Simple numerical techniques for mesoscale polymer models
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Chapter 5

The nature of a collapsed solvated polymer

The application of the Lowe-Andersen thermostat described in this chapter is based on a theoretical model developed by Dreischor and Lowe in [70]. The model and its derivation are reproduced in a slightly modified form in sections 5.1 and 5.2.

5.1 Introduction

The temperature and pressure dependence of the conformational properties of a polymer are linked to its interaction with the solvent. These interactions also determine when dissolving the polymer is, or is not, possible. As it states in the review paper by Williams et al. [71], in 1953 Flory [1] wrote: “The better the solvent, the greater the “swelling” of the molecule. Conversely the poorer the solvent, the smaller the molecule.” To a large extent this chapter addresses how generally true this second statement is. Flory is describing here the evolution of the average polymer dimensions as the effective pair interaction between monomers, mediated by the solvent, changes. Significantly, his work showed that generally at low enough temperature this interaction becomes attractive and the otherwise spindly expanded polymer “coil” collapses into a dense spherical blob, the “globule”. The first experimental observation of this coil to globule transition was probably the denaturation of proteins on heating. Here, the protein goes from its compact active state at low temperatures to an inactive coil state at higher temperatures. In fact, the important role of the coil to globule transition in configurational changes of proteins, such as folding and unfolding, is an active area of research to this day [72, 73]. Generally the coil-to-globule transition is experimentally observed by measuring the polymer radius of gyration, while varying the temperature. Slagowski, Thai
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and McIntyre were the first to report measurements of the coil to globule transition via measurements of the radius of gyration of polystyrene solvated in cyclohexane [74]. In the globular state the size $l$ of the chain is seen to scale with the molecular weight $M$ as $l \propto M^{1/3}$ as opposed to $l \propto M^{0.58}$ where the effective monomer interaction is repulsive. These two regimes are delineated by the theta temperature, at which the effective interaction is zero and the polymer behaves like an ideal chain, with $l \propto M^{1/2}$.

The original theoretical model for these configurational properties is the lattice model based on Flory-Huggins equation of state, often referred to as the mean field model [75]. It models the polymer and solvent as a fully occupying a lattice. Because of this it considers the incompressible (or infinite pressure) limit. Here we give the derivation as presented by De Gennes [76]. The approach then proceeds as follows. A chain made up of $N_m$ monomers is modelled as a spherical domain of volume $V$ containing a homogeneous mixture of monomers and solvent (the “polymer domain”). Outside this domain there is pure solvent. The Free energy of mixing per lattice site according to the Flory-Huggins theory is given by

$$\frac{\Delta F}{nk_BT} = (1 - \phi_m) \ln(1 - \phi_m) + \chi \phi_m (1 - \phi_m)$$ (5.1)

where $n$ is the total number of lattice sites in the system, $\phi_m$ is the monomer volume fraction in the polymer domain and $\chi$ is the well known Flory-Huggins parameter, which is always inversely proportional to the temperature, $T$. This parameter determines the “goodness” of the solvent at a given temperature. If the polymer is expanded, the fraction of space occupied by the monomers, $\phi_m$, is small so we can expand this expression as

$$\frac{\Delta F}{nk_BT} \simeq (\chi - 1) \phi_m + \frac{1}{2} \phi_m (1 - 2\chi) + \frac{1}{6} \phi_m^2 + \ldots$$ (5.2)

or alternatively

$$\frac{\Delta F}{k_BT} \simeq (\chi - 1)N_m + \frac{1}{2} v_L (1 - 2\chi)N_m \rho_m + \frac{1}{6} v_L^2 N_m \rho_m^2 + \ldots$$ (5.3)

Here we have made use of the fact that $\phi_m = v_L \rho_m$, where $\rho_m$ is the monomer density and $v_L$ the lattice site volume. The connectivity of the chain is only taken into account in the form of an additional contribution to the free energy due to changes in the volume occupied by the polymer $V$ relative to the volume occupied by the equivalent ideal chain $V_0 \propto b^3 N_m^{3/2}$, where $b$ is the root mean separation between connected monomers. According to Flory the change in the free energy due to a change in the polymer volume, $\Delta F_v$, is

$$\Delta F_v = \frac{3}{2} \left( \alpha^2 - 1 \right) - \ln \left( \alpha^2 \right)$$ (5.4)
Here $\alpha = (V/V_0)^{1/3}$ is the expansion factor. Minimizing the free energy with respect to $\alpha$, using $\rho_m = N_m/(\alpha^3 V_0)$, yields the result

$$\alpha^5 - \alpha^3 - \frac{v_L^2 N_m^3}{3\alpha^3 V_0^2} = v_L \left( \frac{1}{2} - \chi \right) \frac{N_m^2}{V_0}$$

(5.5)

At high temperatures $\chi < 1/2$, and the chain is expanded, such that lengths scale as $l \propto N_m^{3/5}$. As the temperature is lowered $\chi$ becomes larger. When $\chi = 1/2$ the right hand term in equation 5.5 is zero and the chain will have a size proportional to its ideal chain size, where lengths scale as $l \propto N_m^{1/2}$. The temperature for which this happens, is known as the theta temperature $\Theta$.

Below this temperature, the assumption that $\phi_m$ is small is invalid. However, using the full Flory-Huggins equation of state, the limit of zero temperature yields a polymer volume $V = N_m v_L$ and there is no solvent within the polymer domain, only the monomers of the polymer itself. The Flory model thus predicts that below the theta temperature a polymer collapses and expels the solvent. Polymer collapse can therefore be seen as a type of de-mixing of the polymer and the solvent. Indeed, as equation 5.1 shows, the coil to globule transition is linked to the mixing and demixing of the polymers themselves. Generally collapse will be accompanied by de-mixing of the polymers themselves from the solvent.

The coil to globule transition has also been studied more recently with computer simulation, often to test the assumptions of the mean field theory. Although in some cases an explicit solvent was used [77–85], in most cases the solvent was integrated out by using a simple potential such as the Lennard-Jones potential to describe the interactions between the monomers [86–110]. Alternatively integral equation theory has been used to calculate effective solvation potentials [111–113]. Further, rigorous calculations yielding exact results through a complete enumeration of polymer configurations have been applied to study the collapse transition [114–116]. These calculations, however, are limited to very short chains and again neglect the explicit effect of the solvent. In most cases a reasonable qualitative agreement between the mean field theory and simulation was found. Although progress has been made, it still remains computationally quite demanding to simulate the collapse of polymers in dense liquid solvents because of the amount of solvent required.

For this reason theoretical descriptions are useful to guide us. However, the Flory approach, or any approach that assumes incompressibility, are of limited applicability. There are two main reasons for this. Firstly, they yield only one theta temperature at a given pressure (except for the special case where $\chi$ is zero). In practice there can be as many as three. There is always the one the liquid phase that the Flory theory predicts, because here the incompressibility assumption holds to a good approximation. However,
 Further coil to globule transitions can occur at elevated temperatures where the solvent is a gas or a supercritical fluid. Interestingly, in the supercritical regime as the temperature is raised above the theta temperature there is a second coil to globule transition. So, this time the polymer goes from being expanded to collapsed upon a small increase in the temperature. These effects at elevated temperature are not irrelevant either. The “almost mystical” [117] properties of supercritical solvents make them very interesting for applications in processing. Spice extraction and coffee decaffeination are two examples where this technology is used. Understanding the nature of the coil to globule transition in this regime, is therefore of practical relevance. Secondly, the theta temperatures generally depend on the pressure— even in the liquid phase. Incompressible models apply only in the high pressure limit, so only a model that does not assume incompressibility can tell us something about the effects of pressure.

Dreischor and Lowe [19,118] developed a simple off-lattice thermodynamic model for the size of an isolated solvated polymer, based on Flory’s lattice model [19,118] that can account for the effects of compressibility of the solvent. This model indeed shows a far richer behaviour in terms of solvation effects, than is predicted by Flory’s model. Using an appropriate equation of state this model, amongst other things, predicts under what conditions a coil to globule transition should occur free of the incompressibility assumption. These predictions are in good agreement with the results of computer simulation. Solving this model analytically requires that the fraction of space occupied by the monomers in the polymer domain is small. As such, it can predict where there is a globular state. It cannot, however, predict analytically its precise nature because for the collapsed state this assumption is invalid. Our aim in this chapter is to extend this model to predict the properties of a collapsed solvated polymer in the supercritical regime. The predictions of the model will be compared to the results of computer simulation. To facilitate this comparison we consider the simplest system. That is, the “best” solvent there is—a solvent composed of the monomers of the polymer itself.

5.2 Developing a simple thermodynamic model

The model derived by Dreischor and Lowe [118] follows in the spirit of Flory and views the solvated polymer as a spherical domain, containing a homogeneous mixture of monomers and solvent, surrounded by pure solvent. Rather than assuming incompressibility, the amount of solvent in the polymer domain is determined from the thermodynamic equilibrium condition, that the chemical potential of the solvent in both domains is equal. The interactions between the monomers and the solvent in both phases are included by taking an ap-
propriate equation of state for the monomer fluid/solvent mixture. As with the Flory theory, the connectivity of the monomers is only taken into account in the form of an additional contribution to the free energy due to changes in the volume occupied by the polymer $V$ relative to the volume occupied by the equivalent ideal chain $V_0$ (using equation 5.4). We then write the total free energy of the system as

$$G(\alpha) = N_s \mu_s + N_s \tilde{\mu}_m(\alpha) + \Delta G_v(\alpha) - k_B T \ln(V_{sys})$$  \hspace{1cm} (5.6)$$

with $N_s$ the total number of solvent particles in the system, $\mu_s$ the chemical potential of the solvent, $\tilde{\mu}_m(\alpha)$ the excess chemical potential of the monomers, $\Delta G_v(\alpha)$ the configurational free energy given by equation 5.4, and $V_{sys}$ the system volume. Here, we take the limit of infinite dilution ($V_{sys} \gg V$), so $V_{sys}$ is independent of $\alpha$. Because the monomers are part of a chain, they do not have an ideal contribution to the chemical potential. The polymer is one molecule. If the chain is expanded the monomer density $\rho_m$ in the polymer domain is very low, such that we can write both the monomer and the solvent chemical potential using a Taylor expansion. The condition that the chemical potential of the solvent is the same within and without the polymer domain then implies a slight difference in density between the two domains,

$$\rho_s - \rho^0 = -\frac{u_{ms} \rho_m \rho^0}{1 + u_{ss} \rho^0}$$  \hspace{1cm} (5.7)$$

where $\rho^0$ is the bulk solvent density and $\rho_s$ the solvent density in the polymer domain. The coefficients $u_{ms}$ and $u_{ss}$ are

$$u_{ms} = \left( \partial \tilde{\mu}_m / \partial \rho_s \right)_{\rho^0,0} = \left( \partial \tilde{\mu}_m / \partial \rho_m \right)_{\rho^0,0}$$  \hspace{1cm} (5.8)$$

$$u_{ss} = \left( \partial \tilde{\mu}_s / \partial \rho_s \right)_{\rho^0,0}$$  \hspace{1cm} (5.9)$$

Both generally depend on the solvent density and temperature but their values are specified given an equation of state. To this order in the monomer density the condition of equal chemical potential also implies that the condition for mechanical equilibrium. Namely, that the pressure is the same in both domains. By minimizing the free energy with respect to $\alpha$, we then obtain the result derived in a previous publication [118], namely

$$\alpha^5 - \alpha^3 = \nu \frac{N_m^2}{V_0}$$  \hspace{1cm} (5.10)$$

where $\nu$ is the excluded volume parameter

$$\nu = u_{mm} - \frac{u_{ms} \rho^0}{1 + u_{ss} \rho^0}$$  \hspace{1cm} (5.11)$$
and the coefficient \( u_{mm} \) is

\[
u_{mm} = (\partial \mu_m / \partial \rho_m)_{T, \rho_m} \tag{5.12}\]

Again, this is a density and temperature dependent quantity specified by an equation of state.

For the idealized case of a polymer solvated by fluid of its own monomers (the "symmetric" case) the above results simplify and both the solvent density in the polymer domain and the excluded volume parameter can be written in terms of the dimensionless compressibility of the solvent \( \kappa \), where

\[
\kappa^{-1} = \frac{1}{k_B T} \left( \frac{\partial P}{\partial \rho_0} \right) \tag{5.13}\]

This leads to

\[
\rho_s - \rho_0 = (\kappa - 1) \rho_m \tag{5.14}\]

and

\[
v = \frac{1 - \kappa}{\rho_0} \tag{5.15}\]

The interesting thing about this is that \( v \) is negative, so the polymer wants to collapse, when \( \kappa > 1 \). This being the case \( \rho_s - \rho_0 > 0 \), that is the density of the solvent around the polymer is higher than the bulk solvent density. This is a very different scenario than the mechanism predicted by the Flory model. There, the coil to globule transition is driven by a de-mixing of the solvent from around the polymer and the solvent is expelled as the polymer collapses to the globular state. Here, this analysis suggests, the solvent almost becomes too good a solvent and the collapse is favourable because it allows the polymer to "suck" more solvent into its domain. We use "suggests" here because the theory makes use of a Taylor expansion of the equation of state about the limit \( \rho_m \to 0, \rho_s \to \rho_0 \). However, as the polymer collapses \( \rho_m \) increases so this approach breaks down. All we can really say is that the initial state of the collapse must be accompanied by an increase in the amount of solvent around the polymer because in the initial stages \( \rho_m \) is still small.

Although we cannot solve the model analytically to determine the nature of the globule state, if we know the free energy as a function of the polymer size it is straightforward to minimize this function numerically. In terms of our model, the polymer is essentially treated as a droplet of size \( r \sim V^{1/3} \). Unlike for the the case of an expanded polymer, we can no longer be sure that the pressure in both domains is equal if there is additional contribution to the free energy, in the form of a surface free energy \( \Delta G_o \). This contribution is given by

\[
\Delta G_o = 4 \pi r^2 \gamma \tag{5.16}\]
where $\gamma$ is the surface tension. According to Laplace's law this is directly related to the pressure difference between the two domains via

$$\Delta P = \frac{2\gamma}{r}$$  \hspace{1cm} (5.17)

![Graph showing expanded and collapsed regions as a function of temperature and pressure as calculated from the Johnson equation of state. The thick solid line represents the (estimated) boiling points for the Lennard-Jones fluid.](image)

We now have two routes to proceed. The first route is to treat this problem as we would treat a normal liquid droplet. We will assume the surface tension is a constant independent of the polymer size. Although this surface tension is not known, we can assume an infinitely long chain (meaning $r \rightarrow \infty$), such that the surface free energy is zero. Therefore, the pressure in both phases will be equal. We can thus find the size of the chain, by imposing that the pressure should be equal in the two phases, in addition to the condition for thermodynamic equilibrium (that the solvent chemical potential in both phases should be equal). Because of this additional condition, we are now
no longer free to minimize the free energy with respect to the size of the polymer. We will refer to this model as model 1. The second route we can take is to minimize the free energy of the system with respect to the size of the polymer, as we did in the case of the expanded chain, forgoing the condition that the pressure should be equal in both phases. In doing so we are in fact calculating a surface tension, which does not have to be independent of the polymer size. This model will be referred to as model 2. We will explore both these routes in the rest of this chapter and hopefully be able to conclude which of these is the more realistic, by comparing them to the results of computer simulation. Note that there is some ambiguity comparing simulation results with the theory because the concept of a polymer “volume” is somewhat ambiguous in a simulation. The approach that we used was to take for the theory a spherical volume with a radius of gyration equal to that calculated from the simulations.

5.3 Computational details

The theoretical model was derived using the Lennard Jones equation of state, so we will use that pair potential also in the simulations. The Lennard-Jones potential $u_{ij}$ has the following form:

$$u_{ij}(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

The reason for choosing this potential is the existence of a known equation of state, so we can choose the smallest “typical” value for the cut-off radius often used in literature, in this case $r_c = 2.5\sigma$. Note that the calculations performed by Johnson were done at a cut-off radius of $r_c = 4.0\sigma$, so there will a small discrepancy between the theoretical model and the simulations. We have attempted to correct for this by working relative to the critical temperature and pressure. The configurational entropy is relatively insensitive to the potential, so we choose the simple harmonic potential

$$f_{spring}(r_{ij}^*) = -k d r_{ij}^*$$

where $k = \frac{25}{6} T$. This spring constant $k$ is chosen so that the Kuhn length for an ideal chain with this constant coincides with the minimum of the Lennard Jones potential. To look for the effects predicted by the theory we obviously need to include the solvent explicitly.

This problem will also give us an opportunity to test the new Lowe-Andersen thermostat and the constant pressure algorithm described in Chapter 3 on a slightly more involved problem. Remembering that the Lowe-Andersen thermostat does not suppress diffusion as much as the Andersen...
thermostat, we expect it to sample phase space more efficiently. The barostat allows us to specify the state points we are studying in terms of the temperature and pressure. As such, we can study the collapsed state for points where the theories above predict that the collapsed state is solvent rich and test this prediction.

We ran simulations at different state points and chose one for which the solvent density of solvent in the collapsed polymer was predicted to significant. Because the simulations took a large amount of computer time, we choose the points based on 5.1 in the extreme region of the "Collapsed" region (i.e. bottom left, top left, extreme right, centre). The point we chose was $T = 0.85T_c$ and $P = 0.15P_c$. Under these conditions the polymer chain would collapse to a globule allowing for long chains to be simulated. However, since an expanded self avoiding chain has a size which scales with $R_g \propto N^{\frac{7}{12}}$, the amount of solvent required to fill a minimal box encapsulating this chain scales with $N_s \propto N^{\frac{21}{12}}$. Even in the best case, computational time scales linear with the amount of particles, so the computational effort required to calculate longer uncollapsed chains is almost quadratic. For a collapsed chain the size scales with $R_g \propto N^{\frac{1}{3}}$ and hence the amount of solvent needed as $N_s \propto N$ implying that the computational effort can scale linearly. Of course the computational time will never actually be linear due to cache effects and so on, but large chains are feasible with relatively little computational time.

Now there is the question of how to generate an initial configuration. The easiest way to generate a long self avoiding chain is by simply brute force. Start with the current chain and try to add one bead to the end, if that fails, start all over again with a one bead chain. Now such a configuration will not be a collapsed configuration. To get there we did a number of simulations for which we started with a very low density (and pressure) solvent and equilibrated the system at constant volume until the chain is collapsed. At this point the barostat (as described we used in Frenkel and Smit [5]) was enabled. It then slowly shrinks the box in such a way that it goes to the pressure we require. This effectively results in the desired equilibrium configuration, although the actual path of getting there was slightly un-physical. The main justification is that also for a low density system, where it is practical to simulate with a relatively large quantity of solvent, the polymer would collapse to a globule also when coupled to the barostat from the start. This approach makes the simulations, at the state-point we require, practical using an explicit solvent.

One important observation here was that the choice of the thermostat has a very major effect on the time needed for the chain to collapse. As can be seen in figure 5.2 the commonly used Andersen thermostat results in much slower dynamics. In fact, for the longer chains studied here the collapse is so slow
Figure 5.2: The radius of gyration of a chain consisting of 4096 particles over time. The lower value for the Lowe-Andersen reaches a dense packed spherical configuration on this time scale, whereas for the Andersen thermostat it does not.

that the simulations are almost impractical using it. The probable reason is that, because it is momentum conserving, the Lowe-Andersen thermostat preserves hydrodynamic behaviour. It is the hydrodynamic interactions between monomers that lead to the Zimm scaling of the polymer diffusion coefficient $D \propto 1/\sqrt{N}$. Without this hydrodynamic effect (as with the Andersen thermostat) the scaling is Rouse-like, $D \propto 1/N$ [119]. Obviously, for large $N$ there is a big difference between the two and the hydrodynamics significantly speeds up the configurational dynamics of the polymer [120]. Interestingly, this effect has also been observed in the folding of proteins [121]. We are only interested in the static properties of the collapsed state here, but by using a more dynamically realistic methodology, at little additional overhead, we note that we can do this significantly more efficiently.

Once a collapsed configuration has been found, we can use that as a starting point from which we do the simulations to test the theory. The spherical symmetry of the problem allows us to map the data on just a single quantity, the distance to the centre of mass of the polymer. For the density this is a simple mapping, the pressure was slightly more complicated since it is not
by definition a local quantity. By dividing the system into spherical shells centred on the polymer centre of mass we could still obtain a “local” pressure. This way also allowed us to split the pressure into two parts. One radial part parallel to the vector pointing away from the centre of mass, and one tangential part perpendicular to this. We did this with this alternative equation for the radial virial pressure:

\[
P_{||} = \frac{1}{3V} \left( \sum_{i<j} \frac{\tilde{f}(\tilde{r}_{ij}) \cdot \tilde{p}_i + \tilde{f}(\tilde{r}_{ij}) \cdot \tilde{p}_j}{2} \right)
\]

with \( \tilde{p}_i \) being the projection of \( \tilde{r}_{ij} \) on the unit length vector pointing away from the center of mass through particle \( i \). The tangential virial pressure is then simply the difference between the normal virial pressure and the radial pressure:

\[
P_T = P - P_{||}
\]

. The results of the simulations will be discussed in the next section.

## 5.4 Results

<table>
<thead>
<tr>
<th></th>
<th>Model 1 isolated/solvated</th>
<th>Model 2 isolated/solvated</th>
<th>Simulation isolated/solvated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho^0 )</td>
<td>0/0.019</td>
<td>0/0.019</td>
<td>0/0.019</td>
</tr>
<tr>
<td>( \rho_m )</td>
<td>0.748/0.592</td>
<td>0.527/0.253</td>
<td>( \sim ) 0.82/( \sim ) 0.65-0.66</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>0.0/0.141</td>
<td>0.0/0.288</td>
<td>0/( \sim ) 0.12-0.13</td>
</tr>
<tr>
<td>( \rho_m + \rho_s )</td>
<td>0.748/0.733</td>
<td>0.527/0.541</td>
<td>( \sim ) 0.82/0.78</td>
</tr>
<tr>
<td>( \rho_s/\rho^0 )</td>
<td>-/7.468</td>
<td>-/15.22</td>
<td>-/( \sim ) 6.32-6.84</td>
</tr>
</tbody>
</table>

*Table 5.1: The bulk solvent density \( \rho^0 \), monomer density \( \rho_m \), solvent density \( \rho_s \) and total density \( \rho_m + \rho_s \) inside the polymer globule at \( T/T_c = 0.85 \) and \( P/P_c = 0.15 \) for an isolated Lennard-Jones chain and a Lennard-Jones chain in a symmetric Lennard-Jones solvent as predicted by both models for the collapsed state and the results of simulation.*

As was stated in the introduction, we will consider the simplest case of a collapsed solvated polymer, namely a polymer in a symmetric solvent (a polymer solvated by its own monomers). We opt to use the Lennard-Jones potential to describe the interactions between the monomers and the solvent

\[
u(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right)
\]  \( (5.18) \)
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where \( \sigma \) is characteristic length and \( \epsilon \) the characteristic energy of the particles. In order to make a direct comparison between our two models and the results of simulation, we will need to use an accurate equation of state for the Lennard-Jones fluid in the two models. We will use the equation of state developed by Johnson et al. [30]. This equation of state takes the form

\[
\frac{P}{\rho k_B T} = 1 + \left( a_1 + \frac{a_2}{T^{*1/2}} + \frac{a_3}{T^*} + \frac{a_4}{T^{*2}} + \frac{a_5}{T^{*3}} \right) \rho^* + \\
\left( \frac{a_6}{T^*} + \frac{a_7}{T^{*2}} + \frac{a_8}{T^{*3}} + \frac{a_9}{T^{*4}} \right) \rho^{*2} + \\
\left( \frac{a_{10}}{T^*} + \frac{a_{11}}{T^{*2}} + \frac{a_{12}}{T^{*3}} \right) \rho^{*3} + \frac{a_{13}}{T^{*2}} \rho^{*4} + \\
\left( \frac{a_{14}}{T^{*2}} + \frac{a_{15}}{T^{*3}} \right) \rho^{*5} + \frac{a_{16}}{T^{*2}} \rho^{*6} + \left( \frac{a_{17}}{T^{*2}} + \frac{a_{18}}{T^{*3}} \right) \rho^{*7} + \\
\frac{a_{19}}{T^{*3}} \rho^{*8} + \frac{\exp(-\gamma^2 \rho^{*2})}{\rho^* T^*} \left\{ \left( \frac{a_{20}}{T^{*2}} + \frac{a_{21}}{T^{*3}} \right) \rho^{*3} \right\} + \\
\frac{\exp(-\gamma^2 \rho^{*2})}{\rho^* T^*} \left\{ \left( \frac{a_{22}}{T^{*2}} + \frac{a_{23}}{T^{*3}} \right) \rho^{*5} + \left( \frac{a_{24}}{T^{*2}} + \frac{a_{25}}{T^{*3}} \right) \rho^{*7} \right\} + \\
\frac{\exp(-\gamma^2 \rho^{*2})}{\rho^* T^*} \left\{ \left( \frac{a_{26}}{T^{*2}} + \frac{a_{27}}{T^{*3}} \right) \rho^{*9} + \left( \frac{a_{28}}{T^{*2}} + \frac{a_{29}}{T^{*3}} \right) \rho^{*11} \right\} + \\
\frac{\exp(-\gamma^2 \rho^{*2})}{\rho^* T^*} \left\{ \left( \frac{a_{30}}{T^{*2}} + \frac{a_{31}}{T^{*3}} + \frac{a_{32}}{T^{*4}} \right) \rho^{*13} \right\}
\]

where \( \rho^* = \rho \sigma^3 \) is the reduced density and \( T^* = k_B T / \epsilon \) is the reduced temperature of the system. The parameters \( a_1 - a_{32} \) can be found in [30]. The first thing we have to do, is calculate a phase diagram, to see in what regions of phase space the polymer is expanded or collapsed. We can obtain the theta temperature by setting the excluded volume parameter \( \nu = 0 \) in equation 5.10. The excluded volume parameter itself is obtained using equation 5.20. The resulting phase diagram is presented in figure 5.1. In this figure the theta temperature \( \Theta \) is plotted as a function of the pressure. These quantities have been made dimensionless by the critical properties of the solvent (for a Lennard-Jones fluid, \( T_c^* = 1.32, P_c^* = 0.13 \)). For this system there can be up to two theta temperatures at constant pressure. For the symmetric case the Flory model predicts that there is no theta temperature, and indeed the low temperature theta point in the liquid phase is absent for this model.

In order to obtain an idea what the globule state might look like, we pick a state point within the collapsed region \((T/T_c = 0.85, P/P_c = 0.15)\). We then calculate the monomer and solvent densities within the polymer domain for both models. The results are presented in table 5.1. At this state point the
5.4. RESULTS

bulk solvent (the pure solvent phase in terms of the two models) is a dilute gas. Both models predict that the solvent density in the polymer domain is significantly higher than in the pure solvent phase. Model 2 predicts the largest difference in the solvent density. Both models predict that the total density in the polymer domain is liquid-like \( \rho > \rho_c \), where model 1 predicts the highest total density. We would like to note, that for both models the contribution of the configurational free energy \( \Delta G_v \) to the total free energy is negligible. We also looked at the case of an isolated polymer chain, where the monomers interact with the Lennard-Jones potential. In this case both models predict the density of monomers in the polymer domain is approximately equal to the total density of particles predicted for the solvated chain.

For comparison, we also performed simulations. These simulations were done at the same state point as was used for the model predictions \( T/T_c = 0.85, P/P_c = 0.15 \) for a chain consisting of 2048 and of 4096 monomers. In the case of 2048 monomers, 4952 solvent particles were used, and in the case of 4096 monomers, 4904 solvent particles were used. In addition we also simulated a chain consisting of 4096 monomers in vacuum. The simulation results are shown in table 5.1, figure 5.3, and figure 5.4. The results indicate that the solvent density around the polymer is indeed significantly higher than in the bulk solvent. Figure 5.3 shows that if we plot the solvent density as

![Figure 5.3: The solvent and total density \( \rho \) as a function of the distance from the center of mass \( r \) for a Lennard-Jones chain in a symmetric Lennard-Jones solvent at \( T/T_c = 0.85 \) and \( P/P_c = 0.15 \). The x-axis is in units of the polymer radius of gyration. The y-axis is in reduced Lennard-Jones units.](image)
5. THE NATURE OF A COLLAPSED SOLVATED POLYMER

Figure 5.4: The solvent and total pressure $P$ as a function of the distance from the center of mass $r$ for a Lennard-Jones chain in a symmetric Lennard-Jones solvent at $T/T_c = 0.85$ and $P/P_c = 0.15$. The x-axis is in units of the polymer radius of gyration. The y-axis is in reduced Lennard-Jones units.

a function of the distance from the centre of mass of the polymer the density within a distance of approximately $r = 1$ in units of the polymer radius of gyration is roughly six to seven times higher than in the bulk solvent for both the chain of 2048 and 4096 monomers. In table 5.1 the results of the simulation are compared with the predictions of the two models. Although both models show the correct qualitative behaviour in terms of the solvent density, model 1 clearly outperforms model 2 in the quantitative prediction of the different densities, for both the chain in vacuum and the solvated chains. In addition to calculating the radial densities, we also calculated the radial pressure using the virial theorem. These results have been plotted in figure 5.4. The pressure is seen to increase significantly near the polymer centre of mass. In that respect both models are wrong. Although not shown in table 5.1 the pressure that we obtain from model 2 is negative ($P \approx -3.65$). This implies that the surface tension is negative and decreases with an increasing number of monomers (according to equation 5.17 $\gamma \sim -N_m^{1/3}$). For model 1 we had assumed the pressure around the polymer to be equal to the bulk solvent pressure.
In this chapter we extended the model, previously developed for the size of a solvated polymer, to study the nature of the globule state. We derived two similar thermodynamic models. Both of these models treat the collapsed polymer essentially as a two phase problem. The first phase contains of a homogeneous mixture of monomers and solvent (the polymer domain). The second (bulk) phase contains pure solvent. The condition for thermodynamic equilibrium is that the chemical potential of the solvent is equal in both phases. In the first model it is then assumed that we can treat the polymer as we would a liquid droplet. There is a constant surface tension, such that as the number of monomers becomes very large the pressure in the two phases is equal. The polymer size is thus obtained by adding the condition that the pressure in both phases is equal. In the second model the polymer size is obtained by minimizing the free energy with respect to the size of the polymer. The interactions in both phases are described by an appropriate equation of state.

In this chapter we considered a symmetric system, where the monomers and solvent particles interact via a Lennard-Jones potential.

Both models predict that the solvent density inside the polymer domain is significantly higher than the bulk solvent density. The total density of particles in the polymer domain (collapsed polymer plus solvent) is liquid-like. These predictions were confirmed by computer simulation. The simulations also show (see figure 5.1) that, as both theories require, the monomer density and solvent density in the collapsed polymer as a function of the dimensionless distance from the centre of mass are independent of the number of monomers in the polymer for a sufficiently long polymer. The functions are not, however, step functions as the theoretical models require. This is clearly a limitation of the theories. The first model gives the best quantitative agreement with simulation. These results contradict the predictions of the Flory model, which says that a polymer chain always expels the solvent as it collapses. The fact that the Flory-Huggins model predicts this, should be attributed to its underlying assumption of incompressibility. The condition that the total density has to remain constant, by construction implies that as the monomer density increases the solvent density should decrease.

So, which of the two thermodynamic models is the better representation of reality? Although, the first model clearly gives the better prediction for the densities of monomers and solvent within the polymer globule, neither model gives correct (qualitative) predictions for the pressure. The simulations clearly show a significant increase in the calculated pressure within the polymer chain. The first model by construction says that the pressure within the polymer should equal the pressure of the bulk solvent, whereas the second model predicts a negative pressure. According to Sanchez the theta
temperatures of a polymer solution should correlate with the critical solution temperatures, a fact since confirmed by simulation [122, 123]. This implies that the polymer globules will want to coalesce to form a bulk phase. The second model predicts a negative surface tension, which means that the polymers will prefer to stay in their globule state, rather than form a bulk phase. It is for this reason that we believe the first model is the better model, as it does not contradict the results of Sanchez and co-workers. To further improve the model, we need to obtain a better understanding of the surface effects on the properties of a collapsed polymer.

Nonetheless, the simulations confirm that the qualitative predictions of the models that the collapse mechanism for a polymer in a low density solvent is very different in nature to that at liquid-like solvents. The collapsed state is indeed solvent rich rather than being solvent free. This suggests that studying the coil to globule transition for these systems requires that an explicit solvent is included, however computationally inconvenient this is. In addition this chapter gave us a good practical test case for the Lowe-Andersen thermostat and the barostat. Notably, using the former, the collapse dynamics are so much faster, that using a non-momentum conserving thermostat of the Langevin type would have made these simulation impractical.