
</tr>
<tr>
<td>2.2 Dynamic properties</td>
<td>7</td>
</tr>
<tr>
<td>2.3 Pressure</td>
<td>11</td>
</tr>
<tr>
<td>2.3.1 Fluids of monatomic particles</td>
<td>11</td>
</tr>
<tr>
<td>2.3.2 Polymer melts</td>
<td>15</td>
</tr>
<tr>
<td>2.3.2.1 Pressure from chain insertion probability</td>
<td>16</td>
</tr>
<tr>
<td>2.3.2.2 Pressure from end-bead insertion probability</td>
<td>22</td>
</tr>
<tr>
<td>2.3.3 Approximate equations-of-state for polymer melts</td>
<td>25</td>
</tr>
<tr>
<td>III. LATTICE MODEL</td>
<td>28</td>
</tr>
<tr>
<td>IV. METHOD</td>
<td>31</td>
</tr>
<tr>
<td>4.1 Monte Carlo simulations</td>
<td>31</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table                                                                                                                               Page
4.1 Time scales of Monte Carlo simulations .................................................................33
4.2 Time scales in our Monte Carlo simulations ..........................................................34
4.3 Parameters used in the chain insertion method for melts at inverse temperature $\beta = 0, \beta = 0.1$, $\varepsilon_A = 0, \varepsilon_A = 5$ ..............................................................................40
5.1 Results of chain dimensions for polymers in the melt for filling fraction $\phi = 0.5$, inverse temperature $\beta = 0.1$ and different bending energies ($\varepsilon_A$) ........................................................................................................42
5.2 Results of the self-diffusion coefficient and relaxation time for polymer chains of length $N = 20$ in melts with filling fraction $\phi = 0.5$ and inverse temperature $\beta = 0.1$ for different bending energies $\varepsilon_A$ .................................................................46
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Left panel: Illustration of chain conformations of flexible chains, $\varepsilon_l = 0$ in a simulation box. Right panel: Illustration of the conformations of stiffer chains, $\varepsilon_l = 20$ in a simulation box</td>
<td>4</td>
</tr>
<tr>
<td>2.2 The function $g_{d/6t}$ as a function of time, where $g_d$ is the mean square displacement of the center of mass and $t$ is the time</td>
<td>8</td>
</tr>
<tr>
<td>2.3 Time correlation function of the end-to-end vector $\phi_e$ as a function of time for chains with stiffness parameter $\varepsilon_l = 25$</td>
<td>10</td>
</tr>
<tr>
<td>3.1 Illustration of Shaffer’s bond fluctuation model</td>
<td>28</td>
</tr>
<tr>
<td>3.2 Illustration of bead-bead and bond interactions in our lattice model</td>
<td>30</td>
</tr>
<tr>
<td>4.1 Block averaging technique</td>
<td>34</td>
</tr>
<tr>
<td>4.2 Two-dimensional illustration of an end-bead insertion with bead-bead interaction energy $\varepsilon_B$ and bending penalty $\varepsilon_A$</td>
<td>38</td>
</tr>
<tr>
<td>4.3 The probability $P(e_i)$ as a function of the Boltzmann factor $\exp(-\beta e_i)$ for two different temperatures for chain length $N = 20$, bending penalty $\varepsilon_A = 0$ and filling fraction $\phi = 0.5$</td>
<td>39</td>
</tr>
<tr>
<td>5.1 Mean square radius of gyration $R_g^2$ as a function of bending energy $\varepsilon_A$</td>
<td>43</td>
</tr>
<tr>
<td>5.2 The root mean square bond length $b_i$ as a function of bending energy $\varepsilon_A$</td>
<td>44</td>
</tr>
<tr>
<td>5.3 Kuhn segment length $l_k$ as a function of bending energy $\varepsilon_A$</td>
<td>45</td>
</tr>
</tbody>
</table>
5.4 Mean square displacement of the center of mass $g_d$ as a function of time for different bending energies for chains of length $N = 20$ in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.9) ......................................................... 47

5.5 Mean square displacement of the central monomer, $g_1$, as a function of time for different bending energies for chains of length $N = 20$, in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.10) ......................................................... 48

5.6 Time correlation function of the end-to-end vector $e_{\phi}$ as a function of time for different bending energies for chains of length $N = 20$, in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.12) ......................................................... 49

5.7 The self diffusion coefficient as a function of Kuhn segment length for two different densities ................................................................. 50

5.8 The correlation time as a function of Kuhn segment length for two different densities ................................................................. 51

5.9 (Upper panel) Reduced excess chemical potential $\beta \mu_{ex}$ as a function of filling fraction $\phi$ obtained from end-bead and chain insertion methods for athermal polymer melts with chain length $N = 20$. The diamonds and circles represent results from the chain insertion and bead insertion method, respectively; the error bars are seen to be smaller than the symbol size. (Lower panel) The difference between the $\beta \mu_{ex}$ values of the upper figure ........................................ 53

5.10 (Upper panel) Reduced pressure $\beta p$ as a function of filling fraction $\phi$ obtained from end-bead insertion and chain insertion methods for athermal polymer melts with chain length $N = 20$. The diamonds and circles represent results from the chain and end-bead insertion methods, respectively. (Lower panel) The difference between the $\beta p$ values of the upper figure ......................................................... 54
5.11 (Upper panel) Compressibility factor $Z$ of athermal polymer melts with chain length $N = 20$ as a function of filling fraction $\phi$. The diamonds represent simulation results obtained with the chain insertion method; open circles and filled triangles represent results from the Flory theory and the Flory-Huggins theory, respectively. (Lower panel) The difference between simulation results for the compressibility factor ($Z$) and Flory’s approximation ($Z_F$). The open circles and diamonds represent bead and chain insertion differences, respectively .................................................................56

5.12 (Upper panel) Reduced excess chemical potential $\beta \mu_{ex}$ from bead and chain insertion as a function of filling fraction for polymer melts with chain length $N = 20$ at inverse temperature $\beta = 0.1$ and bending energy $\varepsilon_A = 0$. The diamonds and circles represent chain insertion and bead insertion, respectively. (Lower panel) Difference of the $\beta \mu_{ex}$ values of the upper figure .................................................................57

5.13 (Upper panel) Reduced pressure $\beta p$ as a function of filling fraction $\phi$ obtained from bead insertion and chain insertion methods for polymer melts with chain length $N = 20$ at inverse temperature $\beta = 0.1$ and bending energy $\varepsilon_A = 0$. The diamonds and circles represent results of chain and bead insertion methods, respectively. (Lower panel) The difference between the $\beta p$ values of the upper figure .................................................................59

5.14 Relative deviation of reduced pressure values obtained with the two insertion methods as a function of filling fraction for inverse temperatures $\beta = 0$ (circles) and $\beta = 0.1$ (diamonds) for polymer melts with chain length $N = 20$ .................................................................61

5.15 Ratio of the reduced excess chemical potential $\beta \mu_{ex}$ from the chain insertion method and the reduced bead chemical potential $\beta \mu_c$ from the bead insertion method as a function of filling fraction $\phi$ for inverse temperatures $\beta = 0$ (circles) and $\beta = 0.1$ (diamonds) for polymer melts with chain length $N = 20$ .................................................................61

5.16 Compressibility factor $Z$ of polymer melts with chain length $N = 20$ as a function of filling fraction $\phi$ for different inverse temperatures and bending energies .................................................................62
A polymer is a chain molecule composed of a number of repeating chemical units, called monomers, held together by chemical bonds. A polymetric liquid consisting of only one type of chain molecules is known as a polymer melt. The static and dynamic properties of a polymer melt are different from those of a liquid of small molecules. An important feature of polymer chains in a melt is that they can adopt a large number of conformations. Information about different conformations of chain molecules in the melt can be obtained from the study of chain dimensions such as the radius of gyration and the end–to–end distance. The mobility of chains in the system and conformational relaxation can be studied by investigating self diffusion and correlation functions. The stiffness of a polymer chain is characterized by a length called the Kuhn segment length $l_k$, which is the effective monomer size for the equivalent freely jointed chain. Some polymers like 1, 4-polyisoprene are very flexible ($l_k = 0.82$ nm)$^1$, whereas others like double-stranded DNA are very rigid ($l_k = 50$ nm)$^2$. The chain stiffness affects directly the chain dimensions and indirectly the dynamic properties and, to some extent, the thermodynamic properties of a polymer melt. The knowledge of the pressure is very important because experiments are normally performed under constant pressure.
Hence, we need to know the effect of chain stiffness on pressure in order to separate the effect of chain stiffness from those of other quantities like density and temperature.

In this work, we study chain dimensions, dynamic properties and thermodynamic properties of polymer melts for different temperatures, chain stiffness, and densities. We use a lattice model that is an extension of Shaffer’s bond fluctuation model. In Shaffer’s bond fluctuation model each polymer bead occupies a site on a simple cubic lattice. There are three allowed bond lengths values $a$, $\sqrt{2}a$, and $\sqrt{3}a$, where $a$ is the lattice constant, and bonds are not allowed to cross each other. The excluded volume condition is applied, which forbids the double occupancy of lattice sites. Shaffer’s original model included only hard core interactions and bond constraints. In this work, we include attractive interactions between non-bonded monomers and a bending energy for small bond-angles, $\theta \leq 90^\circ$.

In order to investigate static and dynamic properties, we performed Monte Carlo simulations of polymer melts for different filling fractions, bending energies, and temperatures for polymer chains of length $N = 20$. Since the widely used method to calculate the pressure in off-lattice models from the virial is not applicable for lattice models, we implemented two insertions methods based on the Widom test-particle method in order to determine the chemical potential and from there the pressure of the melt. In the first method, an attempt is made at regular intervals to insert a test bead at the end of one of the chains in the melt. In the second method, attempts are made to insert whole chains instead of single beads. In both cases, a histogram of the interaction energy of the test particles with the melt is constructed (taken to be infinite for hard core
overlap), and evaluated to yield the excess chemical potential. The pressure is then obtained from a thermodynamic integration method.

The equation-of-state of a lattice model for athermal polymer melts can be estimated from the Flory and Flory-Huggins theories. In this work, we determine the equation-of-state of athermal melts from chain insertion and bead insertion, and compare with Flory and Flory-Huggins theories. We also compare pressure values obtained from the bead insertion and chain insertion methods for given temperatures.

The outline of this thesis is as follows. The theoretical background for chain dimensions, dynamic properties, and the bead insertion and chain insertion methods is presented in chapter II. The lattice model for polymer melts employed in this work is described in chapter III. The Monte Carlo simulation method, chain insertion method and end-bead insertion method are discussed in chapter IV. Simulation results for static and dynamic properties are presented in chapter V. A discussion of our results is presented in chapter VI.
CHAPTER II
THEORY

This section introduces the theoretical basis for the study of the chain dimensions, dynamic properties and equation-of-state properties of polymer melts.

2.1 Chain Conformation

The study of the different chain dimensions of a polymer chain gives us an idea about the conformations of the chains in a polymer melt. The chain dimensions of flexible chains are different from those of stiffer chains. In the lattice model that will be introduced in detail in chapter III, the bending energy $\varepsilon_A > 0$ represents a bending penalty for bond-angles $\theta \leq 90^\circ$ and determines the stiffness of the chains.

![Figure 2.1](image)

Figure 2.1 Left panel: Illustration of chain conformations of flexible chains, $\varepsilon_A = 0$ in a simulation box. Right panel: Illustration of the conformations of stiffer chains $\varepsilon_A = 20$ in a simulation box.
Figure 2.1 is an illustration of the conformations of flexible and stiffer polymer chains in a simulation box.

In this work, we considered the following chain dimensions of the polymers: the length of the end–to–end vector $R_e$, the bond length $b_l$, the Kuhn segment length $l_k$, and the radius of gyration $R_g$. The positions of the beads of the chain are represented by a set of position vectors $\{\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_N\}$. A bond vector is represented by the vector $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, which is the difference between two position vectors. The end–to–end vector $\vec{R}_e$ of a chain is defined as

$$\vec{R}_e = \vec{r}_N - \vec{r}_1.$$  \hspace{1cm} (2.1)

The average value of $\vec{R}_e$ is zero since the probability of the end–to–end vector being $\vec{R}_e$ is same as it being $-\vec{R}_e$. But the squared end–to–end distance has a finite value. Therefore the root mean square end–to–end distance $R_e$ is calculated by taking the square root of the average squared end–to–end distance of the chain $\langle R_e^2 \rangle$ where

$$R_e^2 = \vec{R}_e \cdot \vec{R}_e.$$  

The average bond length of a polymer chain is calculated with the equation,

$$b_l^2 = \frac{1}{N-1} \sum_{i=1}^{N-1} (\vec{r}_{i+1} - \vec{r}_i)^2.$$  \hspace{1cm} (2.2)

An important characteristic property of a polymer chain is the Kuhn segment length $l_k$, which is calculated as

$$l_k = \frac{R_e^2}{(N-1)b_l}.$$  \hspace{1cm} (2.3)
The Kuhn length represents the length over which the orientation of bonds is correlated. For flexible chains, $l_k$ is typically a few bond lengths; $l_k$ grows with increasing chain stiffness and is used in this work as a measure for the chain stiffness.

Another convenient observable characterizing the chain dimension is the radius of gyration $R_g$, which is equal to the square of the average distance between the segments and the centre of mass of the polymer. This is represented by the equation\(^7\)

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_{c.m.})^2 . \tag{2.4}$$

The position of the center of mass of the polymer is given by the equation

$$\vec{r}_{c.m.} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i . \tag{2.5}$$

On substituting equation (2.5) into equation (2.4), the radius of gyration can also be represented by the equation

$$R_g^2 = \frac{1}{N^2} \sum_{i=0}^{N-1} \sum_{j=i+1}^{N} \vec{r}_{ij}^2 . \tag{2.6}$$

In polymer melts of very long chains, the ratio of the squared radius of gyration and the end–to–end distance is given by

$$\left \langle R_e^2 \right \rangle / \left \langle R_g^2 \right \rangle = 6 . \tag{2.7}$$

The filling fraction of $N_p$ polymer chains of length $N$ on a lattice having $V$ lattice sites is defined as

$$\phi = \frac{NN_p}{V} . \tag{2.8}$$
2.2 Dynamic properties

The mobility of polymer chains in the melt depends on the density and the stiffness of the chains. The single-chain dynamics in the melt can be described with the aid of the self diffusion coefficient $D$ and the correlation time of the end–to–end vector $\tau_{ee}$. The higher the chain mobility, the larger the self-diffusion coefficient and the smaller the correlation time $\tau_{ee}$. Both an increase in the density and an increase of the chain stiffness are expected to slow the dynamics and therefore decrease the self diffusion coefficient and increase the correlation time of the end–to–end vector $\tau_{ee}$. The self diffusion coefficient $D$ is calculated from the mean square displacement of the center of mass $g_d(t)$ while the relaxation time $\tau_{ee}$ is derived from the time correlation function of the end–to–end vector $\phi_e(t)$.

The mean square displacement $g_d(t)$ is used to measure the displacement of the center of mass of the chain as a function of time. It is defined as

$$g_d(t) = \left\langle (\vec{r}_{c.m.}(t) - \vec{r}_{c.m.}(0))^2 \right\rangle,$$

where $r_{c.m.}(t)$ is the position of the center of mass of the chain at time $t$ and $r_{c.m.}(0)$ is the initial position of the center of mass of the same chain. The angular bracket represents two averages: first the displacements of individual chains are averaged over many time origins then an average over all chains is calculated. Figure 2.2 shows simulation results for $g_d/6t$ of polymer chains of length $N = 20$ with chain stiffness parameter $\varepsilon_A = 25$ in a melt of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ as a function of time. The graph shows that $g_d/6t$ decreases with time, attains a constant
value after some time and becomes irregular at long times. The self-diffusion coefficient is evaluated from the data range where $g_d/6t$ is constant.

The mean square displacement of the central monomer of the chains over a time $t$ is obtained from\(^9\)

$$g_1(t) = \left\langle \left( \vec{r}_{N/2}(t) - \vec{r}_{N/2}(0) \right)^2 \right\rangle,$$

where $\vec{r}_{N/2}(t)$ is the position of the central monomer of a chain at time $t$, $\vec{r}_{N/2}(0)$ is the initial position of the central monomer of the same chain, and the average is calculated as before.

**Figure 2.2** The function $g_d/6t$ as a function of time, where $g_d$ is the mean square displacement of the center of mass and $t$ is the time. The symbols represent simulation results for chains of length $N = 20$, with stiffness parameter $\varepsilon_d = 25$ in a melt of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ evaluated with equation (2.9). The light colored symbols indicate the range of values from which the self-diffusion coefficient was determined.
The self–diffusion coefficient is determined from the long–time limit of the mean squared displacement \( g_d(t) \) of the center of mass shown in figure 2.2,

\[
D = \lim_{t \to \infty} \frac{g_d(t)}{6t}.
\]  

(2.11)

The time correlation function of the end–to–end vector \( \phi_e(t) \) is calculated using the equation

\[
\phi_e(t) = \frac{\langle \vec{R}_e(t) \cdot \vec{R}_e(0) \rangle}{\langle (\vec{R}_e(0))^2 \rangle}.
\]  

(2.12)

where \( \vec{R}_e(t) \) is the end–to–end vector at time \( t \) and \( \vec{R}_e(0) \) is the end–to–end vector at time \( t = 0 \). Figure 2.3 shows a graph of \( \phi_e(t) \) as a function of time for the same condition of the polymer as in figure (2.2).
Figure 2.3 Time correlation function of the end-to-end vector $\phi_e$ as a function of time for chains with stiffness parameter $\varepsilon_A = 25$. The broken line represents simulation results for chains of length $N = 20$ in a melt of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ evaluated with equation (2.12). The solid line indicates the value $\phi_e = 0.298$ that determines the relaxation time.

“The relaxation time $\tau_{ee}$ is the time at which the correlation function with Rouse prediction

$$\phi_e(t) = \frac{\langle R_e(t)R_e(0) \rangle}{\langle R_e(0)^2 \rangle} = \sum_{p=1}^{\langle p^2 \pi^2 \rangle} \frac{8}{p^2 \pi^2} \exp(-p^2 t / \tau_{ee})$$

has the value $\phi_e(\tau_{ee}) = \sum_{p=1}^{\langle p^2 \pi^2 \rangle} \frac{8}{p^2 \pi^2} \exp(-p^2) = 0.298221$ i.e., the time at which the correlation function decays to 30% of its original value”.

In this work, we determined self diffusion coefficients and correlation times to investigate the effect of chain stiffness and density on chain mobility.
2.3 Pressure

The density of polymer chains in a melt has a small effect on the chain dimensions and a large effect on the dynamic properties. Since experiments are typically performed under controlled pressure we need to know the effect of chain stiffness on the pressure in order to separate density effects from chain stiffness effects.

In lattice models, the pressure cannot be calculated directly from the simulations at a single density but it can be deduced with special simulation techniques, which will be introduced here. We will start by reviewing some required statistical mechanics relations.

2.3.1 Fluids of monatomic particles

We start with an ideal gas of classical monatomic particles. The ideal gas canonical partition function is given by\(^\text{11}\)

\[
Q(n, V, T) = \frac{1}{n!} \left( \frac{V}{\Lambda^3} \right)^n, \quad (2.13)
\]

where \(\Lambda = \left( \frac{2\pi \hbar^2 \beta}{m} \right)^{1/2}\) is the thermal wavelength of the atoms, \(n\) is the number of particles, \(V\) is the volume of the system, \(T\) is the temperature, and the factor \(1/n!\) accounts for the indistinguishability of the particles. Here \(\beta = (k_B T)^{-1}\), where \(k_B\) is the Boltzmann constant, \(m\) is the mass of a particle and \(\hbar = h/2\pi\), \(h\) being Planck’s constant. The Helmholtz free energy is related to the partition function through,

\[
F = -\frac{\ln(Q(n, V, T))}{\beta} \quad . \quad (2.14)
\]

With equation (2.13), equation (2.14) becomes,
\[-\beta F = \ln \left( \frac{1}{n!} \left( \frac{V}{\Lambda^3} \right)^n \right) = \ln \left( \frac{V}{\Lambda^3} \right)^n - \ln n! . \quad (2.15)\]

With Sterling’s approximation of $\ln n! = n \ln n - n$, it follows that

\[F = -\frac{n}{\beta} \ln \left( \frac{V}{\Lambda^3} \right) + \frac{n}{\beta} \ln n - \frac{n}{\beta} . \quad (2.16)\]

The chemical potential $\mu$ and pressure $p$ are obtained from the Helmholtz free energy through,

\[\mu = \left( \frac{\partial F}{\partial n} \right)_{VT} , \quad (2.17)\]

\[p = -\left( \frac{\partial F}{\partial V} \right)_{nT} . \quad (2.18)\]

With the help of equation (2.16), we find the chemical potential and pressure of the ideal gas,

\[\mu_{id} = -\frac{1}{\beta} \ln \left( \frac{V}{\Lambda^3 n} \right) , \quad (2.19)\]

\[p_{id} = \frac{n}{V\beta} . \quad (2.20)\]

The pressure of an interacting (non-ideal) fluid can be calculated by a thermodynamic integration if the chemical potential is known. The chemical potential may be calculated from the interactions of a “test” particle, as we will now show following Frenkel and Smit. 12

For any system of $n$ classical identical monatomic particles in a box of volume $V$ at temperature $T$, the partition function $Q$ in the canonical $(nVT)$ ensemble is given by\(^{12}\)

\[Q = \frac{1}{\Lambda^{3n} n!} \int \frac{d^3 r_1 \ldots d^3 r_n}{V} \exp\left( -\beta U(r_1 \ldots r_n) \right) , \quad (2.21)\]
where \( U(r_1...r_N) \) is the potential energy of the particles. In the absence of an external field, the potential energy is typically described by a sum over pairwise contributions

\[
U(r_1...r_N) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} U_{ij}.
\]

In general, equation (2.17) can be written in the form

\[
\mu = -\frac{1}{\beta} \frac{\partial \ln(Q(n,V,T))}{\partial n}.
\]  

(2.22)

For sufficiently large \( n \), the partial derivative with respect to \( n \) can be replaced by a difference, therefore,

\[
\mu = -\frac{1}{\beta} \frac{\ln(Q(n+1,V,T)) - \ln(Q(n,V,T))}{(n+1-n)} = -\frac{1}{\beta} \ln\left(\frac{Q_{n+1}}{Q_n}\right).
\]  

(2.23)

Now, from equation (2.21), we can write,

\[
\frac{Q_{n+1}}{Q_n} = \frac{1}{\Lambda^3(n+1)(n+1)!V} \int_{V} d^3r_1...d^3r_{n+1} \exp(-\beta U(r_1...r_{n+1}))
\]

\[
\int_{V} d^3r_1...d^3r_n \exp(-\beta U(r_1...r_n))
\]

\[
= \frac{1}{\Lambda^3(n+1)} \int_{V} d^3r_1...d^3r_{n+1} \exp(-\beta U(r_1...r_{n+1}))
\]

\[
\int_{V} d^3r_1...d^3r_n \exp(-\beta U(r_1...r_n)).
\]  

(2.24)

The potential energy \( U \) of the \( (n+1) \)-particle system may be separated into the energy of the \( n \)-particle system and the interaction energy \( \Delta U \) of the \( (n+1) \)st particle (the “test” particle) with the rest of the system,

\[
U(r_1...r_{n+1}) = U(r_1...r_n) + \Delta U.
\]  

(2.26)

Inserting equation (2.26) into equation (2.25), we find
\[
\frac{Q_{n+1}}{Q_n} = \frac{1}{\Lambda^3(n+1)} \frac{\left\{\int_V d^3 r_1 \ldots d^3 r_n \exp(-\beta U(r_1 \ldots r_n))\right\} \int_V d^3 r_{n+1} \exp(-\beta \Delta U)}{\left\{\int_V d^3 r_1 \ldots d^3 r_n \exp(-\beta U(r_1 \ldots r_n))\right\}}.
\]

(2.27)

The right hand side of equation (2.27) is, up to a prefactor, the canonical ensemble average,

\[
\left\langle \int_V d^3 r_{n+1} \exp(-\beta \Delta U) \right\rangle_n = \frac{1}{\Lambda^3(n+1)} \left\{\int_0^1 d^3 r_1 \ldots d^3 r_n \exp(-\beta U(r_1 \ldots r_n)) \int_0^1 d^3 r_{n+1} \exp(-\beta \Delta U)\right\}.
\]

(2.28)

Hence, equation (2.27) may be expressed as,

\[
\frac{Q_{n+1}}{Q_n} = \frac{1}{\Lambda^3(n+1)} \left\langle \int_V d^3 r_{n+1} \exp(-\beta \Delta U) \right\rangle_n.
\]

(2.29)

For a homogeneous fluid, the integral over space yields a factor of the volume \(V\) so that equation (2.29) becomes

\[
\frac{Q_{n+1}}{Q_n} = \frac{V}{\Lambda^3(n+1)} \langle \exp(-\beta \Delta U) \rangle_n.
\]

(2.30)

On substituting equation (2.30) into equation (2.23), we obtain,

\[
\mu = -\frac{1}{\beta} \ln \left(\frac{V}{\Lambda^3(n+1)} \langle \exp(-\beta \Delta U) \rangle_n\right)
\]

(2.31)

\[
= -\frac{1}{\beta} \ln \left(\frac{V}{\Lambda^3(n+1)}\right) - \frac{1}{\beta} \ln \left(\langle \exp(-\beta \Delta U) \rangle_n\right).
\]

(2.32)

For large \(n\), where \(n+1 \approx n\), we have
\[
\mu = -\frac{1}{\beta} \ln \left( \frac{V}{\Lambda^3 n} \right) - \frac{1}{\beta} \ln \left( \langle \exp(-\beta \Delta U) \rangle_n \right), \quad (2.33)
\]

where the first term is the ideal gas contribution (see equation (2.19)) and the second term is the so-called excess chemical potential,

\[
\mu = \mu_{id} + \mu_{ex}, \quad (2.34)
\]

with

\[
\mu_{ex} = -\frac{1}{\beta} \ln \left( \langle \exp(-\beta \Delta U) \rangle_n \right). \quad (2.35)
\]

The average value \( \langle \exp(-\beta \Delta U) \rangle_n \) represents the probability \( P(n,V,T) \) that an additional particle may be inserted into a fluid of density \( \rho = n/V \) at temperature \( T \). The relation between this probability and the excess chemical potential is the basis of the Widom test particle insertion method.4

2.3.2 Polymer melts

Just as the excess chemical potential of a small-molecule fluid may be obtained from the Widom test particle insertion method, the excess chemical potential of a polymer melt may be obtained from the probability of insertion of a chain molecule. In addition, the excess chemical potential of a polymer melt may also be estimated from the probability of insertion of a test bead at the end of one of the chains. In this section we derive the relations between insertion probabilities, chemical potentials, and the pressure of a polymer melt.
2.3.2.1 Pressure from chain insertion probability

To derive an expression for the excess chemical potential of a polymer melt, we consider a system with \( N_p \) chains of length \( N \) on a lattice of volume \( V \). The (configurational) partition function of the system can be written in the form,

\[
Z(N_p, N, V, \beta) = \frac{1}{N_p!} \sum_{X_{N_p}} \exp(-\beta U_{N_p}),
\]  

(2.36)

where the sum is over all possible configurations \( X_{N_p} \) of the \( N_p \) chains, \( U_{N_p} \) is the total interaction energy experienced by all chains in the melt, \( \beta = (k_B T)^{-1} \), \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

When an attempt is made to insert a test chain of length \( N \) into the melt, the probability of insertion can be expressed as

\[
P(N_p, N, V, \beta) = \left\langle \exp(-\beta \Delta U_{N_p+1}) \right\rangle_{X_{N_p}} \left\langle X_1 \right\rangle_{X_{N_p}},
\]  

(2.37)

where \( \Delta U_{N_p+1} \) is the interaction energy of the test chain with the other chains in the system. The inner bracket indicates the average over the test chain configurations and the outer bracket the average over the configurations of \( N_p \) chains. We will now show how the insertion probability is related to the excess chemical potential and the pressure of the polymer melt.

The average represented by the inner bracket of equation (2.37) over different configurations of the test chain may be written as,
\[
\left\langle \exp(-\beta U_{N_p+1}) \right\rangle_{X_1}^{X_1} = \frac{\sum \exp(-\beta U_1) \exp(-\beta \Delta U_{N_p+1})}{\sum \exp(-\beta U_1)},
\] 

where \( U_1 \) is the intra-chain energy of the test chain and \( X_1 \) represents all single-chain conformation.

The expression for the insertion probability, equation (2.37) then becomes

\[
\left\langle \left\langle \exp(-\beta \Delta U_{N_p+1}) \right\rangle \right\rangle_{X_1}^{X_{N_p}} = \frac{\sum \sum \exp(-\beta U_1) \exp(-\beta \Delta U_{N_p+1}) \exp(-\beta U_{N_p})}{\sum \sum \exp(-\beta U_{N_p}) \sum \exp(-\beta U_1)}. 
\]

\( \text{(2.39)} \)

Since the energy \( U_{N_p+1} \) of a system with \( N_p + 1 \) chains is the sum of the energies of \( N_p \) chains, a single chain, and the interaction of the single chain with the \( N_p \) chains,

\( U_{N_p+1} = U_{N_p} + U_1 + \Delta U_{N_p+1} \), equation (2.39) becomes

\[
\left\langle \left\langle \exp(-\beta \Delta U_{N_p+1}) \right\rangle \right\rangle_{X_1}^{X_{N_p}} = \frac{\sum \exp(-\beta U_{N_p+1})}{\sum \exp(-\beta U_{N_p}) \sum \exp(-\beta U_1)}. 
\]

\( \text{(2.40)} \)

Combining equations (2.37) and (2.40) we obtain an expression for the insertion probability in terms of partition functions

\[
P(N_p, N, V, \beta) = (N_p + 1) \frac{Z_{N_p+1}(N_p + 1, N, V, \beta)}{Z_{N_p}(N_p, N, V, \beta) Z_1(1, N, V, \beta)},
\]

\( \text{(2.41)} \)

which may be rearranged to yield

\[
Z_{N_p+1}(N_p + 1, N, V, \beta) = \frac{Z_{N_p}(N_p, N, V, \beta) Z_1(1, N, V, \beta)}{(N_p + 1)} P(N_p, N, V, \beta).
\]

\( \text{(2.42)} \)
This is a recursion relation for the partition function $Z_{N_{p+1}}$ in terms of $Z_{N_p}$, $Z_1$, and the insertion probability for $N_p$.

If we write the relation (2.42) for $Z_{N_p}$ instead of $Z_{N_{p+1}}$,

$$Z_{N_p}(N_p, N, V, \beta) = \frac{Z_{N_{p-1}}(N_p - 1, N, V, \beta)Z_1(1, N, V, \beta)}{N_p} P(N_p - 1, N, V, \beta) \quad (2.43)$$

and substitute equation (2.43) into (2.42), we obtain $Z_{N_{p+1}}$ in terms of $Z_{N_p}$, $Z_1$, and the insertion probability for $N_p - 1$ and $N_p$,

$$Z_{N_{p+1}} = \frac{Z_{N_{p-1}}(N_p - 1, N, V, \beta)(Z_1)^2}{(N_p + 1)N_p} P(N_p - 1, N, V, \beta)P(N_p, N, V, \beta). \quad (2.44)$$

Repeating the process for $Z_{N_{p-1}}$, $Z_{N_{p-2}}$ and so on, we finally obtain,

$$Z_{N_{p+1}} = \frac{(Z_1(1, N, V, \beta))^{N_{p+1}}}{(N_p + 1)!} \prod_{j=1}^{N_p} P(j, N, V, \beta). \quad (2.45)$$

Therefore, we can express $Z_{N_p}$ as

$$Z_{N_p} = \frac{(Z_1(1, N, V, \beta))^{N_p}}{N_p!} \prod_{j=1}^{N_p-1} P(j, N, V, \beta). \quad (2.46)$$

The Helmholtz free energy $F_{N_p} = -(\ln Z_{N_p})/\beta$ is related to the chemical potential $\mu$ and the pressure $p$ through

$$F_{N_p} = \mu N_p - pV. \quad (2.47)$$
Since $\mu = \left( \frac{\partial F_{N_p}}{\partial N_p} \right)_{VT}$, the chemical potential may be written as

$$\mu = F_{N_p+1} - F_{N_p}.$$  \hfill (2.48)

which yields for the pressure

$$pV = -F_{N_p} + N_p (F_{N_p+1} - F_{N_p}) .$$  \hfill (2.49)

Expressing the Helmholtz free energy in terms of the partition function, we obtain

$$\beta pV = \ln(Z_{N_p} (N_p, N, V, \beta)) - N_p \ln(P(N_p + 1, N, V, \beta))$$

$$+ N_p \ln(Z_{N_p} (N_p, N, V, \beta)) .$$ \hfill (2.50)

Substituting the value of $Z_{N_p+1}(N_p+1, N, V, \beta)$ from equation (2.42) into (2.48), we find

$$\beta pV = \ln(Z_{N_p} (N_p, N, V, \beta))$$

$$- N_p \ln \left( \frac{P(N_p, N, V, \beta)Z_{N_p} (N_p + 1, N, V, \beta)Z_{1}(1, N, V, \beta)}{N_p + 1} \right)$$

$$+ N_p \ln(Z_{N_p} (N_p, N, V, \beta))$$

$$= \ln(Z_{N_p} (N_p, N, V, \beta)) - N_p \ln(Z_{N_p} (N_p, N, V, \beta))$$

$$- N_p \ln(Z_{1}(1, N, V, \beta)) + N_p \ln(N_p + 1) .$$ \hfill (2.51)

Substituting $Z_{N_p} (N_p, N, V, \beta)$ from equation (2.46), we obtain

$$\beta pV = \ln \left( \frac{(Z_{1}(1, N, V, \beta))^{N_p} N_p^{-1} \prod_{j=1}^{N_p} P(j, N, V, \beta)}{N_p!} \right) - N_p \ln(P(N_p, N, V, \beta))$$
\[- N_p \ln(Z_1(1, N, V, \beta)) + N_p \ln(N_p + 1) \]

\[= N_p \ln(Z_1(1, N, V, N_p)) + \sum_{j=1}^{N_p - 1} \ln(P(j, N, V, \beta)) - \ln N_p! - N_p \ln(P) \]

\[- N_p \ln(Z_1(1, N, V, \beta)) + N_p \ln(N_p + 1) \]

\[= \sum_{j=1}^{N_p - 1} \ln(P(j, N, V, \beta)) - N_p \ln N_p + N_p - N_p \ln(P(N_p, N, V, \beta)) \]

\[+ N_p \ln(N_p + 1). \quad (2.52) \]

For $N_p \to \infty, V \to \infty$, with $N_p/V$ fixed, the summation over the number of chains can be replaced by a thermodynamic integration over the volume fraction $\phi = \frac{N N_p}{V}$, i.e.,

\[P(N_p, N, V, \beta) \to P(\phi, N, \beta). \quad (2.53)\]

Taking the limit $N_p \to \infty$, equation (2.52) becomes,

\[\beta p = \pi = \frac{\phi}{N} (1 - \ln(P(\phi, N, \beta))) + \frac{1}{N} \int_0^\phi \ln(P(\phi', V, \beta)) d\phi'. \quad (2.54)\]

From equation (2.23), the chemical potential can be written in the form,

\[\mu = -\frac{1}{\beta} \ln \left( \frac{Z_{N_p+1}}{Z_{N_p}} \right) \quad (2.55)\]

Using equation (2.42), we obtain

\[\mu = -\frac{1}{\beta} \ln \left( \frac{Z_{N_p+1}}{Z_{N_p}} \right) \]

\[= -\frac{1}{\beta} \ln \left( \frac{Z_1 P(\phi, N, \beta)}{N_p + 1} \right) \]
\[=- \frac{1}{\beta} \ln \left( \frac{Z_1}{N_p + 1} \right) - \frac{1}{\beta} \ln(P(\phi, N, \beta))\]

\[\approx - \frac{1}{\beta} \ln \left( \frac{Z_1}{N_p} \right) - \frac{1}{\beta} \ln(P(\phi, N, \beta)).\]  

(2.56)

where we have used that \(N_p + 1 \approx N_p\) for large \(N_p\). In this way we have separated the chemical potential into ideal and excess parts, \(\mu = \mu_{id} + \mu_{ex}\),

\[
\mu_{id} = - \frac{1}{\beta} \ln \left( \frac{Z_1}{N_p} \right),
\]

(2.57)

\[
\mu_{ex} = - \frac{1}{\beta} \ln(P).
\]

(2.58)

Substituting the value of \(\ln(P)\) from equation (2.58) into equation (2.54), we obtain

\[
\pi = \frac{\phi}{N} \left( 1 + \beta \mu_{ex} \right) - \frac{1}{N} \int_0^1 \beta \mu_{ex}(\phi')d\phi'.
\]

(2.59)

Discretizing this equation and using \(\rho = \frac{N_p}{V}\), we can write the \(i^{th}\) and \((i-1)^{th}\) terms as follows,

\[
\pi_i = \rho_i \left( 1 + \beta \mu_{ex}^i \right) - \frac{\beta}{N} \sum_{j=1}^i \mu_{ex}^i \Delta \phi_j,
\]

(2.60)

\[
\pi_{i-1} = \rho_{i-1} \left( 1 + \beta \mu_{ex}^{i-1} \right) - \frac{\beta}{N} \sum_{j=1}^{i-1} \mu_{ex}^i \Delta \phi_j.
\]

(2.61)

where \(\Delta \phi_j = \phi_j - \phi_{j-1}\).
Now subtracting equation (2.61) from (2.60), we obtain
\[
\pi_i - \pi_{i-1} = \rho_i \left(1 + \beta \mu_{\text{ex}}^i\right) - \rho_{i-1} \left(1 + \beta \mu_{\text{ex}}^{i-1}\right) - \frac{\beta}{N} \mu_{\text{ex}}^i \Delta \phi_i ,
\]  
(2.62)

Since \( \mu_{\text{ex}}^i \Delta \phi_i = \mu_{\text{ex}}^i (\phi_i - \phi_{i-1}) \approx \frac{1}{2} \left( \mu_{\text{ex}}^i + \mu_{\text{ex}}^{i-1}\right)(\phi_i - \phi_{i-1}) \), equation (2.62) becomes
\[
\pi_i - \pi_{i-1} \approx \rho_i \left(1 + \beta \mu_{\text{ex}}^i\right) - \rho_{i-1} \left(1 + \beta \mu_{\text{ex}}^{i-1}\right) \\
- \frac{1}{N} \left( \beta \mu_{\text{ex}}^i + \beta \mu_{\text{ex}}^{i-1}\right)(\phi_i - \phi_{i-1})/2 .
\]  
(2.63)

Since \( \phi = N \rho = \frac{NN_p}{V} \), equation (2.62) may also be written in terms of the density \( \rho = N_p / V \),
\[
\pi_i \approx \pi_{i-1} + \rho_i \left(1 + \beta \mu_{\text{ex}}^i\right) - \rho_{i-1} \left(1 + \beta \mu_{\text{ex}}^{i-1}\right) \\
- \left( \beta \mu_{\text{ex}}^i + \beta \mu_{\text{ex}}^{i-1}\right)(\rho_i - \rho_{i-1})/2 .
\]  
(2.64)

In this work, we use equation (2.64) with (2.58) to calculate the pressure from the chain insertion probabilities determined from MC simulations on a closely spaced grid of densities.

2.3.2.2 Pressure from end-bead insertion probability

The excess chemical potential of a polymer melt can also be obtained from a system having \( N_p - 1 \) chains of length \( N \) and one chain of length \( N+1 \). For that let us first consider a system of \( N_p \) chains of length \( N \) in a box of volume \( V \) at temperature \( T \). The chemical potential of a single chain can be written as (see equation (2.23))
\[
- \beta \mu(N) = \ln\left(Z(N_p, N, V, \beta)\right) - \ln\left(Z(N_p - 1, N, V, \beta)\right) .
\]  
(2.65)
where $Z(N_p, N, V, \beta) = \frac{1}{N_p!} \sum_{X_{N_p}} \exp(-\beta U_{N_p, N})$ is the partition function for the system of $N_p$ chains and $U_{N_p, N}$ is the total interaction energy of the $N_p$ chains of length $N$.

When a bead is inserted into the melt and attached to an end of one of the chains, there are $N_p - 1$ chains of length $N$ and one chain of length $N+1$. The chemical potential of the single chain of length $N+1$ can be written as

$$-\beta \mu(N + 1) = \ln(Z(N_p - 1, N, 1, N + 1, V, \beta)) - \ln(Z(N_p - 1, N, V, \beta)),$$

where $Z(N_p - 1, N, 1, N + 1, V, \beta) = \frac{1}{N_p!} \sum_{X_{N_p}} \sum_{W_1} \exp(-\beta U_{tot})$ and

$$U_{tot} = U_{N_p - 1, N} + U_{1, N} + \Delta U_{N+1},$$

where the first term is the energy of $N_p - 1$ chains of length $N$, the second term is the energy of only $N$ beads of the chain whose length is $N+1$, and the last term is the energy of the inserted bead i.e., the $(N+1)^{\text{st}}$ bead of the chain of length $N+1$, $W_1$ represents all conformations of the test bead.

Therefore, equation (2.67) can be written in the form,

$$U_{tot} = U_{N_p, N} + \Delta U_{N+1}.$$

Subtracting equation (2.65) from (2.66), we obtain

$$-\beta (\mu(N + 1) - \mu(N)) = \ln(Z(N_p - 1, N, 1, N + 1, V, \beta)) - \ln(Z(N_p, N, V, \beta)).$$

(2. 69)
Let $\mu_c$ be the residual chemical potential between a chain of length $N+1$ and a chain of length $N$, then equation (2.69) becomes

$$- \beta \mu_c = \ln \left( \frac{Z(N_p - 1, N, 1, N + 1, V, \beta)}{Z(N_p, N, V, \beta)} \right)$$  \hspace{1cm} (2.70)$$

$$= \ln \left( \frac{\sum_{X_{N_p}} \exp(-\beta U_{N_p}) \sum_{W_1} \exp(-\beta \Delta U_{N+1})}{\sum_{X_{N_p}} \exp(-\beta U_{N_p})} \right).$$  \hspace{1cm} (2.71)$$

Since

$$\langle \exp(-\beta \Delta U_{N+1}) \rangle = \frac{\sum_{X_{N_p}} \exp(-\beta U_{N_p}) \sum_{W_1} \exp(-\beta \Delta U_{N+1})}{\sum_{X_{N_p}} \exp(-\beta U_{N_p})}.$$$$

Then equation (2.71) becomes

$$- \beta \mu_c = \ln \langle \exp(-\beta \Delta U_{N+1}) \rangle_N,$$  \hspace{1cm} (2.72)$$

where $\langle \exp(-\beta \Delta U_{N+1}) \rangle_N$ is the probability of successful insertion of the bead at the end of any of the chains in the system and is averaged over all the chains present in the box. $\Delta U_{N+1}$ is the interaction energy of the inserted bead with all the other beads in the system. Equation (2.72) has the same form as equation (2.35).

Under the assumption that the chemical potential of a polymer chain can be approximated by the excess chemical potential for a bead times the length of the chain, we can approximate the pressure relation from the bead insertion method by modifying equation (2.64).
\[ \pi_i \approx \pi_{i-1} + \phi_i \left( 1 + \beta N \mu_c^i \right) - \phi_{i-1} \left( 1 + \beta N \mu_c^{i-1} \right) - \left( \beta N \mu_c^i + \beta N \mu_c^{i-1} \right) (\phi_i - \phi_{i-1}) / 2. \]  \hspace{1cm} (2.73)

For fixed volume, the relation between pressure and chemical potential can also be expressed in the form,

\[ \frac{\partial (\beta p)}{\partial \rho} = \rho \frac{\partial (\beta \mu)}{\partial \rho}. \]  \hspace{1cm} (2.74)

Writing only for the excess part, we obtain

\[ \frac{\partial (\beta p_{\text{ex}})}{\partial \rho} = \rho \frac{\partial (\beta \mu_{\text{ex}})}{\partial \rho}. \]  \hspace{1cm} (2.75)

If \( \mu_{\text{ex}}, \mu_{\text{ex}}^I, p_{\text{ex}}, p_{\text{ex}}^I \) and \( p_{\text{ex}}^H \) are chemical potentials and pressures from bead insertion and chain insertion methods respectively, the difference can be expressed in the form

\[ \frac{\partial (\beta p_{\text{ex}}^I - \beta p_{\text{ex}}^H)}{\partial \rho} = \rho \frac{\partial (\beta \mu_{\text{ex}}^I - \beta \mu_{\text{ex}}^H)}{\partial \rho}. \]  \hspace{1cm} (2.76)

2.3.3 Approximate equations-of-state for polymer melts

The pressure can be estimated from the Flory (F) and Flory-Huggins (FH) theories for lattice chains. Following Dickman and Hall\(^6\) we consider a chain molecule of length \( N \) that is inserted randomly into a system of \( N_p \) fully flexible athermal chains with length \( N \) and fixed bond length \( a \) on a simple cubic lattice with lattice constant \( a \) and coordination number \( z \). In this case, the probability of insertion, equation (2.37), is independent of temperature, i.e., the Boltzmann factor inside the brackets is unity if the inserted chain
does not overlap with other existing chains and zero otherwise. The insertion probability may be written in the form,

\[ P(N_p, N, V) = \left\langle \left\langle \chi \right\rangle \right\rangle \left. X_{N_p} \right. \]

(2.77)

where \( \chi \) is 0 for overlap of the test chain with the \( N_p \) chains in the lattice and unity otherwise. The inner bracket indicates the average over the test chain configurations and the outer bracket the average over the configurations of the \( N_p \) chains. If the probability of insertion of a single chain conformation into a randomly chosen configuration of \( N_p \) chains without overlap is \( P(X_1) = \left\langle \chi \right\rangle X_{N_p} \) then equation (2.77) may be written as

\[ P(N_p, N, V) = \left\langle \left\langle P(X_1) \right\rangle \right\rangle X_{N_p} \]

(2.78)

Let \( X_1 = (x_1, x_2, \ldots, x_N) \) be the different sites to be occupied by the test chain, then

\[ P(X_1) = (1 - \phi)P(x_2/x_1)P(x_3/x_1x_2) \cdots P(x_N/x_1x_2 \ldots x_{N-1}) \]

(2.79)

where \( P(x_2/x_1) \) is the probability to find site \( x_2 \) empty given that site \( x_1 \) is empty, \( P(x_3/x_1x_2) \) is the probability for \( x_3 \) to be empty given that \( x_1 \) and \( x_2 \) are empty, and so on. The factor \( (1 - \phi) \) is the probability to find the site for the first bead empty when the lattice has a filling fraction of \( \phi \).

In the Flory approximation, the probabilities for finding sites available for occupation by the beads of the polymer chain are assumed to be given by

\[ P(x_k/x_1x_2 \ldots x_{k-1}) = P(x_1) = (1 - \phi) \]

(2.80)
for all \( k \geq 2 \). Therefore, the probability of insertion in Flory’s approximation may be written as

\[
P_F(\phi, N) = (1 - \phi)^N \tag{2.81}
\]

This probability is the same as the probability for finding \( N \) empty sites scattered randomly over the lattice.

Substituting the probability of insertion, equation (2.81), into equation (2.54), we can estimate the pressure \((\pi)\) due to the inserted test chain in the system. This yields for the compressibility factor \( Z = \frac{\beta n}{\rho} \) in Flory’s approximation,\(^\text{13}\)

\[
Z_F = 1 - N[\ln(1 - \phi) + \phi]/\phi . \tag{2.82}
\]

In the Flory-Huggins approach, the conditional probabilities \( P(x_k / x_1 x_2 \ldots x_{k-1}) \) are approximated by the probabilities for finding pairs of available sites,

\[
P(x_k / x_1 x_2 \ldots x_{k-1}) = P(x_k / x_{k-1}) \text{ for all } k \geq 2 ,
\]

so that the insertion probability becomes

\[
P_{FH}(\phi, N) = (1 - \phi)(1 - \phi_o)^{N-1} . \tag{2.83}
\]

where \( \phi_o \) is the probability that the neighbor of a vacant site is occupied.

With an estimate for \( \phi_o \) suitable for a fixed bond length model, the insertion probability in the FH approximation becomes

\[
P_{FH}(\phi, N) = (1 - \phi)^N \left[ 1 - 2\phi z^{-1}(1 - N^{-1}) \right]^{(N-1)} . \tag{2.84}
\]

This yields for the compressibility factor in the Flory-Huggins approximation\(^\text{13}\)

\[
Z_{FH} = Z_F + \frac{Nz}{2\phi} \left\{ \ln \left[ 1 - 2\phi z \left( 1 - \frac{1}{N} \right) \right] + \frac{2\phi}{z} \left( 1 - \frac{1}{N} \right) \right\} . \tag{2.85}
\]
CHAPTER III
LATTICE MODEL

In this section we discuss the lattice model for polymers that we use in this work, it is an extension of Shaffer’s bond fluctuation model.

Shaffer’s bond fluctuation model is a lattice model for polymer chains, where each polymer bead occupies a site on a simple cubic lattice. We use the lattice constant as the unit of length and set $a = 1$. There are three allowed bond lengths with values $1$, $\sqrt{2}$, and $\sqrt{3}$ for this model and bonds cannot cross each other. The excluded volume interaction between the monomers is applied by forbidding the double occupancy of lattice sites.$^3$

Figure 3.1 Illustration of Shaffer’s bond fluctuation model. The solid circles and lines represent monomers (beads) and bonds of a single polymer chain of $N = 20$ segments.
The allowed set of bond vectors connecting the polymer segments is given by

\[ \vec{b} \in P(1,0,0) \cup P(1,1,0) \cup P(1,1,1), \]  

(3.1)

where the symbol \( P(x, y, z) \) denotes all distinct permutations and inversions of the triplet \((x, y, z)\). For example,

\[ P(1,0,0) = \{(1,0,0),(0,1,0),(0,0,1),(1,0,0),(-1,0,0),(0,-1,0),(0,0,1)\}. \]  

(3.2)

As an illustration, the conformation of a single polymer chain on the lattice is shown in Figure (3.1).

In order to prevent bond crossing, a secondary cubic lattice the “mid-point lattice” with lattice constant \( a = 1/2 \) is added to the existing lattice. Enforcing the excluded volume condition on the secondary lattice sites prohibits bond crossing because bond crossing always occurs at the mid points of the original lattice.

In this work, two types of interactions are added to Shaffer’s bond fluctuation model. First, there is an attractive interaction between non-bonded monomers occupying nearest neighbor sites on the lattice; the corresponding interaction energy is \( \varepsilon_B < 0 \). Second a bending energy \( \varepsilon_A > 0 \) represents a bending penalty for bond-angles \( \theta \leq 90^\circ \). Figure 3.2 illustrates the bead–bead and bending interaction.
Figure 3.2 Illustration of bead-bead and bond interactions in our lattice model. The interaction energy for non-bonded beads on nearest-neighbor sites is $\varepsilon_B$ and the bending energy for bond angles $\theta \leq 90^\circ$ is $\varepsilon_A$.

For our model, the total internal energy of the system is given by

$$E = n_A \varepsilon_A + n_B \varepsilon_B ,$$  \tag{3.3} \]

where $n_A$ denotes the number of bond angles with $\theta \leq 90^\circ$ and $n_B$ is the number of non-bonded bead-bead contacts. Throughout this work, we set $\varepsilon_B = -1$.

In this work, all the polymer chains on the lattice are of the same length. The chain conformations, dynamic properties and equation-of-state properties of polymer melts are studied by Monte Carlo Simulations. Periodic boundary conditions are applied on both the primary and secondary lattice in all three coordinate directions.
4.1 Monte Carlo simulations

A major goal of Monte Carlo simulations is to estimate the static average of an observable in an ensemble at given conditions by generating and evaluating a large number of appropriate configurations\textsuperscript{14}. To this end, one generates an initial configuration and then performs elementary move attempts that are accepted or rejected based on an acceptance criterion. If the elementary moves are chosen carefully, one can also obtain information about the dynamic properties of the system. In our case, the initial configuration for a polymer melt of filling fraction $\phi$ on an $L \times L \times L$ lattice consists of $N_p$ polymer chains of length $N$ so that $\phi = \frac{N N_p}{L^3}$. Periodic boundary conditions are applied in all three coordinate directions. We read pre-equilibrated configurations for the chosen conditions (inverse temperature $\beta$, bead-bead interaction energy $\varepsilon_B$, and bending energy $\varepsilon_A$). In an elementary move, a polymer segment is selected at random and a displacement is attempted to a randomly chosen nearest neighbor site. For the move
to be accepted, the chosen site must be empty, the bond length must be among the
allowed set of bond lengths, and the non-bond crossing condition must be satisfied. If this
is the case, the energy associated with the bead before \( E_1 \) and after \( E_2 \) the move is
calculated according to equation (3.3). If \( \Delta E = E_2 - E_1 \) is less than zero the move is
accepted. Otherwise, if \( (\Delta E > 0) \), the move is accepted with probability \( P = \exp(-\beta\Delta E) \),
where \( \beta = (k_B T)^{-1} \), \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. If the move is
accepted, coordinate and midpoints are updated otherwise the original configuration is
retained. One Monte Carlo step consists of \( N_p \times N \) attempted elementary moves. The
different time scales used in Monte Carlo simulations are tabulated in Table 4.1.
Table 4.1 Time scales of Monte Carlo simulations.\(^{15}\)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau_{\text{move}})</td>
<td>Time for an elementary move of a polymer segment.</td>
</tr>
<tr>
<td>(\tau_{MC} = (N_p \times N)\tau_{\text{move}})</td>
<td>Monte Carlo time step (MC)</td>
</tr>
<tr>
<td>(\tau_{\text{corr}} = k_{\text{corr}}\tau_{MC})</td>
<td>Time over which configurations are correlated.</td>
</tr>
<tr>
<td>(\tau_{\text{equib}} = k_{\text{equib}}\tau_{MC})</td>
<td>Time required for the system to achieve equilibration.</td>
</tr>
<tr>
<td>(\tau_{\text{obs}} = k_{\text{obs}}\tau_{MC})</td>
<td>Time over which the quantities are evaluated.</td>
</tr>
<tr>
<td>(\tau_{\text{run}} = k_{\text{run}}\tau_{MC})</td>
<td>Total run time of the simulation</td>
</tr>
<tr>
<td>(\tau_{\text{block}} = k_{\text{block}}\tau_{MC})</td>
<td>Time for block average</td>
</tr>
<tr>
<td>(\tau_{\text{gap}} = k_{\text{gap}}\tau_{MC})</td>
<td>Time between evaluation of configurations.</td>
</tr>
</tbody>
</table>

Typical times used in our simulations are tabulated in Table 4.2.
Table 4.2 Time scales in our Monte Carlo simulations.

<table>
<thead>
<tr>
<th>Number of Monte Carlo steps</th>
<th>( k_{\text{obs}} = 10^7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of equilibration steps</td>
<td>( k_{\text{equil}} = 10^6 )</td>
</tr>
<tr>
<td>Number of MC steps between evaluation</td>
<td>( k_{\text{gap}} = 10 )</td>
</tr>
</tbody>
</table>

The block averaging technique, see figure 4.1, is used to estimate errors during the simulation. For block averaging, we divide the observation time \( \tau_{\text{obs}} = k_{\text{obs}} \tau_{\text{MC}} \) into blocks and calculate the average of a quantity within each block.

![Figure 4.1 Block averaging technique](image)

For each block \( b \in \{1, \ldots, n_{\text{block}}\} \) the average of a quantity \( A \) within the block is calculated using the equation
\[ A(b) = \frac{1}{k_{block}} \sum_{k=k_b+1}^{k_b+k_{block}} A_k, \]  

(4.1)

with \( k_b = (b-1)k_{block} \). An overall average is calculated with the equation

\[ \langle A \rangle = \frac{1}{n_{block}} \sum_{b=1}^{n_{block}} A(b). \]  

(4.2)

The standard deviation \( \sigma_A \) of block values provides an estimate for the statistical error of the quantity

\[ \sigma_A = \left[ \frac{1}{(n_{block} - 1)} \sum_{b=1}^{n_{block}} (A(b) - \langle A \rangle)^2 \right]^{1/2}. \]  

(4.3)

4.2 Evaluation of chain dimensions

The chain dimensions of the polymers we evaluated are: the length of the end–to–end vector \( R_e \), the bond length \( b_l \), and the radius of gyration \( R_g \). The mean square end–to–end distance is obtained by averaging of the end–to–end distances of the chains over all \( (N_p) \) chains and all evaluated \( (k_{conf} = k_{obs} / (n_{block} \times k_{gap})) \) conformations in a block. The equation is

\[ \langle R_e^2 \rangle = \frac{1}{k_{conf} \times k_{conf}} \sum_{N_p} \frac{1}{N_p} \sum_{N_p} R_e^2, \]  

(4.4)

where \( N_p \) is the number of chains. The mean square radius of gyration is calculated similarly.
The mean square bond-length is calculated by taking the average of the bond length of all bonds \((N-1)\) in a chain and averaging this over all chains \(N_p\) and all \(k_{\text{conf}}\) conformations in a block. The equation is

\[ \left\langle b_i^2 \right\rangle = \frac{1}{k_{\text{conf}}} \sum_{k_{\text{conf}}} \frac{1}{N_p} \sum_{N_p} \left( \frac{1}{N-1} \sum_{N-1} b_i^2 . \right) \]  

(4.5)

4.3 Evaluation of dynamic properties

The dynamic properties we evaluated are: the mean square displacement of the central monomer \(g_1(t)\), the mean square displacement of the center of mass \(g_d(t)\), and the time correlation function \(\phi_e(t)\) of the end-to-end vector. The unit of time is Monte Carlo steps (MCs).

The mean square displacement of the center of mass \(g_d(t)\) is obtained by the equation

\[ g_d(t) = \frac{1}{N_p} \sum_{N_p} \left( \frac{1}{k_{\text{conf}}} \sum_{k_{\text{conf}}} \sum_{n} \left( r_{\text{c.m.}}(t) - r_{\text{c.m.}}(0) \right)^2 , \right) \]  

(4.6)

where \(t = nk_{\text{gap}}\) and \(n\) varies from 0 to \((k_{\text{conf}}/2) - 1\). In equation (4.6) \(k_{\text{conf}}\) denotes the total number of evaluated conformations in the simulation. The mean square displacement of the central monomer \(g_1(t)\) is determined similarly. For the displacement functions, the so-called parent coordinates of the configurations are used to calculate the coordinates of the center of mass and the central monomer without application of periodic boundary conditions.
For the time correlation function $\phi_e(t)$ the following equation is used

$$\phi_e(t) = \frac{1}{N_p N_p} \sum_{k_{conf} = n} \sum_{k_{conf} = n} \frac{1}{\bar{R}_e(0) \cdot \bar{R}_e(0)} \left( \bar{R}_e(t) \cdot \bar{R}_e(0) \right)$$  \hspace{1cm} (4.7)

4.4 End-bead insertion method

The end-bead insertion method is used to estimate the chemical potential of a polymer segment in a polymer melt from Monte Carlo simulations. The trial position for the bead is determined by randomly choosing first one of the $N_p$ chains of the melt, then one of its two chain ends, and finally one of the 26 allowed bond vectors which, added to the position of the chain’s last bead, yields the trial positions of the test bead.

After each Monte Carlo step an attempt is made to insert a bead at a trial position. If the trial position is occupied or results in bond-crossing, an interaction energy $\Delta U_{N+1} = \infty$ (overlap) is assigned, otherwise the number of contacts with non-bonded nearest neighbors is determined and the energy $(\Delta U_{N+1})$ is calculated. $\Delta U_{N+1}$ is the sum of the interaction energy of the test bead with all non-bonded beads in nearest neighbors distance and the bending energy, if the bond angle between the end bead and the inserted bead is less than $90^\circ$.

A two dimensional illustration of the end-bead insertion method is shown in figure (4.2). The position of the test bead is the nearest neighbor site of a chain end. The new bond makes a bond angle of $90^\circ$ which results in a bending energy $\varepsilon_A$. The non-bonded bead-bead interaction with a segment of a different chain at a nearest neighbor distance is shown as $\varepsilon_B$ in the figure.
Figure 4.2: Two-dimensional illustration of an end-bead insertion with bead-bead interaction energy $\varepsilon_B$ and bending penalty $\varepsilon_A$.

A histogram of the energy $\Delta U_{N+1}$ is generated from the results of all insertion attempts. For example, when $\varepsilon_A = 0$, the possible energy values $e_i$ for the test bead are $e_i \in \{-6, -5, \ldots, 0, \infty\}$. If $h(e_i)$ is the number of times the energy $e_i$ was encountered, then $P(e_i) = \frac{h(e_i)}{\sum_i h(e_i)}$ is the probability for $e_i$. The probability of insertion is then determined by the relation

$$P = \sum_i P(e_i) \exp(-\beta e_i) .$$

(4.8)

In figure 4.3 we present results for the probability $P(e_i)$ as a function of the Boltzmann factor for two different temperatures.
Figure 4.3 The probability $P(e_i)$ as a function of the Boltzmann factor $\exp(-\beta e_i)$ for two different temperatures for chain length $N = 20$, bending penalty $\varepsilon_A = 0$ and filling fraction $\phi = 0.5$. The color filled and open bars correspond to $\beta = 0.1$ and $\beta = 0.2$, respectively.

The excess chemical potential is calculated from equation (2.72) and the pressure from equation (2.73).

4.5 Chain insertion method

In this technique, attempts are made to insert a test chain at random into a polymer melt containing $N_p$, polymer chains of length $N$. The test chain conformations are those of isolated chains at the same temperature and energy parameters. In order to generate the test chain conformations, a Monte Carlo simulation for a single chain is performed at the required temperature for $10^8$ MC steps and conformations are recorded every ten MC
steps. For filling fractions smaller than $\phi = 0.3$, ten insertion attempts with different stored conformations are made after each MC step. For higher densities, we generated new configurations of the test chain which is discussed below. Parameters used in the chain insertion method for density higher than $\phi = 0.3$ are presented in table 4.3 where $N_p$ is the number of chains, $\phi$ the filling fraction, $k_{obs}$ the number of observation Monte Carlo steps, $k_{equib}$ the number of equilibration steps, $k_{gap}$ the number of Monte Carlo steps between evaluations, $N_{ins}$ the number of insertion attempts in each Monte Carlo step, $N_{single}$ the number of new configurations made from one existing chain conformation, and $N_{success}$ the number of successful insertions. In order to create new configurations from the existing chain, $N$ local and five pivot moves are performed.

Table 4.3 Parameters used in the chain insertion method for melts at inverse temperature $\beta = 0$, $\beta = 0.1$ ($\varepsilon_A = 0$, $\varepsilon_A = 5$). The last column shows representative results for the number of successful insertions for $\beta = 0$.

<table>
<thead>
<tr>
<th>$N_p$</th>
<th>$\phi$</th>
<th>$k_{obs}$</th>
<th>$k_{equib}$</th>
<th>$k_{gap}$</th>
<th>$N_{ins}$</th>
<th>$N_{single}$</th>
<th>$N_{success}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.325</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>76402</td>
</tr>
<tr>
<td>140</td>
<td>0.35</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>35853</td>
</tr>
<tr>
<td>150</td>
<td>0.375</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>32657</td>
</tr>
<tr>
<td>160</td>
<td>0.4</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>50</td>
<td>35486</td>
</tr>
<tr>
<td>170</td>
<td>0.425</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>30060</td>
</tr>
<tr>
<td>180</td>
<td>0.45</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>200</td>
<td>24777</td>
</tr>
<tr>
<td>190</td>
<td>0.475</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>500</td>
<td>24003</td>
</tr>
<tr>
<td>200</td>
<td>0.5</td>
<td>$10^7$</td>
<td>$10^7$</td>
<td>10</td>
<td>10</td>
<td>1000</td>
<td>17617</td>
</tr>
</tbody>
</table>
For every insertion attempt it is tested whether the inserted test chain would overlap with any of the chains in the melt. If this is the case, an interaction energy $\Delta U_{Np+1} = \infty$ (overlap) is assigned, otherwise the number of contacts of all beads in the test chain with the other chains in the melt is determined and the interaction energy $\left( \Delta U_{Np+1} \right)$ is computed. As in the case of end-bead insertion, we generate a histogram of the energy $\Delta U_{Np+1}$ and determine the insertion probability. The number of intervals in the histogram is 70 with minimum energy -6 and maximum energy 1 for bending energy zero. For the case with bending energy, the number of intervals in the histogram is 120 with minimum energy -6 and maximum energy $1 + \varepsilon_A$. The probability of insertion is calculated from equation (2.37) and the pressure from equation (2.64).
CHAPTER V
RESULTS AND DISCUSSION

5.1 Chain dimensions

In this section we present the results for chain dimensions obtained from the Monte Carlo simulations for lattice size $L = 20$, chain length $N = 20$, density $\phi = 0.5$ and inverse temperature $\beta = 0.1$. For chain dimensions, errors are estimated by the method of block averaging. Table 5.1 displays the results of chain dimensions and their error estimates for bending energy $\varepsilon_A = 0$ to 30.

Table 5.1 Results of chain dimensions for polymers in the melt for filling fraction $\phi = 0.5$, inverse temperature $\beta = 0.1$ and different bending energies ($\varepsilon_A$).

<table>
<thead>
<tr>
<th>Bending energy $\varepsilon_A$</th>
<th>MC steps for production (equilibration)</th>
<th>Number of simulations</th>
<th>(end-to-end distance)$^2$</th>
<th>(Radius of gyration)$^2$</th>
<th>(Bond length)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1\times10^7(10^6)$</td>
<td>3</td>
<td>45.9±0.13</td>
<td>7.89±0.015</td>
<td>2.0688±0.0003</td>
</tr>
<tr>
<td>5</td>
<td>$1\times10^7(10^6)$</td>
<td>3</td>
<td>55.5±0.14</td>
<td>9.39±0.019</td>
<td>2.0758±0.0004</td>
</tr>
<tr>
<td>10</td>
<td>$1\times10^7(10^6)$</td>
<td>3</td>
<td>68.6±0.29</td>
<td>11.35±0.034</td>
<td>2.084±0.0004</td>
</tr>
<tr>
<td>15</td>
<td>$1\times10^7(10^6)$</td>
<td>3</td>
<td>84.5±0.43</td>
<td>13.65±0.05</td>
<td>2.0922±0.0004</td>
</tr>
<tr>
<td>20</td>
<td>$1\times10^7(10^6)$</td>
<td>3</td>
<td>101.8±0.58</td>
<td>16.04±0.06</td>
<td>2.0994±0.0005</td>
</tr>
<tr>
<td>25</td>
<td>$1\times10^7(10^6)$</td>
<td>3</td>
<td>118.4±0.75</td>
<td>18.24±0.078</td>
<td>2.1051±0.0006</td>
</tr>
<tr>
<td>30</td>
<td>$1\times10^8(10^7)$</td>
<td>3</td>
<td>132.3±0.36</td>
<td>20.02±0.039</td>
<td>2.1095±0.0002</td>
</tr>
</tbody>
</table>
Figure 5.1 Mean square radius of gyration $R_g^2$ as a function of bending energy $\varepsilon_A$. The symbols represent simulation results with error bars for chains of length $N = 20$, in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.6). The solid line connects the data points.

Figure 5.1 shows the radius of gyration as a function of bending energy. The graph shows that, as the bending energy increases the $R_g^2$ value of the chain increases. The root mean square bond length of the polymer chains as a function of bending energy is shown in figure 5.2. It is seen from the graph that the root mean square bond length increases slightly with increasing bending energy.
Figure 5.2 The root mean square bond length $b_i$ as a function of bending energy $\varepsilon_A$. The symbols represent simulation results with error bars for chains of length $N = 20$ in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.2). The solid line connects the data points.

The Kuhn segment length may be calculated from the mean square end-to-end distance and the bond length of a polymer chain of given length as shown in equation (2.3). Figure 5.3 is a graph of the Kuhn segment length as a function of bending energy. The figure shows that the Kuhn segment length increases monotonically with increasing bending energy. Since the Kuhn segment length is a measure of chain stiffness the present model allows us to describe semiflexible polymers with varying degree of stiffness by adjusting the bending energy $\varepsilon_A$. We have also calculated the chain dimensions for lattice size $L = 20$, chain length $N = 20$, density $\phi = 0.6$ and inverse
temperature $\beta = 0.1$ and found that the density has no significant effect on the chain dimensions for polymer melts in this density range.

![Diagram](image)

**Figure 5.3** Kuhn segment length $l_k$ as a function of bending energy $\varepsilon_A$. The symbols represent simulation results with error bars for chains of length $N = 20$ in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.3). The solid line connects the data points.

5.2 Dynamic properties

The results of dynamic properties obtained from the Monte Carlo simulations for lattice size $L = 20$, chain length $N = 20$, density $\phi = 0.5$ and inverse temperature $\beta = 0.1$ are presented in this section. The mean square displacements and time-correlation...
function for different chain stiffness are evaluated during the Monte-Carlo simulation. From graphs of these functions we determine values for the self-diffusion coefficient $D$ and relaxation time $\tau_{ee}$ of polymer chains in the melt. The values and uncertainties of the self-diffusion coefficient $D$ and the relaxation time $\tau_{ee}$ are obtained by taking the average and standard deviation from three sets of simulation results. Table 5.2 displays the results for the self-diffusion coefficient and the relaxation time $\tau_{ee}$ and their error estimates for bending energy $\varepsilon_A = 0$ to $\varepsilon_A = 30$.

Table 5.2 Results of the self-diffusion coefficient and relaxation time for polymer chains of length $N = 20$ in melts with filling fraction $\phi = 0.5$ and inverse temperature $\beta = 0.1$ for different bending energies $\varepsilon_A$.

<table>
<thead>
<tr>
<th>Bending energy $\varepsilon_A$</th>
<th>MC steps for production (equilibration)</th>
<th>Number of simulations</th>
<th>Self-diffusion coefficient $D \times 10^{-3}$</th>
<th>Relaxation Time $\tau_{ee} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1 \times 10^7 (10^6)$</td>
<td>3</td>
<td>$0.41 \pm 0.0016$</td>
<td>$3.51 \pm 0.050$</td>
</tr>
<tr>
<td>5</td>
<td>$1 \times 10^7 (10^6)$</td>
<td>3</td>
<td>$0.32 \pm 0.0017$</td>
<td>$5.11 \pm 0.066$</td>
</tr>
<tr>
<td>10</td>
<td>$1 \times 10^7 (10^6)$</td>
<td>3</td>
<td>$0.22 \pm 0.0028$</td>
<td>$8.90 \pm 0.0$</td>
</tr>
<tr>
<td>15</td>
<td>$1 \times 10^7 (10^6)$</td>
<td>3</td>
<td>$0.14 \pm 0.000067$</td>
<td>$17.11 \pm 0.24$</td>
</tr>
<tr>
<td>20</td>
<td>$1 \times 10^7 (10^6)$</td>
<td>3</td>
<td>$0.084 \pm 0.000026$</td>
<td>$31.60 \pm 0.75$</td>
</tr>
<tr>
<td>25</td>
<td>$1 \times 10^7 (10^6)$</td>
<td>3</td>
<td>$0.050 \pm 0.000026$</td>
<td>$57.88 \pm 1.37$</td>
</tr>
<tr>
<td>30</td>
<td>$1 \times 10^7 (10^5)$</td>
<td>3</td>
<td>$0.031 \pm 0.00044$</td>
<td>$107.92 \pm 3.93$</td>
</tr>
</tbody>
</table>
Graphs of the mean square displacement of the center of mass $g_d$ as a function of time for different bending energies are shown in figure 5.4. It is seen from the figure that the mean square displacement of the center of mass $g_d$ increases with increasing time and decreases with increasing bending energy. The results show that the stiffer chains reach the diffusion regime, where $g_d$ is a linear function of time, at a later time than the more flexible chains. The diffusive region is indicated by a thick solid line of slope one.

Figure 5.4 Mean square displacement of the center of mass $g_d$ as a function of time for different bending energies for chains of length $N = 20$ in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.9). The thick solid line is of slope one and illustrates diffusive behavior.
Figure 5.5 shows graphs of the mean square displacement of the central monomer, $g_1$, as a function of time for different bending energies. As in the case of the center of mass displacement, the mean square displacement of the central monomer increases with increasing time and decreases with increasing bending energy. The graphs of $g_1(t)$ in log-log representation show a decrease in slope around $t = 10^3$ MCs for the most flexible chains. This change in slope has been interpreted as the onset of entanglement\(^9\) and appears to be missing for the stiffer chains.

![Graph of $g_1(t)$ for different bending energies](image)

Figure 5.5 Mean square displacement of the central monomer, $g_1$, as a function of time for different bending energies for chains of length $N = 20$, in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.10).
Figure 5.6 Time correlation function of the end-to-end vector $\phi_e$ as a function of time for different bending energies for chains of length $N = 20$, in melts of filling fraction $\phi = 0.5$ at inverse temperature $\beta = 0.1$ calculated with equation (2.12).

Figure 5.6 shows the correlation function of the end-to-end vector as a function of time for different values of the bending energy. It is seen that the correlation function of the end-to-end vector decays less rapidly with time as the bending energy is increased.

We have also calculated dynamic properties for lattice size $L = 20$, chain length $N = 20$, density $\phi = 0.6$ and inverse temperature $\beta = 0.1$. Results for the self-diffusion coefficients as a function of Kuhn segment length for two densities, $\phi = 0.5$ and $\phi = 0.6$ are shown in figure 5.7. The graphs show that the logarithm of the self-diffusion coefficient decreases almost linearly with increasing Kuhn segment length. It is also observed that the self-diffusion coefficient decreases with density for all Kuhn segment lengths. Figure 5.8 shows the correlation time of the end-to-end vector as a function of
Kuhn segment length for two densities $\phi = 0.5$ and $\phi = 0.6$. The graphs show that the correlation time increases with increasing Kuhn segment length and density.

![Figure 5.7](image-url)

Figure 5.7 The self diffusion coefficient as a function of Kuhn segment length for two different densities. The symbols (triangles for filling fraction $\phi = 0.5$ and squares for filling fraction $\phi = 0.6$) represent simulation results with error bars for chains of length $N = 20$ at inverse temperature $\beta = 0.1$. The solid lines connect the data points.
Figure 5.8 The correlation time as a function of Kuhn segment length for two different densities. The symbols (triangles for filling fraction $\phi = 0.5$ and squares for filling fraction $\phi = 0.6$) represent simulation results with error bars for chains of length $N = 20$ at inverse temperature $\beta = 0.1$. The solid lines connect the data points.

5.3 Results of end-bead and chain insertion methods

In this section we present results obtained with the end-bead insertion and chain insertion methods in Monte Carlo simulations of a system of lattice size $L = 20$, chain length $N = 20$ for different filling fractions and temperatures.

The upper panel of figure 5.9 shows results for the reduced excess chemical potential $\beta\mu_{ex}$ as a function of filling fraction obtained from end-bead and chain insertion methods for athermal polymer melts. The graphs show that $\beta\mu_{ex}$ increases with increasing filling fraction and that there is a difference between the values of $\beta\mu_{ex}$ obtained from the end-
bead and the chain insertion methods. This contradicts the assumption that the chemical potential of a polymer chain can be approximated by the chemical potential of a bead times the chain length. This difference, which is shown in the lower panel of figure 5.9, decreases initially with increasing filling fraction and remains constant within the uncertainty of the results for filling fractions larger than about $\phi = 0.35$.

Results for the reduced pressure $\beta p$ obtained from the reduced excess chemical potentials $\beta \mu_{ex}$ of figure (5.9) with equation (2.64) are shown in the upper panel of figure 5.10. Figure 5.10 shows that, as expected, $\beta p$ increases with increasing filling fraction and that the $\beta p$ values obtained from bead and chain insertion methods are very similar for all filling fractions. The difference between the values of $\beta p$ obtained from the two methods is shown in the lower panel of figure 5.10. The magnitude of the difference initially increases with increasing filling fraction and approaches a small value that is constant within the uncertainty of the results for higher filling fractions.

Since for higher filling fractions, the difference between the reduced excess chemical potential from bead insertion and chain insertion method is constant within simulation uncertainties, we expect from equation (2.76) that the pressure difference remains constant. This is indeed what we find in figures 5.9 and 5.10. Since the pressure difference remains constant as the density increases, and since the pressure increases with increasing density, the relative deviations between the pressure results from the two methods decrease (see figure 5.14). This means that the bead insertion method becomes more reliable with increasing density for densities larger than about $\phi = 0.3$. 

52
Figure 5.9 (Upper panel) Reduced excess chemical potential $\beta\mu_{ex}$ as a function of filling fraction $\phi$ obtained from end-bead and chain insertion methods for athermal polymer melts with chain length $N = 20$. The diamonds and circles represent results from the chain insertion and bead insertion method, respectively; the error bars are seen to be smaller than the symbol size. (Lower panel) The difference between the $\beta\mu_{ex}$ values of the upper figure.

53
Figure 5.10 (Upper panel) Reduced pressure $\beta p$ as a function of filling fraction $\phi$ obtained from end-bead insertion and chain insertion methods for athermal polymer melts with chain length $N = 20$. The diamonds and circles represent results from the chain and end-bead insertion methods, respectively. (Lower panel) The difference between the $\beta p$ values of the upper figure.
In the upper panel of figure 5.11 we compare values of the compressibility factor

\[ Z = \frac{\beta p}{\rho} \]

taken from the chain insertion method for athermal polymer melts with values calculated from the Flory and Flory-Huggins theories, see equations (2.82) and (2.85). The graphs show a significant difference between the simulation results and the Flory-Huggins approximation at all densities, and much closer agreement between the simulation results and the Flory approximation. The difference between the Flory compressibility factors and those obtained from the bead and chain insertion methods are presented in the lower panel of figure 5.11. It is seen that the magnitude of the difference is small for small filling fractions and has a maximum near \( \phi = 0.2 \) for both methods.

The difference between the simulation results and the Flory-Huggins theory might be due to the approximation used to describe the correlation of suitable pairs of vacant sites. Since the Flory-Huggins theory assumes a fixed bond length, the occupation probability of a nearest neighbor site of any site excluding pairs of sites occupied by segments of the inserted chain is calculated. With these considerations, the insertion probability in the Flory-Huggins approximation is expressed in the form given by equation (2.81). Since our lattice model does not require neighboring chain segments to occupy nearest neighbor sites, the Flory-Huggins theory cannot be expected to give a better description than the Flory theory.
Figure 5.11 (Upper panel) Compressibility factor $Z$ of athermal polymer melts with chain length $N = 20$ as a function of filling fraction $\phi$. The diamonds represent simulation results obtained with the chain insertion method; open circles and filled triangles represent results from the Flory theory and the Flory-Huggins theory, respectively. (Lower panel) The difference between simulation results for the compressibility factor $(Z)$ and Flory’s approximation $(Z_F)$. The open circles and diamonds represent bead and chain insertion differences, respectively.
Figure 5.12 (Upper panel) Reduced excess chemical potential $\beta\mu_{ex}$ from bead and chain insertion as a function of filling fraction for polymer melts with chain length $N = 20$ at inverse temperature $\beta = 0.1$ and bending energy $\epsilon_A = 0$. The diamonds and circles represent chain insertion and bead insertion, respectively. (Lower panel) Difference of the $\beta\mu_{ex}$ values of the upper figure.
The upper panel of figure 5.12 shows values of the reduced excess chemical potential \( \beta \mu_{ex} \) as a function of filling fraction obtained from bead insertion and chain insertion methods for polymer melts with chain length \( N = 20 \), at inverse temperature \( \beta = 0.1 \) and bending energy \( \varepsilon_A = 0 \). As in the case of the athermal melts, \( \beta \mu_{ex} \) increases with increasing filling fraction and there is a difference between the values of \( \beta \mu_{ex} \) obtained from the two insertion methods. This difference is shown in the lower panel of figure 5.12 the difference decreases slightly with increasing filling fraction and remains constant within the uncertainty of the results for higher filling fractions. This behavior is very similar to that for athermal melts.

Simulation results for the reduced pressure \( \beta p \) as a function of filling fraction \( \phi \) calculated from the excess chemical potentials of figure (5.12) with equation (2.64) are shown in the upper panel of figure 5.13. As in the athermal melts, the \( \beta p \) values obtained from the two methods are very similar for all filling fractions. The differences between the \( \beta p \) values obtained with the two simulation methods are shown in the lower panel of figure 5.13. They show that the difference is very small and zero within the uncertainty at the highest filling fractions.
Figure 5.13 (Upper panel) Reduced pressure $\beta p$ as a function of filling fraction $\phi$ obtained from bead insertion and chain insertion methods for polymer melts with chain length $N = 20$ at inverse temperature $\beta = 0.1$ and bending energy $\epsilon_A = 0$. The diamonds and circles represent results of chain and bead insertion methods, respectively. The error bars are seen to be smaller than the symbol size. (Lower panel) The difference between the $\beta p$ values of the upper figure.
The relative deviation of reduced pressure results obtained with the two insertion methods for athermal melts and melts at $\beta = 0.1$ are shown in figure 5.14. The graphs show that the relative deviations are smaller than 2% for most densities.

The end-bead insertion probabilities are evaluated under the assumption that the excess chemical potential of the chain $\mu_{ex}$ may be approximated as $N$ times the excess chemical potential $\mu_c$ of the test bead. To test this assumption we calculated the ratio of $\mu_{ex}$, obtained by chain insertion, to $\mu_c$, obtain by bead insertion. In figure 5.15, we show the results for $\beta = 0.0$ and $\beta = 0.1$. The graphs for $\epsilon_A = 0$ show that the ratio is much smaller than $N = 20$ for the lowest densities, where the relative deviations of the pressure values are also largest. With increasing density, the ratio increases and approaches a constant value for the largest densities. For bending energy $\epsilon_A = 5$, on the other hand, the ratio $\mu_{ex}/\mu_c$ increases with increasing density for all filling fractions leading to large deviations in the calculated pressure.
Figure 5.14 Relative deviation of reduced pressure values obtained with the two insertion methods as a function of filling fraction for inverse temperatures $\beta = 0$ (circles) and $\beta = 0.1$ (diamonds) for polymer melts with chain length $N = 20$.

Figure 5.15 Ratio of the reduced excess chemical potential $\beta\mu_{ex}$ from the chain insertion method and the reduced bead chemical potential $\beta\mu_{c}$ from the bead insertion method as a function of filling fraction $\phi$ for inverse temperatures $\beta = 0$ (circles) and $\beta = 0.1$ (diamonds) for polymer melts with chain length $N = 20$. 
Figure 5.16 Compressibility factor $Z$ of polymer melts with chain length $N = 20$ as a function of filling fraction $\phi$ for different inverse temperatures and bending energies. The symbols represent results for athermal melts (diamonds), $\beta = 0.1$ and $\epsilon_A = 0.0$ (circles), $\beta = 0.1$ and $\epsilon_A = 5$ (triangle up), and $\beta = 0.2$ and $\epsilon_A = 0$ (triangle down).

In figure 5.16 we present simulation results for the compressibility factor $Z$ of polymer melts of different inverse temperatures and bending energies. The results for $\beta = 0.2$ were obtained with the bead insertion method, all others with the chain insertion method. As expected, the athermal melts have the highest compressibility factors. For $\beta = 0.1$ and $\beta = 0.2$, the attractive interactions between the beads reduce the pressure. Since the bending energy is $\epsilon_A$ is positive, one expects bending to make a positive contribution to the pressure. The observed pressure for $\epsilon_A = 5$ is indeed higher than for $\epsilon_A = 0$, however the effect is very small.
CHAPTER VI
SUMMARY AND CONCLUSION

In this work we investigated the effect of chain stiffness, density, and temperature on chain dimensions, dynamic properties, and pressure of polymer melts with Monte Carlo simulations of a lattice model. The model is a generalization of Shaffer’s bond fluctuation model that takes hard-core repulsion, attractive bead-bead interactions, and a bending penalty for narrow bond angles into account.

Results for static properties show that the end-to-end distance, the radius of gyration and the root-mean-square bond length increase with increasing bending energy. The Kuhn segment length is a measure for the chain stiffness that may be calculated from the chain dimensions. In our model, the Kuhn segment length is found to increase nearly linearly with $\epsilon_A$ for a broad range of bending energy values. In contrast, the density has a very small effect on the chain dimensions for chains in the melt. Results for dynamic properties show that an increase in chain stiffness decreases the mobility of the chains. The logarithm of the self-diffusion coefficient decreases (and the logarithm of the end-to-end correlation time increases) almost linearly with the Kuhn segment length. The density has a strong effect on the dynamic properties; the self-diffusion coefficient decreases and the end-to-end correlation time increases with density.
Two methods to determine the pressure of our lattice model for polymer melts were implemented. The first is an end-bead insertion method developed by Kumar and coworkers.\textsuperscript{5} This method has the advantage that the probability for inserting an end bead is sufficiently high to give good statistics even at high densities. The disadvantage is that the evaluation relies on the approximation that the excess chemical potential of the chain is $N$ (chain length) times the excess chemical potential of the last bead. The second method implemented in this work is a chain insertion method. This method is theoretically well founded and reliable. Unfortunately, the probability for chain insertion decreases rapidly with increasing density so that it is not practical to apply it at higher densities. From results for the excess chemical potential obtained with the end-bead insertion and the chain insertion methods, we have calculated the pressure of the polymer melt. For athermal melts, results for the pressure obtained by the two insertion methods agree almost quantitatively with each other at higher densities. For inverse temperature $\beta = 0.1$ with bending energy $\epsilon_A = 0$, values of the reduced pressure $\beta p$ from both insertion methods agree within their uncertainties for most densities.

The compressibility factor obtained athermal melts of this model are better described by the Flory approximation than by the Flory-Huggins theory. A likely reason for the deviations between the simulation results and the Flory-Huggins theory are the underlying lattice models. The Flory-Huggins theory was developed for a fixed bond-length model, where neighboring chain segments occupy nearest neighbor lattice sites, whereas the lattice model employed in this work allows neighboring chain segments to be on first, second and third nearest-neighbor lattice sites.
Our simulation work has resulted in reliable values for the pressure for flexible polymer melts up to very high filling fractions. Our results for athermal chains will form the basis of an investigation of the equation-of-state properties of semiflexible melts that will be carried out in future work.
REFERENCES


