The dynamics of polymers by novel mesoscopic methods
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CHAPTER 6

Long polymer thermodynamics from short blobby chains

ABSTRACT

We construct a model for long polymers that treats each “blob” monomer in the model as a long polymer in its own right. A simple theoretical analysis shows that the interaction between these blobs when they make up part of a longer chain is of the same form as the interaction between them in isolation from the rest of the chain. The analysis allows us to determine the appropriate coarse grained Kuhn length for the model. We simulated the model in an NVT ensemble using a momentum conserving thermostat that acts on the internal modes. To test the model, we increase the number of blob monomers in the chain until observables are independent of this number. We argue that from the point of view of minimizing this number our model is about as good as it is possible to get. The model is tested for two problems. First, the osmotic pressure of a polymer solution as a function of concentration. Here we find that with a relatively small number of blob monomers we recover the correct thermodynamic behaviour in the semi-dilute regime. Second, the pressure required to confine a polymer in a spherical cavity. Again, a relatively short blob polymer reproduces the behaviour of long polymers. We observe that the scaling of the pressure is analogous to the scaling of the osmotic pressure with concentration for semi-dilute polymer solutions. Directly comparing the results with the osmotic pressure of a semi-dilute solution, we conclude that the analogy is only approximate. Finally, we observe that for degrees of confinement so high that the model begins to break down, the pressure increases more slowly with increasing confinement than it should do. The opposite is true if one uses hard sphere monomers. This indicates that in this limit the behaviour is not universal but model dependent.
6.1 INTRODUCTION

In previous chapters we have considered ideal chains. That is, polymers where the monomers do not interact with each other (other than hydrodynamically). In the real world this corresponds to a polymer solution specifically at its theta temperature. Although we successfully developed and validated the methodology for this case, our approach thus far is somewhat restricted. What we would like is the ability to simulate the more general case where the monomers do interact with each other. That is, where the chains are “real” or “excluded volume” chains. This being the case, the scaling of the polymer size, \( l_p \), with the number of monomers, \( N_b \), changes relative to the ideal case. Specifically we now have \( l_p \sim N_b^{\nu} \), where the scaling exponent \( \nu \) is probably \( 7/12 \) in three dimensions \(^{150}\) (remember that for the ideal chain it is \( 1/2 \)). The other basic problems we encounter for the ideal case still apply. Simulating long polymers numerically in atomistic detail is impractical. With increasing number of monomers both the computational effort required to model the polymer, and the number of configurations that then need to be sampled, increases rapidly. Fortunately, the behaviour of even real polymers on long enough length scales is generally independent on the atomic details of the monomers. More coarse-grained parameters, such as the polymer size, are the only relevant variables. The explanation for this comes from renormalization group theory. This theory basically considers the behaviour of polymers when monomers are grouped together to form a smaller number of longer monomers. Because the definition of a monomer is not unique, the properties of the polymer system should not change under this transformation. This begs the following question: is taking a “blobby view”, where monomers in a model real polymer are themselves considered as shorter real polymers, a plausible method to recover long polymer behaviour from short model polymers? If the answer is yes, then this offers the prospect of an extremely efficient computational method for simulating them.

At this point we should emphasize that this is the crucial point. According to theory \(^{17,151}\) (and this is extensively validated experimentally \(^{152}\)) all linear polymers behave in essentially the same way if they are long enough. That is, the detailed structure at the monomeric level is eventually irrelevant. This point is particularly well made if we consider perhaps the simplest and most widely studied model of the real polymer chain - the self avoiding walk on a cubic lattice. \(^{153-157}\) This can hardly be considered realistic on a monomer level and yet long self avoiding walks yield results that are in agreement with experiments on “real world” polymers. Given this, it is unsurprising that there are a wealth of models that claim to simulate coarse grained polymers because they use a monomer-monomer interaction potential that does not
include this detail. Two examples are using a Lennard-Jones potential or the DPD conservative potential. These potentials are introduced without any physical justification but ultimately this does not matter. By throwing enough monomers at the problem the correct long polymer behaviour will always be recovered. The question is how many is enough? What we hope here is that by constructing a more rational model this number will be as small as possible. Our starting point is that in a coarse grained polymer model the “monomers” are themselves polymers and the interactions are consequently of the polymer-polymer type.

This idea is not new. Louis et al. took the idea to its extreme extent and modelled polymers as single “effective” particles. To do so, they calculated the potential of mean force between self-avoiding random walk chains to obtain the effective interaction potential between polymers in the dilute limit. To a good approximation, for a large number of beads ($N_b$), the potential $U(R)$ takes the form

$$
\frac{U(R)}{k_B T} = A \exp \left( -\frac{BR^2}{R_g^2} \right)
$$

(6.1)

where $k_B$ is Boltzmann’s constant, $T$ is the temperature, $R$ is the separation of the centres-of-mass of the two chains, $R_g^2$ the mean squared radius of gyration and $A$ and $B$ are dimensionless constants with values $A = 1.8$ and $B = 0.8$. Because this potential has a maximum at full overlap ($R = 0$) that is $1.8k_B T$, independent of $N_b$, they refer to it as a “soft” interaction (there is no hard core repulsion, and the energy penalty for polymers completely overlapping is quite modest). By modelling long polymers in this way they could study the phase behaviour of polymer-colloid mixtures. This is impractical without a highly coarse grained model of the polymer, illustrating the potential power of this methodology. One complication with their approach, however, is that for concentrated polymer solutions, the interaction potential is density dependent. It has to be re-calculated at each density.

The fact that a density independent potential does not describe the polymer interaction potential above the dilute limit suggests the idea that one constructs a model where the polymers are represented as chains of “polymer-monomers” instead. These “polymer-monomers” we subsequently refer to as “blobs”. Using this approach, it is not necessary to specify the polymer-polymer interaction. It arises naturally from the blob-blob interaction (correctly one hopes). De Pablo et al. described a model for DNA based on this philosophy. That is, they coarse-grained DNA into a model where each bead itself represents a shorter piece of DNA. Fitting the various parameters they were able to reproduce experimental results for the shear induced deformation.
In their approach they used the uniformly expanded Flory-Krigbaum potential to describe the interaction between blobs. The Flory-Krigbaum model is a “smooth density model”. Smoothed density models approximate the polymer-polymer potential of mean force as the interaction free energy $U(R)$ of two overlapping dilute thermodynamic systems with centres-of-masses separated by a distance $R$:

$$\frac{U(R)}{k_B T} = N_b^2 \nu \int_0^\infty P(\mathbf{r}) P(\mathbf{r} - \mathbf{R}) d\mathbf{r}$$

(6.2)

where $P(\mathbf{r}) d\mathbf{r}$ is the probability of a monomer being located at a position $\mathbf{r}$ from the centre-of-mass and $\nu$ is the monomer second virial coefficient. To characterize the degree of expansion of the chain we introduce the expansion factor, $\alpha = \frac{l_p}{l_0}$, where $l_p$ is the “size” of the excluded volume chain, and $l_0$ the equivalent size of the ideal chain. The Flory-Krigbaum potential is a smooth density model that treats two excluded volume chains with negligible expansion ($\alpha \to 1$). This being the case, $P(\mathbf{r})$ is the ideal chain distribution, leading to

$$\frac{U(R)}{k_B T} = N_b^2 \nu \left(\frac{3}{4\pi R_g^2}\right)^{3/2} \exp \left(-\frac{3R^2}{4R_g^2}\right)$$

(6.3)

where $R_g$ is the radius of gyration of the ideal chain. The Flory-Krigbaum potential is only accurate if the blobs are real polymer chains that are not significantly expanded relative to their ideal chain size ($\alpha \to 1$). The “uniform expansion” variant used by De Pablo et al. takes into account the expansion of the chain by approximating $P(\mathbf{r})$ by the distribution of mass for an ideal chain expanded by a factor of $\alpha$. This leads to

$$\frac{U(R)}{k_B T} = N_b^2 \nu \left(\frac{3}{4\pi R_g^2}\right)^{3/2} \exp \left(-\frac{3R^2}{4R_g^2}\right)$$

(6.4)

where $R_g^2$ is now the mean square radius of gyration of the expanded chain ($R_g^2 = \alpha^2 R_{g0}^2$). This represents a significant improvement over the Flory-Krigbaum potential. It gives the correct result for the polymer second virial coefficient, $B_2$, in the limit where the chain is hardly expanded (as does the Flory-Krigbaum potential). Namely, it predicts

$$B_2(\alpha \to 1) = N_b^2 \nu$$

(6.5)

In the limit of long chains it predicts that

$$B_2(\alpha \to \infty) \propto (R_g^2)^{3/2}$$

(6.6)

Again, this is correct (in this limit Flory-Krigbaum gives $B_2 \propto (R_{g0}^2)^{3/2}$, which
is wrong). However, this potential has two drawbacks. First, it gives a poor estimate for the constant of proportionality in Eq. 6.6. Second, for the potential at full overlap it gives

$$\frac{U(R = 0)}{k_B T} \sim N_b^{2-3\nu}$$

(6.7)

which (since the scaling exponent $\nu < 2/3$) diverges to infinity with increasing $N_b$. That is, the potential becomes increasingly hard sphere like. This is both wrong and computationally inconvenient. Given these shortcomings this potential does not seem the best starting point for constructing a blob model.

More recently, Dreischor\textsuperscript{150} pointed out that if one views a polymer solution as a homogeneous distribution of monomers the effect is to scale the monomer second virial coefficient by a factor of $\alpha^{(6\nu - 4)/(2\nu - 1)}$. Applying this idea to the smooth density model yields a potential of the form

$$U(R) = \frac{N_b^2 \nu}{\alpha^{2-3\nu}} \left( \frac{3}{4\pi R_g^2} \right)^{3/2} \exp \left( \frac{-3R^2}{4R_g^2} \right)$$

(6.8)

This potential represents a significant improvement over the uniformly expanded Flory-Krigbaum potential because it (correctly) predicts that the potential at full overlap is a constant independent of $N_b$ in the highly expanded ($\alpha \rightarrow \infty$) limit. That is, a potential of the form observed for the self avoiding walk (Eq. 6.1). Furthermore, using Muthukumar’s\textsuperscript{19} expression for the expansion factor it predicts constants that closely match the simulated values, and a second virial coefficient of

$$B_2(\alpha \rightarrow \infty) = 6.6R_g^3$$

(6.9)

This is in agreement with other estimates. In addition, it is exact for the negligibly expanded case (Eq. 6.5) and accurate for the “slightly” expanded case where $\alpha$ is slightly greater than unity. This can be shown by using Eq. 6.8 to calculate the coefficients in the expansion of the second virial coefficient in terms of the degree of expansion. They agree with formal expansion results to an accuracy of better than 1%. For these reasons, it is this potential that we will use as the basis for our model.

An important consideration now is; does it make sense to consider that the interaction between polymers in the dilute limit accurately models the interaction between polymeric monomers making up a longer polymer? As a first step to developing the blob model, this is the first question we have to address. Once we have the model, we need an efficient methodology for sim-
ulating it. Finally, with all this in place we can test our approach. To do this we consider the following questions. The first is, how well does it describe the structure (more specifically the distribution of mass) in dilute blob chains? The second is, how well can the methodology capture the thermodynamics of semi-dilute polymer solutions? Finally, we consider the important case of confined polymers. Specifically, we study the pressure required to confine a polymer in a small spherical cavity. This is the programme we pursue in the remainder of this chapter.

6.2 EFFECTIVE INTERACTIONS IN A BLOB CHAIN

An excluded volume polymer chain is characterized by the number of monomers, \( N_b \), the root mean squared separation between adjacent monomers, \( b \), and an excluded volume parameter \( \nu \). In the previous section we defined \( \nu \) to be the monomer second virial coefficient, from now on we use \( \nu = 2B_2 \) where \( B_2 \) is the second virial coefficient of a monomer gas. Following this definition, \( \nu \) is a measure of the effective monomer volume. If we specifically define the expansion factor \( \alpha \) in terms of the end-to-end vector (the reason will become apparent later). That is,

\[
\alpha^2 = \frac{L^2}{L_0^2}
\]  

where \( L^2 \) is the mean squared end-to-end distance of the excluded volume chain and \( L_0^2 = N_b b^2 \) is the mean squared end-to-end distance of the ideal chain (i.e. in the limit \( \nu \to 0 \)).

What follows is in the spirit of de Gennes’ treatment of a long polymer as a polymer of “blobs”, each blob itself being a shorter polymer. The main difference is that we will not assume how the blob interaction depends on the blob size. We construct such a blob model of a single long polymer with given \( N_b, b \) and \( \nu \) by grouping monomers into blobs that consist of \( \lambda \) monomers. Quantities referring to the blob chain are indicated with a bar, so \( \bar{N}_b(\lambda) = N_b/\lambda \). The blobs are now themselves excluded volume chains. To separate the effects of expansion within the blobs and expansion due to interactions between the blobs, we introduce the concept of the “ideal blob chain”. This is a chain in which monomers within the same blob interact with each other in the normal way, but there is no interaction between monomers in different blobs. Because there are no blob-blob interactions this will be an
ideal chain with a modified Kuhn length $\bar{b}$:

$$\bar{b}(\lambda)^2 = \alpha_B(\lambda)^2 \lambda b^2$$  \hspace{1cm} (6.11)

where the subscript $B$ indicates a property of the blob itself (in this case the expansion factor). The quantity $\bar{b}$ is explicitly the root mean squared end-to-end distance for a blob in the ideal blob chain. Since the blobs are free to overlap (it is an ideal chain of blobs), the mean squared end-to-end distance of the ideal blob chain is

$$\bar{L}_0(\lambda)^2 = \frac{N_b}{\lambda} \bar{b}(\lambda)^2 = \alpha_B(\lambda)^2 N_b b^2$$  \hspace{1cm} (6.12)

Because the blob chain is a coarse grained version of the original chain it must have the same size, so

$$\bar{\alpha}(\lambda)^2 \bar{L}_0(\lambda)^2 = \alpha^2 \bar{L}_0^2$$  \hspace{1cm} (6.13)

Substituting the expression for $\bar{L}_0(\lambda)$ from Eq. 6.12 into Eq. 6.13 allows us to relate the expansion factor of the chain of blobs $\bar{\alpha}(\lambda)$ to the expansion factor of the original chain $\alpha$ and the blobs themselves $\alpha_B(\lambda)$

$$\bar{\alpha}(\lambda) \alpha_B(\lambda) = \alpha$$  \hspace{1cm} (6.14)

The expansion factor of an excluded volume chain in three-dimensions is determined by a single parameter $z = N_b^{1/2} v/b^3$. That is, $\alpha = f(z)$, so Eq. 6.14 has the form

$$f \left( \frac{N_b^{1/2} \bar{\upsilon}}{\lambda^{1/2} b^3} \right) f \left( \frac{\lambda^{1/2} \upsilon}{b^3} \right) = f \left( \frac{N_b^{1/2} \upsilon}{b^3} \right)$$  \hspace{1cm} (6.15)

While the exact form of $f(z)$ for all $z$ is unknown, we do know some things about it. First, for small $z$ polymers are not significantly expanded so $f(z \rightarrow 0) = 1$. If $v/b^3 \ll 1$ the condition $\alpha_B(\lambda) = 1$ is satisfied so long as $\lambda^{1/2} v/b^3 \ll 1$. This being the case $\bar{b} \rightarrow \lambda^{1/2} b$ and Eq. 6.15 reduces to

$$f \left( \frac{N_b^{1/2} \bar{\upsilon}}{\lambda^{1/2} b^3} \right) = f \left( \frac{N_b^{1/2} \upsilon}{b^3} \right)$$  \hspace{1cm} (6.16)

Since the degree of expansion always increases with increasing $z$, $df(z)/dz > 0$, we unambiguously have

$$\bar{\upsilon} = \lambda^2 \upsilon$$  \hspace{1cm} (6.17)

For a dilute solution of polymers containing $\lambda$ monomers, in the limit $z \rightarrow 0$
the second virial coefficient is

$$B_2 = \frac{\lambda^2 v}{2}$$

(6.18)

so $\bar{v} = 2B_2$. This shows that the excluded volume interaction between blobs in the polymer is indeed identical to the interaction between a dilute solution of the equivalent polymer chains.

In the "scaling" limit ($z \to \infty$), the polymer size has a power-law dependence on the number of monomers, $L \sim N_b^{\nu_b}$. This means that the expansion factor also has a power-law dependence on $z$, specifically $f(z \to \infty) \sim z^{2\nu - 1}$. We can now consider the case where the blobs are themselves long excluded volume chains, so long that the blob itself is an excluded volume chain in the scaling limit ($\lambda^{1/2}v/b^3 \to \infty$). We now have that the blobs, the blob chain and the explicit chain are all in the scaling limit. This being the case Eq. 6.16 has the form:

$$\left(\frac{N_b^{1/2} \bar{v}}{\lambda^{1/2} b^3}\right)^{2\nu-1} \left(\lambda^{1/2} \frac{v}{b^3}\right)^{2\nu-1} = C \left(\frac{N_b^{1/2} v}{b^3}\right)^{2\nu-1}$$

(6.19)

where $C$ is a constant that is close to unity. From Eq. 6.19 it clearly follows that in this limit $\bar{v} = C\bar{b}^3$. In the scaling limit, the polymer second virial coefficient is proportional to the polymer "volume", so in the limit where the blobs of the blob chain are themselves long polymers, we find that the effective interaction is again proportional to the second virial coefficient of a solution of blob monomers. Remembering that in this case $\bar{b}$ is specifically the end-to-end vector of the blob, we assume that the relation between the magnitude of the end-to-end vector and the radius of gyration for the real chain is the same as for an ideal chain,

$$<\bar{R}_g^2> = \frac{1}{6} \bar{b}^2$$

(6.20)

in which case

$$\bar{B}_2 = \frac{6^{3/2}}{2} \bar{R}_g^3 = 7.35 \bar{R}_g^3$$

(6.21)

The above assumes that the constant $C$ is unity. More accurately, we can use Muthukumar's result for the SAW, $C = 1.04$, in which case we have

$$\bar{B}_2 = \frac{6^{3/2}}{2} \bar{R}_g^3 = 6.6 \bar{R}_g^3$$

(6.22)

This is in quantitative agreement with the idea that when the blobs in the blob chain are themselves long polymers, the blob-blob interaction has the same strength as the interaction between blob polymers in the dilute limit. We arrived at the same conclusion for the limit where the blobs were hardly expanded. From this we can conclude that when we consider the monomers
making up a polymer to be shorter polymers, the interactions between these blob “polymer monomers” are the same as the interactions between them when they are simply in solution and not part of a larger polymer. We should stress that this is frequently assumed, but not shown, to be the case.

Although we now know the magnitude of the Kuhn length in the blob chain, we have to chose the form of the bonding potential $U_b$. The logical choice is the harmonic potential that gives the correct end distribution of the end-to-end vector for any $N_b$ in the limit that the chain is ideal, that is

$$\frac{U_b}{k_B T} = \frac{3}{2} \sum_{i=1}^{N_b-1} \left( \frac{r_i - r_{i+1}}{\sqrt{6} R_g} \right)^2$$

(6.23)

Combining this with the blob-blob potential (Eq. 6.8), the potential energy we finally arrive at is therefore

$$\frac{U_b}{k_B T} = \sum_{i=1}^{N_b-1} \sum_{j=i+1}^{N_b} 1.8 \exp \left( -\frac{3 (r_i - r_j)^2}{4 R_g^2} \right) + \frac{3}{2} \sum_{i=1}^{N_b-1} \left( \frac{r_i - r_{i+1}}{\sqrt{6} R_g} \right)^2$$

(6.24)

Armed with this potential we can now proceed to calculate the properties of these blobby chains.

### 6.3 SIMULATION METHOD

We now need a method to simulate our blob model. Initially we are interested in only static quantities. For this we could use either dynamic or Monte-Carlo methods. Using the latter, calculating the static properties in the confined polymer case is a difficult task: the acceptance rate of the trial moves decreases rapidly with increasing confinement so the computational effort involved increases accordingly. A full dynamic simulation, on the other hand, can also require a large amount of computational resources. The reason for this is that the relevant simulation time is how long we have simulated the system relative to the time required for the polymer chain to have “significantly” changed its configuration. One can argue that this is the case once the end-to-end distance at some time $t + \tau$ is uncorrelated with the end-to-end distance at the initial time $t$. Here $\tau$ is the decay time of the end-to-end distance. We determine $\tau$ by calculating the autocorrelation function of the end-to-end distance:

$$C(\delta) = \langle r_{e2e}(t) \cdot r_{e2e}(t + \delta) \rangle$$

(6.25)
The characteristic time is then given by $\tau = \int_0^\infty C(\delta)/C(0) \, d\delta$. This time increases as the number of blob monomers in the model polymer increases (hence the desireability of reducing the number of beads to a minimum). It is known\(^1\) that if one neglects hydrodynamic interactions

$$\tau \sim \eta N_b^2 b^3$$

whereas including hydrodynamic interactions

$$\tau \sim \eta N_b^{3/2} b^3$$

We use a modified version of the Lowe-Andersen (LA) thermostat\(^7\) as a means of accelerating the rate at which our dynamic method samples configurations of polymer chains. Usually, the LA thermostat works on all pairs of particles in the system, within a certain cut-off radius. Each time step, these pairs have a certain probability of undergoing a virtual collision with the heat bath. A virtual collision involves generating a new relative velocity $\mathbf{v}^*(t)$ from the Maxwell-Boltzmann distribution along the line of centres. Furthermore, the new relative velocity is imposed in such a way that linear momentum is conserved. After a bath collision of particle $i$ and $j$, the new velocity of the latter is

$$\mathbf{v}_j^* = \mathbf{v}_j - (\mu_{ij}/m_j)(\mathbf{v}_i - \mathbf{v}_j) \cdot \hat{\sigma}_{ij} \sigma_{ij}$$

where $\hat{\sigma}_{ij}$ is the unit separation vector ($\hat{\sigma}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$ and $\mathbf{r}_i$ is the position of particle $i$), $m_j$ is the mass of particle $j$, $\mu_{ij}$ is the reduced mass of the particle pair ($\mu_{ij} = m_i m_j/(m_i + m_j)$) and $\theta$ is a stochastic variable.\(^7,162\) We modify this scheme such that only particle pairs adjacent to each other along the polymer chain are allowed to undergo a virtual collision. In other words, bead number five can only interact with beads number four and six via the LA thermostat. All other interactions between all beads, such as a spring potential or an excluded volume potential, are treated in the normal manner.

The final ingredient in our simulation scheme is a random interaction of a (random) single bead $i$ with a virtual heat bath

$$\mathbf{v}_i = \sqrt{\frac{k_B T}{m_i}} [\xi_1, \xi_2, \xi_3]$$

with $\xi_i$ being independent random numbers taken from a Gaussian distribution of unit variance.\(^162\) Such an interaction is comparable with an Andersen thermostating interaction.\(^23\) If we did not introduce this latter possibility, the centre-of-mass kinetic energy of the polymer chain would not change throughout the simulation because the LA thermostat acts on relative veloc-
The decay time of the end-to-end distance, $\tau_{E2E}$ (expressed in units of the time step), as a function of the number of beads, $N_b$, in the polymer model chain. The circles represent the results from the simulations using the Andersen thermostat, the diamond shaped symbols represent the simulations using the Lowe-Andersen thermostat. The filled symbols represent the results from the simulations using the blob chain model, the open symbols represent the Lennard-Jones model.

We will now compare the scaling of the decay time of the end-to-end distance of two different polymer models using the modified LA thermostat scheme and the original Andersen thermostat. For the modified LA thermostat we set the collision frequency to be $0.05$ and for the incidental Andersen interaction to be $0.005$. For the system coupled to an Andersen thermostat we set the collision frequency to be $0.05$. In Fig. 6.1 we demonstrate the potential benefits of the new thermostat procedure on two types of polymer chains. First we consider the polymer model for excluded volume chains as presented in this chapter, second we look at an alternative to this model,
namely a polymer chain consisting of Lennard-Jones particles. The latter is not strictly relevant to the study here, but is an example of a more realistic explicit monomer potential. We include it to assess whether the methodology could be more generally useful.

Once the blobby chain is long enough, $N_b > 20$, the decay time of the end-to-end distance scales as $\tau \propto N_b^{1.51 \pm 0.01}$ for the modified LA thermostat. In all cases $\tau$ is expressed in units of the time step. For the Andersen thermostat it scales as $\tau \propto N_b^{1.98 \pm 0.02}$. Interestingly, these two scalings actually correspond with respectively the hydrodynamic (Eq. 6.27) and non-hydrodynamic (Eq. 6.26) theoretical results. Consequently, the dynamics of a blobby polymer chain are effectively a factor $\sim \sqrt{N_b}$ faster using the novel thermostat than using the Andersen thermostat. For simulations with a given number of time steps this means that the results using the modified LA thermostat will be more accurate because we have sampled more independent configurations. Looking at the results for the Lennard-Jones chains we see the same trend. For the novel thermostat the decay time of the end-to-end distance scales as $\tau \propto N_b^{0.84 \pm 0.01}$ whereas for the Andersen thermostat it scales as $\tau \propto N_b^{0.94 \pm 0.03}$. For the Lennard-Jones chains the results appear less impressive, but one has to keep in mind that in most simulations the chains are much longer than in this test case. Because we look at the scaling with the number of beads, the actual difference in time needed to obtain a given degree of accuracy increases rapidly with increasing number of beads.

Later in this chapter we investigate excluded volume chains in spherical confinement. The interaction potential between the blobs and the wall is of the following form:

$$U(r) = -2 \ln \left( \frac{r}{\sqrt{2} R_g} \right)$$  \hspace{1cm} (6.30)

where $r$ is the distance between the centre of the blob and the wall. Because this is a relatively soft wall-potential, the time steps in the simulations must be small. If we make the time step too big then, because of the errors involved in numerically integrating the equations of motion, the polymer beads can “escape” from the confinement. However, if we make the time step too small the computational time involved increases drastically. We choose to use a varying time step, depending on the distance from the wall. If all particles are far from the wall we use a long time step ($\Delta t_0 = 0.1$). If one of the particles gets within a set distance $\delta$ from the wall, the time step (for all particles) is decreased according to

$$\Delta t(r) = \frac{\Delta t_0 r^2}{\delta}$$  \hspace{1cm} (6.31)

The combination of this methodology and the modified LA thermostat scheme
enables us to perform simulation on confined chains with a very limited amount of computational resources (typically less than one day per single simulation run on a desktop computer).

6.4 RESULTS

We have examined how useful the blob methodology is as a means of simulating long excluded volume polymers at a more modest computational cost by considering three problems. The first is how well can it describe the structure (more specifically the distribution of mass) in dilute blob chains? The second is how well can the methodology capture the thermodynamics of semi-dilute polymer solutions. Here we have the advantage of having experimental data to compare with. Finally, we consider the pressure required to confine a polymer in a spherical cavity.

6.4.1 STRUCTURE IN THE DILUTE LIMIT

We begin by considering the properties of our blob chains in the dilute limit. The quantity we concentrate on is the structure factor (the Fourier transform
of the density-density correlation)

\[ s(k) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \exp \left( i k \cdot r_{ij} \right) \]  \hspace{1cm} (6.32)

where \( N \) is the total number of monomers in the system and \( i \) indexes all monomers in the system. The reasons for this are twofold. First, the structure factor is the response function for density fluctuations. That is, where the structure factor of the blob model is correct, the response of the model to an external perturbation will also be correct. Second, theoretically there is a lot known about how this function behaves for long excluded volume chains. For \( k \ll 1/R_g \) it takes the form of the Fourier transform of a Gaussian of width \( R_g \) in the same limit:

\[ s(k) = 1 - (kR_g)^2/2 \]  \hspace{1cm} (6.33)

Therefore, on long enough length scales the structure of the excluded polymer chain is simply equivalent to that of an expanded ideal chain. On the other hand, in the intermediate limit \( 1/b \gg k \gg 1/R_g \) the fractal nature of the excluded volume chain determines the distribution and renormalization arguments lead to

\[ s(k) \sim \frac{1}{(kb)^{1/\nu}} \]  \hspace{1cm} (6.34)

Finally, we know that on very short length scales (in this case less than the typical separation between adjacent blobs, \( \bar{b} \), i.e. \( k > 1/\bar{b} \)) we only have the self term in Eq. 6.32 so that \( s(k) = 1 \). In Fig. 6.2 we have plotted the normalized structure factor \( s(k)/N \) as a function of the dimensionless wavevector \( kR_g \) for blobby model polymers consisting of a number of blobs ranging from \( N_b = 25 \) to \( 400 \). As the figure shows, it is a single unique function at small \( k \). Where the function does not depend on \( N_b \), that is the curves coincide, a given blobby chain is reproducing the behaviour of a chain with arbitrarily larger \( N_b \): a short model chain is reproducing the behaviour of any larger chain, even an infinitely long chain. Put simply, the method is working. What we see is that this is the case up to increasingly large \( kR_g \) as we increase \( N_b \). This means that we reproduce the correct behaviour on progressively short length scales as we use more blob monomers. This is the number of blobs behaving in an analogous way to the grid spacing in a finite difference scheme for example. It determines the “degree of resolution” we have in the model. To resolve the correct structure to a given accuracy on increasing short length scales we inevitably have to increase \( N_b \). On shorter length scales (\( kR_g \gg 1 \)), as Fig. 6.3 shows, the structure factor is a unique function of the dimensionless wave vector \( kb \). Also plotted is the theoretical
Figure 6.3: Structure factor for blob chains, with various numbers of blobs, as a function of the dimensionless wavevector $k_b$. Also shown is the theoretical renormalization group result for a real polymer chain in the scaling limit and, for comparison, the small $k$ scaling ($1/(k^2)$).

renormalization group results for a polymer in the scaling limit. As the figure shows, the agreement is excellent. With increasing $N_b$ this behaviour is recovered to progressively smaller values of $k_b$ (that is, longer length scales). As the region where $k_b = 1$ is approached, and this scaling must break down, there is very little additional structure introduced by the blob-blob potential.

6.4.2 THE OSMOTIC PRESSURE

Perhaps the most important property of a polymer solution is its osmotic pressure $\Pi$. It is widely used for the determination of molecular weights of large molecules such as polymers and proteins. Even very dilute polymer solutions display large deviations from ideality (van 't Hoff's law) because of their very low entropy of mixing. Renormalization arguments show that the dimensionless osmotic pressure $\Pi R_\text{B}^3 / k_B T$ is a unique function of the variable $\rho / \rho^*$, where $\rho$ is the monomer concentration and $\rho^* = R_\text{B}^3 / N_p$ (with $N_p$ the number of polymers) is the “overlap” concentration. This is the monomer concentration at which, when increasing the concentration of the solution, polymers start to significantly overlap each other (and consequently polymer-polymer interactions become important). When $\rho / \rho^* \gg 1$, i.e. when the polymer solution looks like a monomer soup, the number of monomers in a
Figure 6.4: Dimensionless osmotic pressure as a function of the polymer concentration relative to the overlap concentration calculated for the blob chains with various numbers of blobs. Also shown are the equivalent data for the self avoiding walk (SAW) and experimental results.

given polymer is irrelevant and this leads to a scaling

\[
\frac{\Pi R^3}{k_B T} \sim \left( \frac{\rho}{\rho^*} \right)^{\frac{3-\nu}{\nu}}
\]  

(6.35)

In Fig. 6.4 we have plotted the dimensionless osmotic pressure we calculated for solutions of blob model chains, \( \Pi V_p / k_B T \), as a function of the concentration relative to the overlap concentration \( \rho / \rho^* = \rho_p V_p \). Here \( V_p \) is a polymer "volume", \( V_p = (4/3)\pi R^3 \), and \( \rho_p \) is the polymer concentration. In these dimensionless terms, for a given number of blob monomers \( N_b \) in the chain the results fall onto one unique curve up to a given value of \( \rho / \rho^* \). In the interest of clarity, we show data for a given \( N_b \) just up to the value of \( \rho / \rho^* \) for which deviations from the unique \( (N_b \to \infty) \) curve become significant. As an example, for \( N_b = 10 \) the last point plotted is for \( \rho / \rho^* \sim 4 \). Here, as the figure shows, the calculated osmotic pressure is slightly below the universal curve. This shows that at this concentration the blob 10-mer is starting to provide an inadequate description of the system. On the positive side, this means that a model chain of ten blobs adequately describes the thermodynamics of a polymer solution for values of the concentration up to four-fold the overlap concentration. At this point the osmotic pressure is almost an order of magnitude greater than its ideal value. The polymer-polymer interactions are the dominant contribution to the osmotic pressure, so this is no mean achievement. In the plot we also show the equivalent data for the self avoiding random walk (SAW) on a cubic lattice for \( N_b = 10 \) and \( N_b = 500 \).
the figure shows, even the blob model with \( N_b = 10 \) is a vast improvement of the \( N_b = 40 \) self avoiding walk.

As we increase the number of blob monomers in the model the correct behaviour is recovered up to higher values of \( \rho/\rho^* \). For example \( N_b = 40 \) is adequate up until \( \rho/\rho^* \sim 20 \). In other words: we can always recover the long polymer result but with increasing concentration we need more blobs in the model to do so. This is not really surprising because we simply need to capture the correct behaviour on increasingly short length scales. That is, use more blobs. This is consistent with the observation that in the dilute limit it requires more monomers to resolve \( s(k) \) on shorter length scales.

Examining the configurational behaviour of the blob polymers in concentrated solutions, in Fig. 6.5 (A) we have plotted the normalized structure factor as a function of the dimensionless wavevector \( kR_g \) for two relatively long blob chains \( (N_b = 50 \text{ and } N_b = 100) \). As we see, for a given value of \( \rho/\rho^* \) the curves coincide, indicating that the blob polymers are producing correct (independent of \( N_b \)) behaviour. The two curves coincide up to a lower value of \( kR_g \) with increasing concentration. That is, with increasing concentrations the correct behaviour is only recovered on longer length scales. This is consistent with the conclusion that with increasing \( \rho/\rho^* \) more blobs are necessary to resolve the correct behaviour. Generally, we see that in the small \( k \) limit density fluctuations are strongly suppressed and the polymer shrinks. To some extent these results confirm the osmotic pressure results because the osmotic compressibility is related to \( s(k) \) in this limit. If one is correct, so is the other. In Fig. 6.5 (B) we have plotted the structure factor as a function of the dimensionless wavevector \( kb \). Notice that for large \( k \) the data approach a function independent of the concentration with increasing values of \( kb \).
Because this function is independent of concentration it is the dilute limit function (i.e. it is the same as that plotted in Fig. 6.2). In other words, on short enough length scales the structure of the polymer is the same as it is in the dilute limit. This is consistent with de Gennes’ model for the screening of excluded volume interactions above the overlap concentration. In this limit, de Gennes’ view is that the polymers behave as an ideal chain of expanded blobs. Within the blob itself the polymer has the same structure as it does in the dilute limit, precisely as we observe. The one thing we should note is that, while this picture is supported by our results, there is nothing special about the overlap concentration. The same mechanism seems to operate even significantly below it.

6.4.3 THE PRESSURE OF A SPHERICALLY CONFINED POLYMER

Placing polymers under confinement dramatically reduces the number of accessible configurations. Consequently, there is a steep increase of the free energy and the polymer exerts a pressure resisting the confinement. The magnitude of the effect is an important factor in a number of important problems, notably in the field of bio-physics. Two obvious examples are the translocation of proteins through narrow channels\textsuperscript{166,167} and the packaging of DNA inside virus capsids.\textsuperscript{168–170} From a computational point of view, as noted above, it also makes Monte Carlo methods less efficient. From this standpoint, it is a good example of a problem where the dynamic method we discussed in paragraph 6.3 could well be advantageous. Using this method we have calculated the pressure exerted on a spherical container by a single polymer modelled. This system was considered by Luijten and Cacciuto.\textsuperscript{171} They used a model polymer with hard sphere monomers confined by a steeply repulsive potential (this represented the container). Using this model they were able to confirm a recent theoretical prediction\textsuperscript{172} that the pressure of confinement $P\textsubscript{s}$ scales in an analogous manner to the osmotic pressure of a semi-dilute polymer solution. That is,

$$\frac{P R_g^3}{k_B T} \sim \left( \frac{R_g^3}{V} \right)^{\frac{1}{3-\nu}}$$

where $V$ is the container volume and the “degree of confinement” $R_g^3/V$ plays the analogous role to the concentration relative to the overlap concentration in the semi-dilute solution case. In Fig. 6.6 we have plotted the pressure a confined blobby polymer exerts on the spherical cavity. The pressure was calculated directly as the monomer-container force per unit area. As the figure shows, the results follow a very similar pattern to those we observe for
Figure 6.6: Dimensionless pressure of confinement of a single blob polymer chain for various numbers of blobs. Also shown is the theoretical scaling \( \sim (V_p/V)^{7/3} \), the dashed line and the osmotic pressure of a dilute polymer solution (the continuous line) plotted in the same terms.

the osmotic pressure. For a given number of blob monomers we recover the correct result up until some degree of confinement. Subsequently the model breaks down and more blobs are needed in the model to calculate the correct pressure of confinement. For the universal \( (N_b \text{ independent}) \) curve obtained, we observe that the scaling is indeed similar to that of a polymer solution above the overlap concentration. Plotting the actual osmotic pressure of a polymer solution (the data plotted in Fig. 6.4), in analogous terms we see that although the scaling for high degrees of confinement is the same, the functional form away from this limit is not. Further, where the blob model breaks down the pressure of confinement increases at a slower rate. It does not show the same behaviour \( PR_g^3 \sim (V/R_g^3)^3 \) that was observed by Luijten et al.\(^{171}\) This shows that the behaviour in this limit is not universal.

6.4.4 RHEOLOGY

All the preceding results we described concern static properties of polymeric systems. This is in contrast to the rest of the thesis that deals with dynamic properties. In principle, combining the blob model with the simple solvent model is straightforward. This then allows us to achieve our goal of a realistic dynamic mesoscopic model for real polymers. However, it is not obvious that the reasoning underlying the “magic” hydrodynamic radius\(^9\) is sound in this case. Proceeding with this project requires careful analysis of this
Figure 6.7: The relative solvent viscosity (left) and the component of the radius of gyration along the flow axis (right), both as a function of the dimensionless shear rate $\tau \dot{\gamma}$, where $\tau$ is defined as $R_g^2/D_0$ and $\dot{\gamma} = 4V_{\text{max}}/L$. All simulations were performed on polymer chains of 32 beads at a volume fraction of 0.51. The squares represent simulations on ideal chains, the circles on excluded volume chains. The viscosity is measured using the periodic Poiseuille flow method. In both figures the errorbars are smaller than the symbol size.

question. Nonetheless, we can at least show that such a methodology is in principle practical. Further, we can examine how important the role of excluded volume interactions are in determining the dynamic behaviour of real polymers.

To this end we consider the following. In chapter 5 we demonstrated that solutions of ideal polymer model chains show shear thickening behaviour. What happens if we repeat these simulations for the excluded volume model chains we introduce in the current chapter? In Fig. 6.7 we plot the results of the simulations for both types. Contrary to the ideal chains, the excluded volume chains show shear thinning behaviour. This is in agreement with other simulations. Furthermore, in Fig. 6.7, we look at the component of $R_g$ along the flow axis, relative to that component for chains in equilibrium. For ideal polymer chains, this ratio increases to $\sim 9$ for a dimensionless shear rate of $\sim 4$. This means that the chain is nine times longer than that same chain in equilibrium. For the excluded volume chain this ratio increases much slower, to a value of $\sim 2.5$ at a shear rate slightly below $\tau \dot{\gamma} = 5$. In both cases, the differences between the ideal chains and the excluded volume chains can only be caused by the excluded volume potential because all other parameters in the system were kept the same.
6.5 DISCUSSION AND CONCLUSIONS

We have developed a model for real polymer chains (polymers that actually interact with each other) based on treating the monomers as blob monomers that are themselves long polymer chains. A simple theoretical analysis showed that this view is valid. The potentials that result are soft, this makes simulating blobby chains dynamically relatively straightforward. We note that this fact would also make Monte Carlo simulations of the blob chains very efficient. The novel “internal” thermostat we developed gives a relaxation time $\tau$ for the end-to-end distance that scales with the number of monomers as the “Zimm-like” $\tau \propto N_b^{1.5}$. For a normal stochastic thermostat it is the “Rouse-like” $\tau \propto N_b^2$. For small $N_b$ the internal thermostat is notably more efficient, and, given the above, it is increasingly advantageous with increasing $N_b$. Therefore, this approach might well be very useful for simulations of more detailed polymer models (proteins for example) where $N_b$ is typically much larger than the modest values used for the mesoscopic model studied here. In the context we have used it here, we are not interested in whether the dynamics are realistic or not. It is simply a means to an end (calculating the static properties). While we do not claim that the dynamics are necessarily realistic, there is an argument that it is at least more realistic than using a normal stochastic thermostat. This is because it is at least possible to set one parameter correctly, specifically, the ratio of the diffusive time to the relaxation time. This is not possible simply using a stochastic thermostat.

Testing the model we find that it reproduces the thermodynamics of long linear polymers using a very small number of blob monomers. In fact, we now argue that it is hard to imagine that one could do any better. The reason is as follows. The behaviour of long linear polymer chains is generic (i.e. $\Pi R_g^2/k_B T$ is a universal function of $\rho/\rho^*$) only so long as the monomer “volume fraction” is low. A reasonable definition of the latter is $\rho_v$. So, we can define the concentration at which this assumption breaks down as $\rho^{**} = 1/\rho_v$. That is, for concentrations corresponding to $\rho/\rho^{**} \sim 1$. At concentrations at or above this concentration a typical blob separation is similar to, or less than, the size of the blobs themselves. Because we cannot resolve the structure of the polymer on length scales smaller than the size of the blobs themselves, this places a fundamental upper limit on the concentration up to which the model can work. Namely, the condition $\rho/\rho^{**} \ll 1$ must be satisfied. Returning to the results from the model, we found that with $N_b = 10$ the results were adequate up until $\rho/\rho^* = 4$. In terms of $\rho^{**}$ this concentration corresponds to $\rho/\rho^{**} = 0.25$. That is, the model works up to a point close to the maximum value where it could conceivably work, given the amount of structural information that it resolves.
At concentrations where a typical blob separation is similar to, or less than, the size of the blobs themselves, the system starts to look like a melt of blobs. In this limit the behaviour of the system *does* depend on the form of the explicit monomer-monomer interactions. The same is true for real polymer systems. At melt concentrations the behaviour depends on the explicit atomic detail of the polymer molecules. A good illustration of this is the fact that, for concentrations where the blob model starts to break down, the osmotic pressure increases more slowly than it should (see Fig. 6.4). This is because the model approaches a melt of "soft" particles. For any system of particles with soft interactions, at high enough densities the pressure scales as $\Pi/k_B T \sim \rho^2$. This is a slower rate of increase than the true semi-dilute scaling $\Pi/k_B T \sim \rho^{7/3}$. This is in contrast with the SAW, for which the monomers do have excluded volume, so a "hard melt" rather than a soft melt is approached. In this case, at high concentrations the deviations from the semi-dilute result show up as a more rapid rate of increase (see Fig. 6.4).

A peculiarity of the results for the osmotic pressure is that the universal curve we find for the osmotic pressure does not agree quantitatively with the results for the long ($N_b = 500$) SAW. Although the scaling with $\rho/\rho^*$ is similar, the curves disagree by a factor of almost two. However, the results for the blob model do agree extremely well with experimental results (noticeably better than those for the SAW). There are two possible explanations for this. First, that the function is not in fact unique. That is, in the limit of large $N_b$ the curves do not coincide. This would mean that the form of the monomer-monomer potential matters even in the scaling limit and the blob potential is more representative of the real potential. The second is that the $N_b = 500$ SAW is not quite representative of the long SAW limit. Because simulations of even longer SAW’s (up to $N_b = 80000$) give values for the second virial coefficient that are in agreement with experimentally measured values (and the simulations reported here) we believe that the latter is the more probable explanation.

We were also able to show that the methodology works for confined polymers. For high degrees of confinement, we see the theoretically predicted scaling of the pressure of confinement with degree of confinement. While this essentially confirms the central result of Luijten et al., it is at a significantly lower computational cost. We do not have detailed enough information available to quantify by how much, but their calculations required several weeks of computing on a cluster. The (more accurate) calculations reported here required days on a desktop PC. Furthermore, we could directly simulate a "hard" confining potential, whereas their methodology used steep confining potentials. This means that the "volume" of the cavity is a somewhat ill-defined quantity that can also vary depending on the nominal degree
of confinement. To eliminate any such effect requires running multiple simulations with progressively steeper confining potentials until the results are independent of the potential. This is an additional computational overhead that our method does not have.

The results for the confinement pressure are qualitatively but not quantitatively similar to the osmotic pressure of a polymer solution. The blob model itself behaves in an analogue fashion. A given number of blobs in the chain will produce the true (long polymer) result up until \( V_p = 3V \), at which point the pressure of confinement is two orders of magnitude greater than the ideal pressure. At higher degrees of confinement it starts to underestimate the pressure. As with the osmotic pressure, for a given \( N_b \), as \( \rho/\rho^* \) approaches unity the model must break down and more blobs are required. Where our results do disagree with those of Luijten et al. is in the limit where the model breaks down \( \rho/\rho^* > 1 \). We see a slower rate of increase, again because the soft melt has a pressure that increases more slowly. For the model with hard monomers, the converse was true. In this limit they found that \( PV_p \sim (V_p/V)^3 \), as opposed to \( PV_p \sim (V_p/V)^{7/3} \) in the "universal" regime. From this we conclude that in this limit the behaviour is not universal, because it does depend on the exact form of the monomer-monomer potential. The blob analysis they carried out to explain the scaling that they observed similarly cannot be universally valid.

In the final section we reported preliminary results for the blob model with more realistic dynamics. That is, coupled to the simple model fluid we used in earlier chapters. We were able to show that this is in principle straightforward and that the interactions in a real polymer chain significantly influence the dynamics. This is illustrated by the significant difference in both the viscosity and the deformation in shear flow between the blob model and the ideal model we introduced earlier. At the very least this illustrates the importance of including polymer interaction for recovering correct dynamics. What we did not do was carefully validate that these results are truly representative of a long real polymer. To do so would require a careful analysis of the results for simulations using different numbers of blob monomers, along the lines we pursued for the ideal case. This remains a subject for future research, as does extending the methodology to the "intermediate" regime. That is, where the polymer is neither ideal nor in the scaling limit. Given that the potential (Eq. 6.8) is accurate for both limits and the regime in between, this should be possible. What we can conclude is that based simply on physical and theoretical arguments we have developed a blobby model for a polymer in the scaling limit that is about as good as you can get.