Structure and Thermodynamics of Lattice Polymers in Bulk and at Interfaces

A Comparison of Ornstein-Zernike-like Approaches to Monte Carlo Simulations
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Chapter 1
Introduction

1.1 Polymers

Polymers can be divided into natural (e.g., wool, silk, cotton, cellulose) and synthetic materials (plastics, rubbers). A main characteristic of the materials is that they consist of extremely large molecules. Their molecular weight is generally $10^4$ to $10^6$ g/mole, in contrast to substances like water (18g/mole) or alcohol (46g/mole).

Polymer molecules are formed during step or chain polymerization reactions [1] in which low molecular weight compounds are coupled into polymers. In a reaction mostly linear, but also branched and ring-shaped molecules, or a 3-dimensional network, can be formed. This is highly dependent on the type of low molecular weight compound that is used in the polymerization reaction. The low molecular compound from which the polymer molecules are built is called the chemical repeat- or monomeric unit.

Depending on the type of low molecular weight compound, a wide variety of chemical properties with many applications in the optical, electronic, medical and coatings industries can be obtained. The materials also exhibit many interesting physical phenomena [2] among which crystallization, vitrification, aging, visco-elasticity, (micro) phase separation and liquid crystallinity. These macroscopically observable physical material properties have their importance in many applications of polymeric materials, and can be explained in terms of the molecular organization of the materials.

The molecular organization of (polymeric) materials in bulk and at interfaces can be probed by X-ray or neutron scattering experiments [3]. In such experiments one measures the intensity $I(\Theta)$ of the radiation scattered by a polymer sample at angle $\Theta$ with the primary beam, normalized to the scattered radiation at $\Theta = 0$, $S(\Theta) = I(\Theta)/I(0)$. The quantity $S(\Theta)$ is called the structure factor. The scattering pattern or structure factor is a direct measure of the molecular organization because another configuration of the scatterers, i.e. a different ordering of
the molecules in the polymeric material, results in a different scattering pattern. From the structure factor, the distribution of the scatterers in the sample can be obtained by Fourier transformation [4].

In the work described in this thesis we have been concerned with the (macroscopic) thermal and interfacial properties of polymeric materials and their quantitative relation to the molecular organization of the materials. Such relations are provided by statistical mechanics.

1.2 Classical statistical mechanics of liquids

A description of the thermal equilibrium properties of a macroscopic amount of material is provided by thermodynamics [5,6]. It is well known from thermodynamics that the variables that determine the macroscopic state of a material such as the mechanical variables pressure $p$, energy $U$ and volume $V$, and the thermal variables temperature $T$, chemical potential $\mu$ and entropy $S$, are interrelated in such a way that an amount of material consisting of $N$ molecules is in principle fully characterized by its free energy $\mathcal{A} = \mathcal{A}(N,V,T)$. All thermodynamic state variables can be derived from the free energy.

The objective of statistical mechanics is to obtain these macroscopic state variables of a material from its molecular organization and interactions. According to classical mechanics, this can in principle be accomplished in a completely deterministic way by constructing and integrating the equations of motion of all molecules in the macroscopic body, although this is virtually impossible because of the extremely large number of molecules in such a body. Statistical mechanics handles this problem by using the fact that because of the large number of particles, new types of regularity appear which can be formulated in statistical mechanical laws that are probabilistic in nature [7]. The probabilistic character implies that all calculated state variables are distributions around an average. For large bodies these distributions are extremely narrow [7,8], and therefore, one does not notice the probabilistic nature of the variables. The average value of a quantity can thus be taken as the value of that quantity, a procedure that is implicit in thermodynamics.

From the free energy it is seen that the state of a material is macroscopically characterized by three variables $N$, $V$ and $T$. Microscopically on the other hand, the material is fully characterized only if we know the positions $\mathbf{r}_i$ and momenta $\mathbf{p}_i$ of all the $N$ molecules in the material. Thus, statistical mechanics deals with an enormous reduction of variables in going from the microscopic to the macroscopic material description. This is illustrated in Eq. 1.1, which is one of the basic equations of statistical mechanics

$$
\exp\left(-\frac{\mathcal{A}(N,V,T)}{k_BT}\right) = \frac{1}{N!\Lambda^N} \int \cdots \int \exp\left(-\frac{U_{N,tot}(\mathbf{r}_i^N)}{k_BT}\right)d\mathbf{r}_i^N
$$

(1.1)
On the left hand side we have the free energy $\mathcal{A}$ which is a representative of the macroscopic world. It only depends on $N$, $V$ and $T$. On the right hand side we see the so called Boltzmann factor $\exp(-U_{N,\text{tot}}(\mathbf{r}^N)/k_BT)$. The Boltzmann factor is a quantity sensitive to details of the microscopic molecular organization and is dependent on the $3N$ variables $\mathbf{r}^N$ via the total configurational energy of the model system $U_{N,\text{tot}}(\mathbf{r}^N)$. The configurational energy $U_{N,\text{tot}}(\mathbf{r}^N)$ is a function of the position of all $N$ molecules $\mathbf{r}^N = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The integration over the momenta $\mathbf{p}_i$ of the particles is independent of the details of the molecular interaction and is already carried out on the right hand side of Eq 1.1. The result is collected in the prefactor $\Lambda^{-N}$.

Note that the Boltzmann factor is a measure of the probability of obtaining a molecular configuration $\mathbf{r}^N$: energetically unfavorable ($U_{N,\text{tot}}(\mathbf{r}^N)$ large) configurations correspond to a Boltzmann factor that is approximately zero. Therefore, such a configuration will not contribute to the free energy of the system, only configurations with favorable internal energies will. Note that the integration over the positions of all molecules in Eq. 1.1 ensures that all configurations are probed.

A second important equation is Eq. 1.2. It provides a numerical measure of the microscopic structural correlations present in the system. The structural correlations between two molecules 1 and 2 can be quantified by leaving out the integrations over the coordinates of these molecules in the left hand side of Eq 1.1. Appropriate normalization results in

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{N!}{(N-2)!\rho^2Q_N} \int \ldots \int \exp\left(-\frac{U_{N,\text{tot}}(\mathbf{r}^N)}{k_BT}\right)d\mathbf{r}_3 \ldots d\mathbf{r}_N$$  \hspace{1cm} (1.2)

in which $Q_N$ is given by

$$Q_N = \int \ldots \int \exp\left(-\frac{U_{N,\text{tot}}(\mathbf{r}^N)}{k_BT}\right)d\mathbf{r}^N$$  \hspace{1cm} (1.3)

The $g(\mathbf{r}_1, \mathbf{r}_2)$ is the 2-particle distribution. Physically, $\rho g(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2$ gives the number of molecules in volume element $(\mathbf{r}_2, \mathbf{r}_2 + d\mathbf{r}_2)$ on condition that there is a molecule in $(\mathbf{r}_1, \mathbf{r}_1 + d\mathbf{r}_1)$, where $\rho = N/V$ is the overall density of the fluid.

Eq. 1.1-1.3 are valid if the molecules are simple, i.e., consisting of a single particle. A linear polymeric molecule is often modelled as a chain of covalently bonded particles. Each particle then corresponds to a segment (chemical repeat unit) of the chain molecule. Thus, in the case of polymeric molecules the integration in Eq 1.1 and Eq 1.2 should be over all segments of all molecules. The configurational energy $U_{N,\text{tot}}(\mathbf{r}^N)$ then consists of interactions between segments of the same molecules and of interactions between segments belonging to different molecules. With this convention, Eq. 1.1 and Eq. 1.2 are still valid, but it is convenient to write an extra equation of type Eq. 1.2: Eq. 1.2 applies if we consider two segments that are not part of the same molecule (the intermolecular
2-particle distribution), and the extra equation for the intramolecular 2-particle distribution, \( \omega(r_1, r_2) \), applies if the two segments are part of the same molecule.

The principal difficulty in statistical mechanics is the calculation of the right hand sides of Eq 1.1 and Eq 1.2. This amounts to the calculation of the contributions of all non-zero Boltzmann factors of the model system. It is seen in Eq 1.1 that the contributing Boltzmann factors are determined by the configurations with the lowest energies. These are the so-called equilibrium configurations of the model system. There are two main routes to "sample" the molecular equilibrium configurations:

- computer simulation:
  In a Monte Carlo (MC) simulation the important configurations are sampled by moving the \( N \) molecules in a box of volume \( V \) and accepting the moves according to the Metropolis acceptance rules [9]. All macroscopic variables can then be calculated from this set of configurations.
  In a molecular dynamics simulation Newton's laws of mechanics are solved to obtain the equilibrium configurations. This is a completely deterministic method, but it can only be applied for very short periods (\( \mathcal{O}(10^{-10}) \)s) of time and to a small number of molecules.
  The simulation methods require a large computational capacity. Another disadvantage is that one always has to deal with statistical uncertainties and finite sizes of the system volume \( V \). Advantageous is that apart from the construction of a model, no approximations are needed, and that the model systems can be chosen to be relatively realistic. Atomistically detailed systems can be handled, which allows for direct comparison of simulation results to laboratory experiments. Nowadays, simulations are considered as computer experiments, thanks to their exact status.

- theory, the construction of analytically or numerically tractable approximations:
  A brief survey of basic approaches to the modelling of polymeric liquids will be given in the next section. It is generally not possible yet to study models that are atomistically detailed. Only idealized models are studied. This drawback is also the strength of the approach: the method is, more than simulations, important in reducing physical phenomena to their bare essence, without focussing on fully quantifying experimentally obtained data.

1.3 Modelling of polymeric liquids

In classical polymer science, statistical mechanics based theories [10-12] have mainly been concerned with the explanation of thermodynamic phenomena ob-
served in polymer fluids. The equation of state, phase separation behavior \cite{11}, and adsorption/desorption characteristics \cite{13} have received a great deal of attention. In these classical approaches the structural correlations that appear between the particles in the polymer fluids are approximated and not considered explicitly.

It is only until about ten years ago that the first polymer fluid theories appeared \cite{14-17} which attempted to calculate the structural correlations between the particles explicitly and from that the macroscopic properties of the fluids.

A polymer fluid is often modelled as a collection of flexible molecules each consisting of a linear sequence of covalently bonded impenetrable segments. Apart from covalent bonding between the segments, all segments also interact with each other via non-covalent interaction potentials e.g., of Lennard-Jones type. The structural correlations present in such a polymeric fluid can then be attributed to three effects. By far the most important are packing effects that appear due to the repulsive interactions between the segments, but also effects due to attractive interactions between segments and chain-connectivity effects caused by the bonding of particles (segments) into molecules are of importance for the fluid structure.

Classical approaches in polymer science are based on Prigogine's cell model \cite{10} or the Flory-Huggins lattice model \cite{11,12}. These approaches adopt approximations for the structural correlations present between the molecule-segments. Space is discretized, and is thought to be build of cells \cite{10} or lattice sites \cite{11,12}. As a result, the packing effects caused by the repulsive cores of the particles are not \cite{11,12} or only partially \cite{10} taken into account. Chain-connectivity is also only included in an approximate fashion via the Flory- \cite{18} or Huggins \cite{19} approximation. The effect of attractive interactions on the correlations is also not (Bragg-Williams random mixing \cite{8}) or only partially (Quasi-Chemical approximation \cite{8,11}) taken into account. If the approximations mentioned above are adopted in the multiple integral of Eq. 1.1, $A(N,V,T)$ can be calculated, together with all other important thermodynamic information \cite{7,8}.

Subsequent approaches have improved upon the pioneering work of Refs. \cite{10-12} by taking chain connectivity- and attractive energy effects into account up to higher order \cite{20}, or by generalizing the results obtained in discretized space to continuum \cite{21}.

Lattice models \cite{11,12}, which do not incorporate packing effects, are not able to predict an accurate equation of state, because of the importance of these effects for the equation of state behavior of real polymeric fluids. Cell models \cite{10}, which do (approximately) account for the packing effects, are more successful in explaining the equation of state-behavior of real polymeric fluids. Both categories of models have been reasonably successful in the description of liquid-liquid and liquid-gas phase separation phenomena \cite{10,11,22-24} (note that liquid-gas phase
separation is only important for relatively low molecular weight systems). This
is mainly because packing effects are not of leading importance for separation
phenomena to occur: phase separation phenomena are largely caused by the at­
ttractive energies between the molecules in the system, and the Quasi-Chemical
approximation, although approximate, is fairly accurate in incorporating these
attractive interactions on the structural correlations of lattice systems. Therefore,
it gives reasonably accurate results in predicting phase separation phenomena.

The more recent theories of Refs. [14-17] rely on integral equation methods
developed in liquid state physics [25-28]. The general method that is employed
focuses on the calculation of structural correlations present in continuum space
models via integral equations. The structural correlations are calculated from
the integral equations by combining them with an approximate closure relation
[26,29,30]. Both the integral equation and the closures can be derived from funda­
mental considerations [31]. Once the structural correlations are known, formally
exact statistical mechanical routes can be applied to obtain the macroscopic ther­
modynamic properties from the structural correlations [32]. The method thus
offers a solid, physically realistic microscopic basis in the explanation and quan­
tification of macroscopic phenomena.

The structural correlations in continuum space fluids are largely determined by
the packing of the molecules and therefore, a lot of attention has been focussed
on accurately incorporating packing effects in the theory. Chain-connectivity and
the effects of attractive interactions are of less influence in determining the struc­
tural correlations and as a result, less attention has been paid to them, although
these effects are very important, especially for the thermodynamic properties of
polymeric molecules. This is thus in contrast to the classical theories where most
attention has been focussed on the thermodynamic properties of model systems
and less on the calculation of the structural correlations.

The most important drawback within integral equation approaches is the ap­
proximate nature of the closure relations, which causes the integral equation
approaches to be thermodynamically inconsistent [32]. Another problem is that
the nature of the approximations in the closure relations is not so much physical
but more mathematical. This makes it difficult to construct more consistent
closures that are still tractable.

1.4 Aim of this thesis

Integral equation models have been introduced less than ten years ago in polymer
science [15,16]. Therefore, the general objective of the work described in this
thesis was to investigate the merits of these relatively new approaches in the
statistical mechanics of polymer systems.
Thus far, all integral equation studies of polymer systems have been concerned with continuum space fluids [14-17]. It is well known that at liquid-like densities, the overall structure of such fluids is largely determined by the repulsive interactions between the cores of the segments (packing effects), and that the effects of the attractive interactions and chain-connectivity only appear as perturbations on the structure caused by the repulsions [33]. Fortunately, it is possible to capture the packing effects to a high degree of accuracy within integral equation approaches, as is seen from our knowledge of the hard sphere model [26,27], for which the repulsion between the particle cores is the sole factor that determines the fluid structure. Although of less importance for the overall fluid structure, it is nevertheless very desirable to incorporate also the effects of the attractive interactions and chain-connectivity in a molecular based theory, because of the decisive importance of these factors in understanding the phase separation phenomena and equation of state behavior of polymers on the basis of the fluid structure [18,19].

A first objective of our work was therefore to provide clearcut tests of how well non-covalent attractive interactions and chain-connectivity are taken into account in integral equation formalisms. In order to single out the effects of the attractive interactions and chain-connectivity, we have discretized configurational space onto a cubic mesh. If we then consider a cubic lattice version of the best known integral equation theory for polymer systems, the polymer-RISM theory [15,16], and if we let each polymer segment occupy exactly one lattice site, we see that all liquid-like ordering effects that are predominant in continuum models disappear. Comparison to Monte Carlo simulations on the same model then provides us with direct answers regarding the effects of chain-connectivity and attractive interactions on the structure and thermal properties of polymer fluids.

A second objective of the work described in this thesis was to address the consistency problem that is inherent in the standard polymer-RISM approach [15,16]. In the standard polymer-RISM approach, the intermolecular ordering (the intermolecular 2-particle distribution) is expressed in terms of the molecular conformations (the intramolecular 2-particle distribution). No relations that, in turn, determine the intramolecular 2-particle distribution in terms of the intermolecular 2-particle distribution are provided by the polymer-RISM theory, although, for flexible molecules, the intramolecular distribution certainly is a function of the intermolecular distribution. Therefore, the intramolecular 2-particle distribution is an input quantity in the theory. This absence of internal consistency is a central problem of the polymer-RISM theory.

Although a self-consistent version of the polymer-RISM theory has been developed [34,35], we have chosen to employ a different route which is not formulated in terms of an inter- and intramolecular distribution. This approach is based on the associating fluid formalism [14,36] by Wertheim. The directional forces
between the particles that appear in this approach are used to construct covalent bonds between the particles, so that (polymer) molecules can be formed. By considering a mixture of two types of particles, it is shown that both the average inter- and intramolecular distributions can be extracted separately from the results of such an approach.

1.5 Outline of this thesis

In chapter 2 the Ornstein-Zernike (OZ) integral equation theory [25] for simple fluids is outlined. The general relations between the structural and thermodynamic properties of a simple fluid are discussed and the OZ-formalism is applied to the 3-dimensional (3D) nearest neighbor lattice fluid (the nearest neighbor lattice gas or Ising model). The 3D nearest neighbor fluid is not a good model for a polymeric fluid, but it is nevertheless studied here to get an indication how well the effects of isotropic attractive interactions on the structural correlations are captured by the OZ-formalism. These non-covalent attractive interactions are one of the three factors that determine the structure of polymeric systems, and the nearest neighbor lattice fluid allows to study them without the interference of packing or chain-connectivity effects, which are the other two factors of importance in polymeric systems. Results for structural and thermal properties of the model are compared to $NpT$-Monte Carlo (MC) simulations and to results for the same model obtained within the Quasi-Chemical approximation [8].

In chapters 3-5, we study polymer models by introducing chain-connectivity on the lattice via the polymer-RISM model. In chapter 3 the structure and the equation of state of athermal, i.e., purely repulsive, polymer molecules are studied. The results indicate how well the polymer-RISM equation is able to capture chain-connectivity effects, without interference of the effects caused by non-covalent attractive and repulsive interactions. In chapter 4 an extension to interacting molecules is made and the equation of state (EoS) and liquid-gas (LG) spinodal are studied. Thus, in this chapter we consider the combined effects of non-covalent and covalent attractions. In chapter 5 the approach is extended to calculate the adsorption of an interacting polymer fluid at an impenetrable wall. Results of chapters 3 to 5 are tested against $NpT$-MC simulations performed by P. Cifra of the Polymer Institute, Slovak Academy of Sciences - Bratislava. The results for the thermal properties of chapters 3 and 4 are also compared to a Non-Random Mixing theory based on the Quasi-Chemical approximation [38]. The adsorption profiles calculated in chapter 5 are compared to the Scheutjens-Fleer theory [39].

The line of work considered in chapters 6-8 is based on the associating fluid theory of Wertheim [14,36], and is meant to provide an alternative to the polymer-RISM theory considered in chapters 3-5. The basic formalism does not use an inter- and intramolecular distribution, and therefore, it is internally consistent. In chapter 6 we calculate the structural correlations in an associating fluid of particles
that can (covalently) bind into dimers, and in chapter 7, particles that form linear polymer molecules are considered. It is shown that both the average inter- and intramolecular structure can be extracted separately from this approach. In chapter 6 and 7 we also present results for the structural correlations obtained from MC-simulations. The simulations also monitor the average chain lengths obtained in the polymerizing fluid. In chapter 8 we have studied the Wertheim-fluids near an impenetrable wall and compared the obtained adsorption/depletion profiles with MC simulations. The simulations of chapters 7 and 8 are based on the Configurational bias scheme [40], but have the additional feature that they sample chain length. The simulations are performed with the help of B. Smit, Shell Research and Technology Centre - Amsterdam.
References


Chapter 2

Ornstein-Zernike approach for simple lattice fluids

2.1 Introduction

Since the late fifties a lot of work has been devoted to the study of the structural properties of simple fluids [1-6]. A simple fluid consists of particles (molecules), that interact via spherically symmetric interaction potentials that can be purely repulsive (hard sphere fluid) [5-7] or also exhibit an attractive part [8-10]. The molecular ordering of simple fluids is in general homogeneous and isotropic and can be characterized as liquid-like, i.e., the molecules are densely packed (when compared to a gas) and their packing shows an apparent lack of organization (when compared to a crystalline material).

Several routes to link the molecular organization of a fluid to the macroscopic properties of the fluid, e.g., the equation of state, and the liquid-gas- and liquid-liquid miscibility behavior, have been established [2,11]. The accurate determination of the molecular organization is therefore important in explaining the macroscopic properties of fluids.

The structural correlations present in simple fluids have been studied in several ways. Experiments on model systems [12,13], and computer simulations [14] have been performed, and from a theoretical point of view, two major routes have been developed: the formal, mathematically based Bogolubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy [2] and the more physical Ornstein-Zernike (OZ) approach [3]. In this and later chapters we want to study the latter.

The Ornstein-Zernike equation for a hard sphere system, has been solved analytically within the approximate Percus-Yevick closure [4], independently by Wertheim [5] and Thiele [6] in 1963. Despite the simplicity of the model, the solution is difficult, and although it compares favorably to simulation results [2], it is not exact due to the approximate nature of the Percus-Yevick closure. Models for much more complex systems have been solved since the solution of the
hard sphere model [10,15,16], but nevertheless, the calculation of the structural correlations of liquid-like model fluids remains a very difficult task. Solutions for the structural correlations in chemically interesting fluids, e.g., polymer melts, strongly associating fluids, and polymer fluids near a surface are even more rare [17-20] and hard to obtain. The complexity of the equations that govern the structural correlations have been an important reason for us to resort to a further approximation: the discretization of the space available to the fluid. It will be shown that this results in a significant reduction of the mathematical complexity. The discretization of space therefore proves to be a fruitful basis for systematically adding further complexities, e.g., chain connectivity, directional attractions, and external fields, to the model.

Discretization of space is common practice in the statistical mechanics of metallic alloys, ferromagnetic systems, and also polymer systems [21-23], which is the second reason why we adopt the lattice approximation: ultimately we are interested in using the OZ-formalism for polymeric fluids, and the use of a lattice will then allow to compare the results of the OZ-formalism directly to the vast body of existing work on lattices. In this chapter we only study the 3-dimensional (3D) nearest neighbor lattice fluid. It is also called the lattice gas or Ising model. Its 2D version is one of the very few statistical models with a dimensionality higher than one for which the free energy has been calculated exactly [24]. The free energy of the 3D model is not known exactly, but the model is commonly used [21,24], and accurate high and low temperature expansions of the free energy of the model are available [25]. The critical properties of the model are also known to a high degree of accuracy [26].

Apart from the above mentioned mathematical simplicity and possibility to compare the OZ-formalism to other theoretical approaches, there is a third reason for adopting a lattice: if the fluid particles occupy exactly one lattice site (as is the case in the nearest neighbor model), all liquid-like ordering effects that dominate the structure of continuum space liquids will vanish. The adoption of a lattice therefore offers a possibility to investigate how well the OZ-formalism is able to account for the effect of attractive interactions on the structural correlations, without an interference of packing effects which are predominant in continuum fluids. Previous work on lattices that uses the OZ-formalism, has been reported in Refs. [27-30].

The objective of the work presented in this chapter is to explore how well the OZ-equation and accompanying closures are able to describe the structural and thermodynamic properties of 3D nearest neighbor lattice fluids. By comparing the results to $NpT$-Monte Carlo simulations, to semi-exact results obtained for the 3D Ising model [26], and to results obtained within the Quasi-Chemical approximation [21], it is possible to accurately test the OZ-theory within MSA- and PY-closures. We have also investigated several routes to the equation of state and the liquid-gas spinodal to get a clear estimate of the thermodynamic consis-
tency problem. The rest of this chapter is outlined as follows. In section 2.2 we will present the statistical mechanical concepts (i.e., spatial correlations, distribution functions, equation of state and liquid-gas spinodal) that are important in understanding the structural and thermodynamic properties of simple fluids. In section 2.3 we will outline some general aspects of the OZ-theory (the formal relations and the closure equations). In section 2.4 we briefly consider the implications of a discretization of space for the general definitions outlined in section 2.2, after which we apply the OZ-formalism to lattice systems in section 2.5. In section 2.6 the $NpT$-simulation method that is used to obtain the structural and EoS properties of the nearest neighbor lattice fluid is discussed shortly. In section 2.7 results for the 2-particle distributions of the lattice model, the equation of state (EoS), and the liquid-gas (LG) spinodal, are presented. The structural correlations and the EoS behavior are compared to simulation results. The EoS results are also compared to results obtained within the Quasi-Chemical approximation [21]. The results for the LG-spinodal are compared to the spinodal obtained within the Quasi-Chemical approximation and to semi-exact results for the binodal of the 3D Ising model [26].

2.2 Statistical mechanical definitions and thermodynamic relations

In this section we outline a general theoretical framework which serves as a basis for the work described later on in this thesis. It is based on Ref. [31]. The section is split in three parts. In the first subsection, some general principles and definitions will be outlined. In the second part the commonly used routes to the equation of state are present, and in the third subsection we briefly discuss liquid-gas phase separation behavior.

2.2.1 General principles

We start within the canonical ensemble: a closed system of $N$ identical particles contained in a volume $V$ at temperature $T$ [11,32]. The variables $N$, $V$, and $T$ fully determine the thermodynamic behavior of the system for a known particle geometry and interparticle potential [33]. The total energy, the Hamiltonian of such a system, is

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_N(r^N) + U_{N,\text{ext}}(r^N)$$

(2.1)

where $p^N = (p_1, \ldots, p_N)$ are the momenta of the $N$ particles and $r^N = (r_1, \ldots, r_N)$ are the positions of the centers of mass of the particles. The first term, in which $p_i^2 = p_i \cdot p_i$, is the kinetic energy contribution to the total energy, $U_N$ is the total
interaction energy (potential energy), and $U_{N,\text{ext}}$ is the contribution of an external field (e.g., a solid adsorbing wall or a gravitational field). For our purposes, the total interaction energy can be divided in pair interactions between particles (see appendix IV of [32])

$$U_N(r_N) = \sum_{i<j}^{N,N} u(r_i, r_j)$$  \hspace{1cm} (2.2)

The influence of the external field is felt by each particle separately

$$U_{N,\text{ext}}(r_N) = \sum_{i=1}^N u_{\text{ext}}(r_i)$$  \hspace{1cm} (2.3)

One of the basic laws of statistical mechanics states that the probability $dW(r_N, p_N)$ to find the $N$ particles at positions $(r_1, r_1 + dr_1), \ldots, (r_N, r_N + dr_N)$ with momenta $(p_1, p_1 + dp_1), \ldots, (p_N, p_N + dp_N)$ is [34]

$$dW(r_N, p_N) = \frac{1}{Z_N} e^{-\beta H_N(r_N, p_N)} d\Gamma_N$$  \hspace{1cm} (2.4)

where $e^{-\beta H_N}$ is the Boltzmann factor and $\beta = 1/k_BT$, in which $k_B$ is the Boltzmann constant. The volume element $d\Gamma_N$ is given by

$$d\Gamma_N = \frac{dr_N dp_N}{(2\pi \hbar)^3N}$$  \hspace{1cm} (2.5)

The factor $(2\pi \hbar)^{3N}$ appears from Heisenberg’s uncertainty principle [34]. The normalizing factor $Z_N$ in Eq. 2.4 is called the canonical partition function and is given by

$$Z_N = \frac{1}{N!} \int \ldots \int e^{-\beta H_N(r_N, p_N)} d\Gamma_N$$  \hspace{1cm} (2.6)

in which the $1/N!$ accounts for the indistinguishability of the $N$ particles. The integration over the momenta in Eq. 2.6 is a multiple Gaussian integral and can be carried out separately from the integration over the positions if it is assumed that $V$ is large enough to extend the integration bounds to $\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} dp_N$. We then obtain

$$Z_N = \frac{1}{N! \Lambda^{3N}} Q_N$$  \hspace{1cm} (2.7)

where $\Lambda = \left( \frac{2\pi \hbar^2}{mk_BT} \right)^{1/2}$ is the DeBroglie thermal wavelength and

$$Q_N = \int \ldots \int e^{-\beta(\sum_{i}U_N(r_N) + U_{N,\text{ext}}(r_N))} dr_N$$  \hspace{1cm} (2.8)
This quantity $Q_N$ is called the configurational integral because it has only configurational and no kinetic contributions. The free energy $A$ of the system is related to the partition function $Z_N$ as \[ A = -k_B T \ln Z_N \] which gives upon combination with Eq. 2.7 \[ A = k_B T \ln (N!\Lambda^{3N}) - k_B T \ln Q_N \] The first term in this equation is the kinetic contribution to the free energy and the second term denotes the configurational part. The kinetic contribution to the free energy will be the same whatever interparticle interaction is considered, and therefore, it is the configurational part of $A$ which will be the subject of further discussion. For that purpose, we integrate $dW(r^N_p^N)$ of Eq. 2.4 over the momenta to obtain a configurational probability \[ dW(r^N) = D_N(r^N)dr^N \] in which the Gibbs distribution function, $D_N$, which is the normalized configurational space probability density, is recognized \[ D_N(r^N) = \frac{1}{Q_N} \exp[-\beta(U_N(r^N) + U_{N,ext}(r^N))] \] The average value of the configurational part of a quantity $X(r^N)$ can then be expressed within the canonical ensemble as \[ < X(r^N) > = \int \ldots \int X(r^N)D_N(r^N)dr^N \] In the thermodynamic limit ($N \to \infty, V \to \infty, N/V = \rho = \text{const}$), the average value $< X >$ becomes the macroscopically observable or thermodynamic value $X$ [34]. Another option, which can be chosen once the free energy $A$ is known for a sufficiently large system, is to obtain the various thermodynamic variables via well established thermodynamic relations [33], e.g., the pressure is obtained from \[ p = -(\partial A/\partial V)_{T,N} \] the internal energy from \[ U = -T^2 (\partial A/T)_{V,N} \] and the entropy from \[ S = -(\partial A/\partial T)_{V,N} \] It is not hard to see that Eq. 2.15 is equivalent to Eq. 2.13 for $A = A_{conf} = -k_B T \ln Q_N$ and $X = U$. Hence, the statistical mechanical route, Eq. 2.13, and the thermodynamic route, Eq. 2.15, are identical.
Instead of working with a canonical ensemble, we can also start from the grand canonical ensemble which governs an open system in which the number of particles is not fixed. The grand canonical ensemble is characterized by fixed values of the chemical potential $\mu$ and again, $V$ and $T$. The probability that the system contains exactly $N$ particles is given in the grand canonical ensemble by

$$P_N = \frac{\lambda^N}{\Xi} Z_N$$  \hspace{1cm} (2.17)

with $\lambda = \exp[\beta \mu]$. The normalization factor $\Xi$ in Eq. 2.17, is the grand partition function. It is given by

$$\Xi = \sum_{N \geq 0} \lambda^N Z_N$$ \hspace{1cm} (2.18)

$\Xi$ is the grand canonical analog of $Z_N$ that was defined in Eq. 2.6. Note that there is no direct analog of $Q_N$. This is due to the summation in Eq. 2.18: the grand partition function $\Xi$, unlike $Z_N$, cannot be written as a product of a function of purely configurational contributions ($Q_N$) and purely kinetic contributions.

From the grand canonical partition function we can make contact with thermodynamics via the grand potential $\Omega(\mu, V, T) = -pV$ [32]

$$\Omega = -k_B T \ln \Xi$$  \hspace{1cm} (2.19)

In the grand canonical ensemble the average value of a variable follows from

$$\langle X \rangle = \sum_N \frac{\lambda^N}{N!} \int \ldots \int X(r^N, p^N) \frac{e^{-\beta U_N}}{\Xi} d\Gamma_N$$  \hspace{1cm} (2.20)

In the thermodynamic limit, the averages of the observables $X$ are independent of the type of ensemble.

From Eq. 2.20 it is seen that

$$\langle N \rangle = \sum_N N \frac{\lambda^N Z_N}{\Xi} = \left( \frac{\partial \ln \Xi}{\partial \ln \lambda} \right)_{V,T}$$ \hspace{1cm} (2.21)

and

$$k_B T \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = \langle N^2 \rangle - \langle N \rangle^2$$  \hspace{1cm} (2.22)

The right hand side of Eq. 2.22 represents the mean square fluctuation of the number of particles in the system. Eq. 2.22 is of fundamental importance due to its direct relation to the system's compressibility. It will be used further on in this section.

Let us now turn to the spatial density fluctuations present in a simple fluid at average density $\rho$. First we define the $s$-particle distribution $\rho^{(s)}(r_1, \ldots, r_s)$ as [34]

$$\rho^{(s)}(r_1, \ldots, r_s) = \frac{N!}{(N-s)!} Q_N \int \ldots \int e^{-\beta U_N(r^N)} dr_{s+1} \ldots dr_N$$  \hspace{1cm} (2.23)
Physically, \( \rho^{(s)}(r_1, \ldots, r_s) dr_1 \ldots dr_s \) denotes the probability of finding a particle at \((r_1, r_1 + dr_1)\), a particle at \((r_2, r_2 + dr_2)\), \ldots , a particle at \((r_s, r_s + dr_s)\), irrespective of the identity of these particles. The 2-particle correlation \( \chi(r_1, r_2) \) between particles at positions \( r_1 \) and \( r_2 \), which is a measure of the density fluctuations in the fluid, is then given by

\[
\chi(r_1, r_2) = \rho^{(2)}(r_1, r_2) - \rho^{(1)}(r_1)\rho^{(1)}(r_2) + \rho^{(1)}(r_1)\delta(r_2 - r_1) \tag{2.24}
\]

in which \( \rho^{(1)}(r_1) \) and \( \rho^{(2)}(r_1, r_2) \) are defined by Eq. 2.23 for respectively \( s = 1 \) and \( s = 2 \). The last term in Eq. 2.24 accounts for the fact that there can only be one particle in \( dr_1 \) if \( r_1 \) and \( r_2 \) coincide. If we define the general \( s \)-particle distribution \( g_s(r_1, \ldots, r_s) \) as

\[
g_s(r_1, \ldots, r_s) = \frac{\rho^{(s)}(r_1, \ldots, r_s)}{\rho^s} \tag{2.25}
\]

we can write Eq. 2.24 as

\[
\chi(r_1, r_2) = \rho^2 h(r_1, r_2) + \rho \delta(r_2 - r_1) \tag{2.26}
\]

where \( h(r_1, r_2) = g_2(r_1, r_2) - 1 \) and \( \rho^{(1)}(r_1) = \rho \). From Eqs. 2.23 and 2.25 it is seen that \( \rho^2 g_2(r_1, r_2) dr_1 dr_2 \) is the probability of finding a molecule at \((r_1, r_1 + dr_1)\) and a molecule at \((r_2, r_2 + dr_2)\). Thus, \( \rho^2/N g_2(r_1, r_2) dr_1 dr_2/(dr_1/\int dr_1) \), which can also be written as \( \rho g_2(r_1, r_2) dr_2 \), is the expected number of molecules in volume element \((r_2, r_2 + dr_2)\) provided a given molecule has been placed at \( r_1 \). From now on we will omit the subscript 2 if \( g_2 \) is considered.

For an isotropic and homogeneous fluid we have

\[
h(r_1, r_2) = h(r_2 - r_1) = h(|r_2 - r_1|) = h(r) \tag{2.27}
\]

The first equality in Eq. 2.27 ensues from the fluid being homogeneous (translational invariance of the structural correlations) and the second equality is valid if, in addition, the fluid is isotropic (angle independence of structural correlations). For a homogeneous and isotropic fluid, \( g(r) = h(r) + 1 \) is called the radial distribution function, and \( r \) denotes the particle-particle separation.

The Fourier transform of \( \rho g(r) \) is the static structure factor \( S(k) \) and is given by

\[
S(k) = 1 + \int dr e^{ikr} \rho(g(r) - 1) \tag{2.28}
\]

The structure factor is a measurable quantity, e.g., by Röntgen- or neutron scattering [35]. As seen from Eq. 2.26, \( S(k) \) clearly measures the fluctuations in the density of the fluid.

It is due to the direct links of \( g(r_1, r_2) \) to the density fluctuations (Eq. 2.26) and the experimentally obtainable structure factor \( S(k) \), but also to the thermodynamic quantities \( p, U \) and \( A \) (see section 2.2.2), that the 2-particle distribution
function plays such a prominent role in statistical mechanics. It demonstrates the essential structural differences between gases, liquids and solids, as shown in Fig. 2.1.

An ideal gas is structureless, its interparticle potential is zero everywhere which

![Figure 2.1: Typical behavior of the 2-particle distribution function in a gaseous-, liquid-, and solid phase.](image)

implies, via Eq. 2.25 with $D_N(r^N) = 1/V^N$, that $g(r) = 1$. For a dilute gas, $g(r)$ has a peak at $r_0$ corresponding to the minimum of the pair potential. Beyond $r_0$, chances to find another molecule are no better than that given by the bulk density $\rho$. Thus, in a real gas there are no structural correlations present apart from those formed by a shell of nearest neighbors. A crystalline solid is characterized by a very regular ordering (apart from lattice defects) of the molecules. Therefore, $g(r)$ is long ranged in a solid and has sharp peaks positioned at regular distances from each other. In the liquid state there is some short range ordering (first-, second- and third neighbor shells) but for larger particle separations, the correlations quickly decay, i.e., $g(r) \rightarrow 1$.

We have already given a general formula, Eq. 2.13, to calculate the average value of a quantity $X(r^N)$ in the canonical ensemble, but let us now consider how to calculate averages of quantities which only involve a subset of the $N$ particles. Here we only consider the pair potential $u(r_1, r_2)$, and the external field contribution to particle 1, $u_{ext}(r_1)$. From Eq. 2.13 we have

$$< u(r_1, r_2) > = \int \ldots \int u(r_1, r_2)D_N(r^N)d^N$$

20
\begin{align*}
\langle u_{\text{ext}}(r_1) \rangle &= \int \ldots \int u_{\text{ext}}(r_1)D_N(r^N)dr^N
\end{align*}

With Eqs. 2.23 and 2.25, for \( s = 2 \) and \( s = 1 \), this can be rewritten as

\begin{align*}
\langle u(r_1, r_2) \rangle &= \frac{1}{V^2} \int \int u(r_1, r_2)g_2(r_1, r_2)dr_1dr_2 \\
\langle u_{\text{ext}}(r_1) \rangle &= \frac{1}{V} \int u_{\text{ext}}(r_1)g_1(r_1)dr_1
\end{align*}

where \( g_1(r_1) = 1 \) for a homogeneous liquid. For \( \langle U_N(r^N) \rangle \) and \( \langle U_{N,\text{ext}}(r^N) \rangle \) we have (Eq. 2.2 and Eq. 2.3)

\begin{align*}
\langle U_N(r^N) \rangle &= \sum_{i<j} < u(r_i, r_j) > = \frac{N!}{(N-2)!2!} < u(r_1, r_2) > \\
\text{and} \quad \langle U_{N,\text{ext}}(r^N) \rangle &= \sum_i < u_{\text{ext}}(r_i) > = \frac{N!}{(N-1)!} < u_{\text{ext}}(r_1) >
\end{align*}

thus

\begin{equation}
\langle U_N(r^N) \rangle = \frac{\rho^2}{2} \int \int u(r_1, r_2)g(r_1, r_2)dr_1dr_2 \quad (2.29)
\end{equation}

and

\begin{equation}
\langle U_{N,\text{ext}}(r^N) \rangle = \rho \int u_{\text{ext}}(r_1)dr_1 \quad (2.30)
\end{equation}

Eqs. 2.29 and 2.30 will be used in the next subsection.

### 2.2.2 Routes to the equation of state

Assume that we are able to calculate the 2-particle distribution function \( g(r_1, r_2) \) that characterizes the fluid. We then want to obtain the thermodynamic properties of this fluid. There are several possible routes [11]. Here we will briefly describe the energy-, pressure- (also named virial-) and compressibility-route.

**Energy equation**

The energy route establishes the relationship between the total energy \( E = \langle \mathcal{E} \rangle \) of the system and its temperature \( T \) and particle density \( \rho \). Averaging the Hamiltonian (Eq. 2.1) within the canonical ensemble gives

\begin{equation}
E = \frac{3}{2}Nk_BT + \langle U_N(r^N) \rangle + \langle U_{N,\text{ext}}(r^N) \rangle \quad (2.31)
\end{equation}

The first term on the right hand side represents the kinetic energy. It follows directly from the standard Gaussian integral

\begin{equation}
\langle \mathcal{H}_{N,\text{kin}} \rangle = \Lambda^{-3N} \int \ldots \int \mathcal{H}_{N,\text{kin}}e^{-\beta\mathcal{H}_{N,\text{kin}}} \frac{dp^N}{(2\pi\hbar)^{3N}} \quad (2.32)
\end{equation}
with $H_{N,\text{kin}} = \sum_{i=1}^{N} \frac{p_i^2}{2m}$.
The other terms are the contributions of the internal energy and the external field to the system’s energy. They are respectively given by Eqs. 2.29 and 2.30. For a homogeneous and isotropic fluid (Eq. 2.27) in the absence of an external field, we then have

$$E = N \left( \frac{3}{2} k_B T + 2\pi \rho \int_0^\infty u(r) g(r) r^2 dr \right)$$

(2.33)

Note that the fluid structure is also implicitly dependent on the density and temperature of the system: $g(r) = g(r; \rho, T)$. If $g(r)$ is known, the energy follows via Eq. 2.33. Eq. 2.33 will be employed later on in this chapter.

### Pressure equation

Although we have not employed the pressure route to obtain an EoS in this work, we will mention it for completeness. The derivation can be found in Ref. [11]. It starts from Eq. 2.14, that can be rewritten as

$$p = k_B T \left( \frac{\partial \ln Q_N}{\partial V} \right)_{N,T}$$

(2.34)

with help of Eq. 2.10. The final result is the pressure or virial equation. It relates the pressure to the temperature and density of the fluid. For an isotropic fluid it is given by

$$p = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr$$

(2.35)

The first term on the right hand side is again the ideal gas contribution, and the second term accounts for the intermolecular forces in the fluid.

### Compressibility equation

The isothermal compressibility of a fluid is defined as

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,N} = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_{T,V}$$

(2.36)

The second equality in Eq. 2.36 follows from thermodynamics: at isothermal conditions we have

$$dp = \left( \frac{\partial p}{\partial N} \right)_{V,T} dN + \left( \frac{\partial p}{\partial V} \right)_{N,T} dV$$

(2.37)

and thus, for an isothermal and isobaric volume change we can write

$$\left( \frac{\partial V}{\partial N} \right)_{p,T} = -\left( \frac{\partial N}{\partial \rho} \right)_{V,T} \left( \frac{\partial \rho}{\partial V} \right)_{N,T}$$

(2.38)
The second equality in Eq. 2.36 is thus immediately verified if it is realized that
\( V = N \cdot (\frac{\partial V}{\partial N})_{p,T} \) for a 1-component system (\( V \) is a homogeneous function of first
order, see Ref. [33]).

In the grand ensemble is \( pV = k_BT \ln \Xi \) (Eq. 2.19). Thus

\[
k_B T \left( \frac{\partial \rho}{\partial p} \right)_{T,V} = k_B T \left( \frac{\partial < N >}{\partial p} \right)_{T,V} = \left( \frac{\partial < N >}{\partial \ln \Xi} \right)_{T,V}
\]

This can be rewritten as \( \left( \frac{\partial < N >}{\partial \mu} \right)_{T,V} / \left( \frac{\ln \Xi}{\partial \mu} \right)_{T,V} \). With help of Eqs. 2.21 and 2.22
we can then write for the isothermal compressibility

\[
\kappa_T = \frac{V}{< N >^2} - \frac{< N >^2}{k_B T}
\]

We also have from Eqs. 2.24 and 2.26

\[
\int \int \chi(r_1, r_2) dr_1 dr_2 = < N^2 > - < N >^2 = \rho^2 \int \int h(r_1, r_2) dr_1 dr_2 + < N >
\]

Combining Eqs. 2.39 and 2.40, and using the fact that we are considering homo­
geneous and isotropic fluids (Eq. 2.27), results in

\[
k_B T \rho \kappa_T = 1 + \rho \int h(r) dr
\]

where the first term on the right again denotes the ideal gas contribution.

From this equation we can find the pressure of a simple fluid by integrating
Eq. 2.36 over the density

\[
\frac{p}{k_B T} = \int_0^\rho \frac{1}{1 + \rho' \int h(r) dr} d\rho'
\]

We will employ Eq. 2.42 frequently in this and later chapters.

### 2.2.3 Liquid-gas equilibrium

Fig. 2.2 schematically shows the thermodynamic regions in the \( pV \)-plane that are
of importance for a 1-component fluid subject to LG-phase separation. They are
the stable, metastable, and unstable regions. The three regions are separated by
two curves (the full lines in Fig. 2.2). The outer curve is the binodal, i.e., the
line that connects all states for which the liquid and the gas are in mechanical
\( (p_L = p_G) \), thermal \( (T_L = T_G) \), and chemical \( (\mu_L = \mu_G) \) equilibrium. The inner
curve is the spinodal. It is defined by

\[
\left( \frac{\partial \rho}{\partial V} \right)_{N,T} = 0
\]
which implies that $\kappa_T \to \infty$ at the spinodal (see Eq. 2.36). From Eq. 2.41, we then see that at the spinodal $\int h(r)dr \to \infty$. Because $h(r)$ is essentially a bounded function (its integral over a finite region is bounded in virtue of the existence of a maximum density arising from the incompressibility of particles), it becomes infinitely long ranged at the spinodal. From Eq. 2.28 for $k = |k| = 0$ and Eq. 2.41 we also see

$$\kappa_T = \frac{S(0)}{\rho k_B T} \quad \text{(2.44)}$$

Thus, at the spinodal we have $S(0) \to \infty$, which is experimentally obtainable by extrapolation.

Let us now briefly discuss the three thermodynamic regions. A fluid at conditions located in the stable region will always remain to be a 1-component system, and an unstable fluid will always phase separate into a liquid and a gaseous phase. Two separate phases located on the binodal will originate from such an unstable state. A metastable fluid on the other hand, is stable with respect to small local density fluctuations, but larger fluctuations, e.g., the formation of a droplet, will cause it to phase separate [33]. Such a larger fluctuation will in principle always occur, and as a result, we will again end up with two separate phases located on the binodal. Although both metastable and unstable fluids will ultimately phase separate, the spinodal is useful as a boundary between the metastable and unstable region, because the phase separation mechanism observable with
scattering techniques (if the metastable states exist long enough to observe the demixing phenomenon) is different in the two regions [36].

A few more things can be seen from Fig. 2.2. The dashed line in Fig. 2.2 is an isotherm. It connects states with the same temperature. The left branch of the isotherm represents liquid states (strong dependence of $p$ on $V$) and the right hand branch gaseous states. From a thermodynamic point of view, the isotherm does not exist in the region enclosed by the binodal (this is denoted by the horizontal dashed line which connects the liquid and vapor phase that result if the isotherm enters the metastable/unstable region). Nevertheless, in Fig. 2.2, the isotherm is shown as a continuous line, because the displayed Van der Waals-loops [33] appear in supersaturated vapors and superheated liquids.

The top of the binodal and spinodal, $(\partial^2 p/\partial V^2)_{N,T} = 0$, is the so-called critical point $C$ (see Fig. 2.2). It is characterized by a critical pressure $p_c$, temperature $T_c$, and volume $V_c$. The critical isotherm for $T = T_c$ passes through $C$, and separates isotherms for $T < T_c$, which display the LG-equilibrium behavior shown by the isotherm in Fig. 2.2, and isotherms for $T > T_c$, which do not enter the metastable/unstable region and do not show signs of a LG-transition. Thus, the critical temperature is the highest temperature for which a LG-transition occurs. In section 2.5 we calculate the spinodal curve (not the binodal curve which is more difficult to access in an integral equation approach) to get an impression of the location of the critical point within the OZ-formalism.

2.3 The Ornstein-Zernike equation: general remarks

The Ornstein-Zernike (OZ) equation [3] offers an elegant means to calculate the structural correlations in a liquid. The OZ-equation divides the total correlation $h(r_1, r_2)$ between two particles 1 and 2 in two parts: a direct correlation $c(r_1, r_2)$, and an indirect correlation due to the presence of a third particle. The latter should be integrated over all positions of the third particle. The OZ-equation is then given by

$$h(r_1, r_2) = c(r_1, r_2) + \int c(r_1, r_3)\rho(r_3)h(r_3, r_2)dr_3$$

(2.45)

with

$$h(r_1, r_2) = g(r_1, r_2) - 1$$

(2.46)

If one recurrently substitutes the OZ equation in the right hand side of Eq. 2.45 one obtains

$$h(r_1, r_2) = c(r_1, r_2) + \int c(r_1, r_3)\rho(r_3)c(r_3, r_2)dr_3 + \int \int c(r_1, r_3)\rho(r_3)c(r_3, r_4)\rho(r_4)c(r_4, r_2)dr_3dr_4 + \ldots$$

(2.47)
Each term in this infinite series represents a part of the total correlation between particle 1 and 2. Higher order terms involve more and more particles. For a homogeneous and isotropic fluid of spherical particles one has $\rho(r_3) = \rho$. Eq. 2.45 can then be written as

$$h(r) = c(r) + \rho \int c(|r' - r|)h(r')dr'$$  \hspace{1cm} (2.48)

in which $r$ is the distance between particle 1 and particle 2. Eq. 2.48 can conveniently be rewritten in Fourier space. The 3-dimensional Fourier transform is defined by

$$\hat{f}(k) = \int f(r)e^{ik \cdot r}dr$$  \hspace{1cm} (2.49)

and the inverse transformation is

$$f(r) = \left(\frac{1}{2\pi}\right)^3 \int \hat{f}(k)e^{-ik \cdot r}dk$$  \hspace{1cm} (2.50)

Fourier transformation of Eq. 2.48 is then given by

$$\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k)\hat{h}(k)$$  \hspace{1cm} (2.51)

or

$$(1 + \rho \hat{h}(k))(1 - \rho \hat{c}(k)) = 1$$  \hspace{1cm} (2.52)

in which $k = |k|$. The isothermal compressibility $\kappa_T$, given by Eq. 2.41, with help of Eq. 2.52, can be written as

$$k_B T \rho \kappa_T = \frac{1}{1 - \rho \hat{c}(0)}$$  \hspace{1cm} (2.53)

It is seen from Eq. 2.41 and Eq. 2.53 that, at the critical point where $\kappa_T \to \infty$ [33], the direct correlation function is shorter ranged than the total correlation function. Generally, the range of the direct correlation function is of the order of the range of the attractive pair potential. This is obviously correct in the limit $\rho \to 0$: the direct correlation between two isolated particles can never reach further than the attractive interaction $u(r_1, r_2)$ between them.

Apart from the physical introduction followed in this section it is also possible to place the OZ-equation in a rigorous mathematical framework with help of graphical techniques [37-39]. Due to this possibility to derive the equation in a precise manner, it is called diagrammatically correct. With the diagrammatic analysis followed in deriving the equation it is mathematically proven that $c(r_1, r_2)$ is shorter ranged than $h(r_1, r_2)$ [40]. The analysis has another advantage: Eq. 2.45 alone is not sufficient to calculate the fluid structure. An extra relation between $h(r_1, r_2)$ and $c(r_1, r_2)$, a closure equation, has to complement Eq. 2.45
for that purpose. It is from the mathematical approach that these approximate closure relations are found. Percus and Yevick proposed the Percus-Yevick (PY) closure which reads [4,41]

\[ c(r_1, r_2) = g(r_1, r_2) \left( 1 - e^\beta u(r_1, r_2) \right) \tag{2.54} \]

Van Leeuwen, Groeneveld and De Boer [38] proposed the Hypernetted Chain closure (HNC)

\[ c(r_1, r_2) = h(r_1, r_2) - \ln g(r_1, r_2) - \beta u(r_1, r_2) \tag{2.55} \]

A third closure can be obtained from Eq. 2.54 if we approximate it by its large \( |r_2 - r_1| \) limit

\[ c(r_1, r_2) = -\beta u(r_1, r_2) \tag{2.56} \]

If Eq. 2.56 is used for all \( |r_2 - r_1| \) larger than the particle diameter \( \sigma \), we speak of the Mean Spherical Approximation (MSA) [42]. Eq. 2.56 needs to be combined with an equation for \( |r_2 - r_1| \leq \sigma \), the non-overlap condition

\[ g(r_1, r_2) = 0 \quad \text{for} \quad |r_2 - r_1| \leq \sigma \tag{2.57} \]

to obtain a closure equation for all \( |r_2 - r_1| \geq 0 \). Eq. 2.57 states that particles cannot overlap and is exact in the region for which \( u(r_1, r_2) \to \infty \). It is not hard to assess that the non-overlap condition is also implicitly contained in Eqs. 2.54 and 2.55.

Combining Eq. 2.45 with the PY- or HNC-closure for \( \rho \to 0 \) shows that \( g(r_1, r_2) = e^{-\beta u(r_1, r_2)} \), thus \( c(r_1, r_2) \to e^{-\beta u(r_1, r_2)} - 1 = f(r_1, r_2) \). It is seen that this is not the case for the MSA-closure. It is also seen that in both the PY- and MSA-closure, \( c(r_1, r_2) \) vanishes if \( u(r_1, r_2) = 0 \). This last property is not present in the HNC-closure, but generally, \( c(r_1, r_2) \) is very small beyond the range of the potential if the HNC-closure is used.

The problem of calculating a fluid structure now simply boils down to solving a set of three equations: The OZ equation (Eq. 2.45), a closure equation (Eq. 2.54, Eq. 2.55, or Eq. 2.56), and Eq. 2.46 for the three \( r_1 \) and \( r_2 \)-dependent unknowns \( h(r_1, r_2), g(r_1, r_2) \) and \( c(r_1, r_2) \). Note from the OZ equation that these variables are also implicitly dependent on the density. The solution of this set has proven to be very hard and is generally only possible for homogeneous and isotropic fluids for which \( |r_2 - r_1| = \sigma \). It was only in 1963 that Wertheim [5] and Thiele [6] independently obtained the analytic solution for the fluid structure of a homogeneous and isotropic fluid of hard, non-attracting spheres within the PY-closure.

Due to the approximations present in the closures, we can only obtain an approximate radial distribution function \( g(r) \). Each closure for the same model fluid will result in a somewhat different \( g(r) \). The approximate nature of \( g(r) \)
has its consequences for the thermodynamics (see section 2.2) calculated from it: the EoS calculated from the pressure route will in general be different for the compressibility-EoS or the energy-EoS (here we assume that we are able to calculate the pressures from the energies that are obtained within the energy route). This is called the thermodynamic consistency problem. There have been several attempts to improve the consistency [43-45], but it remains a central problem associated with integral equation theories.

2.4 Statistical mechanics of lattice fluids

In the previous sections we have considered continuum space fluids. Here we want to have a brief look at the consequences of a discretization of space for the approach outlined in section 2.2.

The approach followed in section 2.2 does not have to be altered if we make the convention that in case of a lattice fluid, \( \int \ldots \int dr \) refers to a summation over the lattice sites: each integration \( \int dr \) should be read as \( v_0 \sum_{r_1} \), with \( v_0 \) being the volume of a lattice site and \( \sum \) denoting the summation over the sites. The only problem that arises concerns the momenta in Eq. 2.6: it is hard to envisage the fluid particles moving through discretized space. There are two ways of dealing with the momenta. One is to simply leave out the momenta from the beginning, i.e., in Eq. 2.1, and to consider only configurational space contributions to \( Z_N \). The other one is to treat the integrations over the momenta in Eq. 2.6 in a continuum fashion, and to discretize configurational space in the resulting Eqs. 2.7 and 2.8. This last approach will be taken here [46]. Despite the inconsistency that occurs in adopting this approach, we do not foresee any problems, for the kinetic contribution to the free energy \( A \) is always the same. Therefore, it has no consequences for the thermodynamic functions that are derived from \( A \).

A second point that needs consideration concerns the spatial density fluctuations in discretized space. In continuum space, \( \rho g_2(r_1, r_2) dr_2 \) denotes the number of particles in volume element \( (r_2, r_2 + dr_2) \) on condition that there is a particle in \( (r_1, r_1 + dr_1) \). On a lattice we have to replace the element \( dr_2 \) by the volume \( v_0 \) of one lattice site. The \( \rho g_2(r_1, r_2) dr_2 \) is then given by \( \eta g_2(r_1, r_2) \) with \( \eta = \rho v_0 \) being the fraction of filled lattice sites. The spatial density fluctuations, given by Eq. 2.26 in continuum space, are for a lattice system thus given by

\[
\chi(r_1, r_2) = \eta^2 h(r_1, r_2) + \eta \delta_{12} \tag{2.58}
\]

where \( \delta_{12} \) is a Kronecker delta.

A last point that should be mentioned considers the pressure equation, Eq. 2.35. The derivative of the pair potential with respect to the distance, in Eq. 2.35, is
not well defined on the lattice. However, a lattice analog of the pressure equation is available [47], and will be briefly outlined below.

Consider a volume $V$ that occupies $L$ lattice sites in the directions $m$ and $n$ and $H$ sites in the remaining $l$-direction: $V = H L^2 v_0$. Imagine there to be an impenetrable wall on both sides of the box that are perpendicular to the $l$-axis. We can obtain a change of the volume accessible to the fluid between the walls by giving the wall at $l = 0$ an infinitely strong repulsion with the fluid particles in the layer closest to the wall. In continuum space such a volume change reads

$$p v_0 = \frac{k_B T}{L^2} \left( \frac{\partial \ln Q_N}{\partial H} \right)_{N,T}$$  \hspace{1cm} (2.59)

The analog of this equation for a lattice fluid in which each particle occupies exactly one lattice site is

$$p v_0 = \frac{k_B T}{L^2} \left( \ln Q_N(N, L, H, T) - \ln Q_N(N, L, H - 1, T) \right)$$  \hspace{1cm} (2.60)

The first term on the right corresponds to the case where the hard wall has no interaction with the fluid (i.e., no exclusion of volume near the wall) and the second term corresponds to an infinitely strong repulsion with the fluid near the wall (full exclusion of layer closest to the wall).

On the lattice $Q_N$ is given by (see Eq. 2.8)

$$Q_N(N, L, H, T) = v_0^N \sum_{r_1} \ldots \sum_{r_N} e^{-\beta (U_N(r^N) + U_{N,ext}(r^N))}$$  \hspace{1cm} (2.61)

with $r_i = (l_i, m_i, n_i)$ denoting the lattice position of particle $i$, and $U_{N,ext}(r^N) = U_{N,wall}(r^N)$. The Eq. 2.61 can be rewritten as

$$Q(N, L, H, T, \phi) = v_0^N \sum_{r_1} \ldots \sum_{r_N} e^{-\beta U_N(r^N) \phi^{N(1)}}$$  \hspace{1cm} (2.62)

with help of Eq. 2.3, where $\phi = e^{-\beta U_{wall}}$ is a function of the wall-particle interaction and $N(1)$ is the number of particles in layer 1 that is closest to the wall. Clearly, $Q(N, L, H, T, \phi = 1) = Q(N, L, H, T)$ and $Q(N, L, H, T, \phi = 0) = Q(N, L, H - 1, T)$ correspond to the situations of no repulsion ($\phi = 1$) and full repulsion ($\phi = 0$). Therefore, for the lattice pressure, we can write a charging formula in which the influence of the wall interpolates between on/off. It is given by

$$\frac{p v_0}{k_B T} = \frac{1}{L^2} \int_{\phi = 0}^{\phi = 1} \frac{\partial \ln Q_N}{\partial \phi} d\phi = \int_{\phi = 0}^{\phi = 1} \frac{\eta(1)}{\phi} d\phi$$  \hspace{1cm} (2.63)

where $\eta(1) = \langle N(1) \rangle / L^2$ is the site occupation fraction in the layer closest to the wall. The second equality in Eq. 2.63 follows directly from Eq. 2.62. Eq. 2.63 is the lattice analog of the virial equation (Eq. 2.35) and will be employed later on in this thesis. It is directly applicable in MC simulations [47,48] if periodic boundary conditions are applied in $m$- and $n$-direction, and also in our theoretical work (for which $L \to \infty$).
2.5 OZ-theory for lattice fluids

2.5.1 OZ-equation for structural correlations on lattices

A homogeneous simple lattice fluid can be studied within the Ornstein-Zernike approach by discretizing the OZ-equation, Eq. 2.45, as [27-29]

\[ h(r) = c(r) + \eta \sum_{r'} c(r' - r)h(r') \tag{2.64} \]

in which the packing fraction \( \eta = \rho v_0 \) is the fraction of filled lattice sites. The distance between the centers of particles 1 and 2 is for a 3D cubic lattice given by \( r = (l, m, n) \). We have from Eq. 2.46

\[ h(r) = g(r) - 1 \tag{2.65} \]

The lattice OZ-equation for homogeneous fluids, Eq. 2.64, can easily be written down for other dimensions, but here we will only consider the 3-dimensional case. Note that the cubic lattice fluid is not fully isotropic, \( g(r) \) is dependent on vector \( r \) which not only has a length, but also a direction. This is in contrast to its continuum analog for which \( g(r) \) only depends on \( r = |r| \).

Let us consider the lattice analog of the Fourier transform given in Eqs. 2.49 and 2.50. For a 3D fluid it is

\[ \hat{f}(k) = \sum_{r} f(r)e^{ikr} \]

and

\[ f(r) = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{f}(k)e^{-ikr}dk \]

where \( k = (u, v, w) \). For the case of symmetric functions \( f(r) = f(-r) \) we can thus write the Fourier series

\[ \hat{f}(u, v, w) = \sum_{l,m,n} f(l, m, n) \cos lu \cos mv \cos nw \tag{2.66} \]

and the inverse series

\[ f(l, m, n) = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} f(u, v, w) \cos lu \cos mv \cos nw \, du \, dv \, dw \tag{2.67} \]

Using Eq. 2.66 to Fourier transform Eq. 2.64 we have the lattice analog of Eq. 2.51

\[ \hat{h}(u, v, w) = \hat{c}(u, v, w) + \eta \hat{c}(u, v, w)\hat{h}(u, v, w) \tag{2.68} \]

where it should be noted that the sum in Eq. 2.64 has disappeared upon Fourier transformation. On the cubic lattice, the PY closure (Eq. 2.54) reads

\[ c(l, m, n) = g(l, m, n) \left( 1 - e^{\beta a(l,m,n)} \right) \tag{2.69} \]
The MSA-closure (Eq. 2.56) is

\[
g(0,0,0) = 0 \\
c(l, m, n) = -\beta u(l, m, n) \quad \text{for } (l, m, n) \neq (0,0,0) \tag{2.70}
\]

Both the PY and MSA closure share the property that the direct correlation function vanishes beyond the range of the pair potential \(u(l, m, n)\), which makes these closures especially suitable for studying lattice fluids. Therefore, we focus on these closures in this study.

In this work, we only consider fluids of non-overlapping particles that occupy exactly one lattice site and that are only allowed to have an attractive interaction with nearest neighbors on the lattice. Such a fluid is generally known as the nearest neighbor lattice fluid. Its particle-particle interaction potential is given by

\[
u(0,0,0) \sim 0 \\
u(l, m, n) = u_{\text{attr}} \quad \text{if } l^2 + m^2 + n^2 = 1 \\
u(l, m, n) = 0 \quad \text{otherwise} \tag{2.71}
\]

The restriction that the particles occupy exactly one lattice site is not of principal importance and can easily be relaxed by altering the interaction potential. If we for instance take \(u(l, m, n) \sim 0\) for \(l^2 + m^2 + n^2 \leq 3\), the space that each particle occupies on the lattice is extended. Such an extension introduces liquid-like packing effects on the lattice.

The solution of the OZ-equation for the nearest neighbor model presented here will be considered in the next section. The solution method is simple due to the discretization of space, and allows for the systematic introduction of higher order complexities, e.g., extension of particle size, extension of the range of the interaction potential, directional attractions, and also chain-connectivity. The cubic lattice model has the additional advantage that it is extensively studied, which allows for comparison to other theories [32,49].

### 2.5.2 Solution procedure

The 2-particle distribution \(g(l, m, n)\) of the fluid with model potential Eq. 2.71 can be obtained by solving the three equations, Eq. 2.64, Eq. 2.65, and one of the closure relations (Eqs. 2.69 or 2.70).

The OZ-equation is solved most conveniently in Fourier space. First consider the case \(u_{\text{attr}} = 0\) in Eq. 2.71, i.e., the non-interacting and non-overlapping lattice fluid. From Eq. 2.69 (or Eq. 2.70, the PY and MSA closures are equivalent for non-interacting systems) we see that the direct correlation function \(c(l, m, n)\) is
non-zero only for \((l, m, n) = (0, 0, 0)\). Thus, from Eq. 2.66 we have \(\hat{c}(u, v, w) = c_0\). Substitution of \(\hat{c}(u, v, w)\) in Eq. 2.68 gives

\[
\hat{h}(u, v, w) = \frac{c_0}{1 - \eta c_0}
\]

(2.72)

Inverse transformation of Eq. 2.72 via Eq. 2.67, and using Eq. 2.65 and the non-overlap condition \(g(0, 0, 0) = 0\) (that is implicit in Eq. 2.69) results in one equation in the unknown \(c_0\)

\[-1 = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{c_0}{1 - \eta c_0} du dv dw
\]

(2.73)

from which we directly find that \(c_0 = -1/(1 - \eta)\). The values of \(g(l, m, n)\) are then directly found for all \((l, m, n)\) from Eq. 2.67

\[
g(l, m, n) = 1 + \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\hat{c}(u, v, w)}{1 - \eta \hat{c}(u, v, w)} \cos lu \cos mv \cos nw du dv dw
\]

(2.74)

in which we still have \(\hat{c}(u, v, w) = c_0\). For the non-interacting hard cubic lattice fluid we thus find

\[
g(0, 0, 0) = 0
\]

\[
g(l, m, n) = 1 \quad \text{for} \quad (l, m, n) \neq (0, 0, 0)
\]

(2.75)

Eq. 2.75 illustrates the complete absence of structural correlations for the non-interacting lattice fluid in which the particles occupy exactly one lattice site. This is in great contrast to the continuous space hard sphere system in which liquid-like packing effects of entropic origin are predominant [5,6].

The general solution procedure for \(u_{\text{attr}} \neq 0\) within the PY-closure is as follows [28]. Eq. 2.68 is used to write \(\hat{h}(u, v, w)\) in terms of \(\hat{c}(u, v, w)\). Subsequently, \(\hat{c}(u, v, w)\) is written in terms of the unknowns \(c_0 = c(0, 0, 0)\) and \(c_1 = c(\pm 1, 0, 0) = c(0, \pm 1, 0) = c(0, 0, \pm 1)\) with help of Eq. 2.66. We only have to consider \(c_0\) and \(c_1\), because the closure relation Eq. 2.69 indicates that \(c(l, m, n)\) is zero beyond the range of the potential. The two unknowns can be found from two equations that are constructed by inverse Fourier transformation (see Eq. 2.67) of \(\hat{h}(u, v, w)\), after which it is combined with the PY-closure for \((l, m, n) = (0, 0, 0)\) and \((l, m, n) = (1, 0, 0)\). The two equations are solved numerically with a standard Newton-Raphson procedure combined with a 3D-quadrature routine. Once \(c_0\) and \(c_1\) are known, \(g(l, m, n)\) follows via Eq. 2.74.

The solution within the MSA-closure is even simpler. The only unknown is \(c_0 = c(0, 0, 0)\) as \(c_1\) follows directly via Eq. 2.70. The procedure thus only involves solving one equation in one unknown for this case. It is completely analogous to the solution of the non-interacting lattice fluid although \(c_0\) has to be obtained numerically if \(u_{\text{attr}} \neq 0\).
The procedure outlined above generally needs less than ten Newton-Raphson iterations, which takes less than a minute of real time on a Silicon Graphics Challenge with a MIPS R4400 processor. A quicker method was nevertheless desired in calculating some of the thermodynamic properties of the fluid, as will become clear in section 2.5.3. Fortunately, such a method exists. We can recast the equations for $c_0$ and $c_1$ in terms of the standard integral $I_{n=0}(b)$ [50]

\[ I_n(b) = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{(\cos u + \cos v + \cos w)^n}{b - (\cos u + \cos v + \cos w)} \, du \, dv \, dw \]  

(2.76)

with help of the recursive relation

\[ \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} (\cos u + \cos v + \cos w)^{n-1} \, du \, dv \, dw = bI_{n-1}(b) - I_n(b) \quad \text{for } n \geq 1 \]  

(2.77)

Tickson has rewritten $I_0(b)$ in the rapidly calculable form [51]

\[ I_0(b) = \frac{1}{\pi^2} \int_0^\pi \frac{2}{b - \cos u} K\left(\frac{2}{b - \cos u}\right) \, du \]  

(2.78)

in which $K$ is the complete elliptic integral of the first kind, defined by

\[ K(v) = \int_0^{\pi/2} \frac{d\Theta}{\sqrt{1 - v^2 \sin^2 \Theta}} \]  

(2.79)

Recasting the solution in terms of Eq. 2.76 reduces the number of integrations required within each Newton-Raphson iteration from three to one (plus a standard integral Eq. 2.79). This significantly speeds up the solution procedure.

2.5.3 Thermodynamic properties

Let us now turn to the thermodynamic properties of the lattice fluid. Once $g(l, m, n)$ and $c(l, m, n)$ are known, one way of obtaining an equation of state is via the compressibility route

\[ \frac{p\nu_0}{k_BT} = \int_0^\eta \frac{1}{1 + \eta' \sum_{l,m,n} h(l, m, n)} \, d\eta' \]  

(2.80)

which is the discretized version of Eq. 2.42. It can be written in terms of the (short ranged) direct correlation function as

\[ \frac{p\nu_0}{k_BT} = \int_0^\eta (1 - \eta' \sum_{l,m,n} c(l, m, n)) \, d\eta' \]  

(2.81)

with help of Eq. 2.68.

Two cases can immediately be verified from Eq. 2.80. First, for an ideal gas
there is a complete absence of correlations: \( g(l, m, n) = 1 \) for all \((l, m, n)\). Thus, Eq. 2.80 immediately yields the ideal gas equation of state \( p v_0 = \eta k_B T \). Secondly, in the case of a lattice system of non-overlapping and non-interacting particles we find upon substitution of Eq. 2.75 in Eq. 2.80 that

\[
\frac{p v_0}{k_B T} = -\ln(1 - \eta)
\]  

(2.82)

Eq. 2.82 is exact as can be verified from direct enumeration of the possible arrangements of the particles on the lattice. Interacting fluids can not be treated directly. However, for an interacting system we can analytically perform the \( \eta \)-integration in the compressibility equation, Eq. 2.81, if it is considered within the PY-closure. The result is [52]

\[
\frac{p v_0}{k_B T} = \eta + \frac{\eta^2}{2} \sum_{l, m, n} c(l, m, n) \left( \frac{c(l, m, n)}{\gamma(l, m, n)} - 2 \right) + \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \eta \hat{c}(u, v, w) + \ln \left( 1 - \eta \hat{c}(u, v, w) \right) dudvdw
\]

(2.83)

with

\[
\begin{align*}
\gamma(0, 0, 0) & \to \infty \\
\gamma(l, m, n) & = 1 - e^{2\piSLT} \quad \text{if } \sqrt{l^2 + m^2 + n^2} = 1 \\
\gamma(l, m, n) & = 0 \quad \text{otherwise}
\end{align*}
\]

(2.84)

Note that Eq. 2.83 is easier to handle than Eq. 2.81 because it does not involve a numerical integration over the packing fraction: it is dependent on a single thermodynamic state. From the PY-closure, \( c(l, m, n) = \gamma(l, m, n)g(l, m, n) \), it is seen that in case of the nearest neighbor model, the second term on the right hand side in Eq. 2.83 is zero for \( l^2 + m^2 + n^2 \geq 2 \).

An expression for the pressure based on the energy route within the MSA-closure is also known [53,54]. In this expression which is again dependent on a single thermodynamic state, the pressure of the non-overlapping non-attracting cubic lattice fluid Eq. 2.82 is involved as an exact reference.

\[
\frac{p v_0}{\eta k_B T} = \frac{p_0 v_0}{\eta k_B T} - \frac{\eta}{2} \left( \hat{c}(0, 0, 0) - \hat{c}_0(0, 0, 0) \right) - \frac{1}{2(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left( \frac{1}{\eta} \ln \left( 1 - \eta \hat{c}(u, v, w) \right) + \frac{\hat{c}(u, v, w)}{1 - \eta \hat{c}(u, v, w)} \right) dudvdw + \frac{1}{2(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left( \frac{1}{\eta} \ln \left( 1 - \eta \hat{c}_0(u, v, w) \right) + \frac{\hat{c}_0(u, v, w)}{1 - \eta \hat{c}_0(u, v, w)} \right) dudvdw
\]

(2.85)
where the subscript 0 denotes the hard reference system.

A third EoS was obtained by combining the compressibility equation, Eq. 2.80, with the MSA-closure. There is no single state expression for this route and therefore, we have performed the integration over the packing fraction in Eq. 2.81 numerically. This is very time consuming because \( c(l, m, n) \) has to be obtained separately for each state point. To facilitate the procedure we have rewritten the solution of the OZ-equation in terms of Eq. 2.76 as outlined in section 2.5.2.

The three routes to the EoS that we have investigated generally produce different answers due to the approximate nature of the closures. In this chapter we investigate how large the differences are. In a later chapter we have employed a fourth EoS based on the wall-route of Dickman [47].

Apart from the EoS behavior of the lattice fluid we also have obtained the Liquid-Gas spinodal curve within the OZ-formalism. In section 2.2.3 it was outlined that \( \kappa_T \) diverges at the spinodal. From the discretized version of Eq. 2.53 we thus obtain the spinodal condition

\[
1 - \eta \bar{c}(0, 0, 0) = 0 \tag{2.86}
\]

The results obtained with this compressibility spinodal will in generally be different for the PY- and MSA-closure. Results for the LG-spinodal obtained within both closures will be presented in section 2.7. We have also estimated the location of the energy-MSA (e-MSA) LG-spinodal by numerically differentiating Eq. 2.85 as in \( (\partial p/\partial \eta)_T = 0 \). In section 2.7 it is pointed out that the \( h(l, m, n) \) are not infinitely long ranged on the e-MSA spinodal which is in contradiction to Eq. 2.41. This inconsistency is again due to the approximate nature of the MSA-closure.

### 2.5.4 Analogies with other approaches

There is a direct analogy between the nearest neighbor lattice fluid and the 3D Ising model for ferromagnetic systems [24]. If the site occupancy \( s_i \) of the nearest neighbor model \( (s_i = 0 \) corresponds to an empty site \( i \) and \( s_i = 1 \) to an occupied site \( i ) \) is related to the spin parameter \( \sigma_i \) of the Ising model \( (\sigma_i = -1 \) corresponds to the spin down state, and \( \sigma_i = 1 \) to the spin up state of site \( i ) \) via

\[
\sigma_i = 2s_i - 1 \tag{2.87}
\]

then the magnetic coupling constant \( J \) is related to the pair interaction energy \( u_{\text{attr}} \) as

\[
J = -\frac{u_{\text{attr}}}{4} \tag{2.88}
\]

and the spontaneous magnetization \( M \) is related to the lattice packing fraction \( \eta \) as

\[
\eta = 2(1 \pm M) \tag{2.89}
\]
The lattice OZ-equation can thus be used to study the correlations in Ising sys­

tems [30]. In section 2.7 we have used the analogy between the two models to

compare the location of the top of the spinodals calculated from the OZ-formalism

to the location of the top of the binodal estimated on the basis of Monte Carlo

data for the Ising model [26].

An analogy with certain mean field theories can be established [29] by ap­

plying a perturbational approach to the direct correlation function [29]. For

that purpose, consider the direct correlation function \( c(l, m, n) \) to be a sum of a

non-attracting reference part and a part that accounts for the attractions

\[
\begin{align*}
  c(l, m, n) &= c_0(l, m, n) - \frac{u_{\text{attr}}(l, m, n)}{k_B T} \\
  \text{Eq. 2.90 is valid for small attractions [29]. Substitution of Eq. 2.90 in Eq. 2.81}
\end{align*}
\]

then leads to a mean field expression for the pressure

\[
\begin{align*}
  pv_0 &= p_0 v_0 + \frac{n^2}{2} \sum_{l,m,n} u_{\text{attr}}(l, m, n) \\
  \text{It is a sum of the reference pressure } p_0, \text{ and a perturbational part determined}
\end{align*}
\]

by the attractions. The form of Eq. 2.91 is identical to the form of the Van der

Waals equation \( p = p_0 - a \rho^2 \) if we identify the constant \( a \) with \( \frac{1}{2} u_{\text{attr}}(0, 0, 0) \) [29].

From Eq. 2.90 and the lattice OZ-equation Eq. 2.64, it is seen what a mean field

(MF) approach amounts to. A MF-assumption of the type Eq. 2.90 implies, via

Eq. 2.64, that the total correlation \( h(\mathbf{r}) \) is set in advance (here we assume that

\( c_0(l, m, n) \) of the reference system is known), without considering it explicitly.

Therefore, attention is generally only paid to the thermodynamic properties of

the system. This is illustrated by the following two examples: the Bragg-Williams

mean field approximation [21], when applied to lattice mixtures of A and B

particles (or a mixture of particles and empty sites), simply neglects all structural

correlations that appear from the differences in A-A, A-B and B-B interactions,

and the Quasi-Chemical MF approximation neglects all correlations for

\( |\mathbf{r}| \geq 2 \) for such a mixture of A and B particles. The Quasi-Chemical approximation does

take the nearest neighbor correlations (\( |\mathbf{r}| = 1 \)) into account [21,32], but it should

be realized that the correlation length reaches further than the nearest neighbor

position, even if the interaction potentials are of nearest neighbor type.

2.6 Monte Carlo simulation

The \( N_pT \)-simulation method that was used to obtain the 2-particle distribution

\( g(l, m, n) \) and the equation of state for the lattice fluid with nearest neighbor

pair interaction strengths of \( u_{\text{attr}} = 0.0 k_B T, -0.2 k_B T, -0.5 k_B T, \) and \(-0.85 k_B T \)
is described in detail elsewhere [55,56]. It consists of condensing a slab of the fluid against a wall in a rectangular section of the cubic lattice with 50 sites in the \( l \)-direction perpendicular to the wall and 22 sites in the other two directions. In the \( m \)- and \( n \)-direction we have applied periodic boundary conditions. The number of particles in the box is \( N = 2420 \). A finite pressure is exerted by fluctuating the total volume of the box. The volume fluctuations are created by building/destroying a solid piston site-by-site with respect to a solid wall located at \( l = 0 \).

Configurational space is sampled by randomly moving the particles over the lattice. Up to \( 1 \times 10^9 \) moves were applied from which the first \( 0.4 \times 10^9 \) were used only for equilibration of the state. Averaging of thermodynamic and structural properties took place every 5000 moves and a volume fluctuation move was applied every 200 particle moves. The simulation method produces a melt with jagged edges at the piston side of the slab [57] and also shows a depletion profile near the solid wall. The \( g(l, m, n) \) was therefore obtained (with standard methods, see e.g., Ref. [14]) from the middle section of the slab, where the influence of the wall and piston are absent. For the case of \( u_{\text{attr}} = -0.85k_B T \), which is close to the liquid-gas critical interaction strength \( u_{\text{attr,c}} = -0.886618k_B T \), the wall-fluid correlations become relatively long ranged which implies that more particles \( (N = 7260) \) are needed to obtain a bulk region large enough to accurately extract \( g(l, m, n) \).

The cut-off distance in the calculations of \( g(l, m, n) \) is 4 lattice spacings. The errors in the \( g(l, m, n) \) and the packing fraction \( \eta \) of the bulk region are smaller than the symbols used in the figures of section 2.7 and are therefore omitted.

The runs were performed on a RISC IBM 6000 machine. We have not monitored CPU times. The simulation results are available on request via e-mail tgpken@urc.tue.nl.

### 2.7 Results and discussion

In this section we present results for the 2-particle distribution function of the 3D nearest neighbor model obtained from the OZ-formalism within the PY- and MSA-closure. The results are compared to MC-simulations. We also consider the EoS obtained within the PY-closure and compressibility route (c-PY), the MSA-closure and the energy route (e-MSA), and MSA-closure and compressibility route (c-MSA). These three different EoS are compared to MC-simulation data and to the EoS obtained within the Quasi-Chemical approximation [32].

Also, the liquid-gas spinodal curves obtained from the c-PY, c-MSA, and e-MSA route are compared to the spinodal obtained within the Quasi-Chemical approximation, and to Monte Carlo data for the binodal of the 3D Ising model [26].

The comparison with the binodal of Ref. [26] indicates how well the different approximations predict the location of the critical point \((T_c, \eta_c)\), the shared top of
spinodal and binodal. Finally, it is shown that the behavior of the c-PY spinodal is unphysical. This seems to be typical for the c-PY spinodal and is not a lattice artifact, it has also been found for continuum models [9,58].

Figure 2.3: 2-Particle distribution as a function of interparticle distance at \( \eta = 0.1 \). Symbols are simulation results. The full lines are obtained within the PY-closure and the dashed lines within the MSA-closure. The simulations are performed for \( U_{\text{attr}} = -1.0 k_B T \) (■), \( U_{\text{attr}} = -0.5 k_B T \) (▲), and \( U_{\text{attr}} = -0.2 k_B T \) (●).

In Fig. 2.3, we show the 2-particle distribution function \( g(r) \) as a function of distance \( r = \sqrt{l^2 + m^2 + n^2} \). The simulation results are depicted by the symbols and the results from the OZ-approach are indicated by the lines. The full line denotes the results obtained within the PY-closure and the dashed lines indicate the results obtained within the MSA-closure. The figure clearly indicates that the deviation from \( g(r) = 1 \) becomes larger for a stronger nearest neighbor attraction. Thus, correlations become more pronounced in case of stronger interactions between the particles. It is also seen that both closures produce excellent results for \( U_{\text{attr}} = -0.2 k_B T \), and also for \( U_{\text{attr}} = -0.5 k_B T \), but that they underestimate the \( g(r) \) for \( U_{\text{attr}} = -1.0 k_B T \), although the PY-closure still behaves reasonably in this case.

In Fig. 2.4, where we have plotted \( g(r) \) versus the interparticle distance \( r \) for \( U_{\text{attr}} = -0.5 k_B T \) at two different lattice packing fractions, it is seen that the correlations also become more pronounced at lower packing fractions. Generally, the PY-closure behaves better than the MSA-closure for the model tested here,
but for situations in which the correlations become strong (strongly interacting systems, low packing fractions) both the PY- and MSA-closure underestimate the correlations.

In Figs. 2.5-2.8 we have plotted the reduced pressure versus packing fraction for four different interaction strengths $u_{\text{attr}} = -0.5k_B T$, $-0.2k_B T$, $-0.85k_B T$. In each figure we have depicted four different routes to the EoS (of the same 3D nearest neighbor model): the full line is the result from the c-PY route, the long dashed line denotes the c-MSA EoS, the short dash is obtained from the e-MSA route and the short-long dashed line is obtained within the Quasi-Chemical approximation. The symbols are the simulation results. The Quasi-Chemical approximation is also termed the Bethe-Peierls approximation in case the model is formulated in Ising language. It is an improvement on the Random Mixing approximation, and takes local composition effects into account by considering a random mixing of pairs of particles, a particle and an empty lattice site, and empty sites, rather than of monomers [32].

In Fig. 2.5 the calculated EoS all reduce to the same exact result given by Eq. 2.82. This case provides a check for the accuracy of the simulations: the symbols are all located on top of the exact EoS-line and we can therefore rely on the accuracy of the simulation method. In Fig. 2.6, in which $u_{\text{attr}} = -0.2k_B T$, all four EoS are
Figure 2.5: Equation of state for 3D nearest neighbor fluid with $u_{\text{attr}} = -0.0k_B T$. The symbols are MC results and the lines (see text) are obtained from the compressibility-PY route (full line), the compressibility-MSA route (long dash), the energy-MSA route (short dash), and the Quasi-Chemical approximation (long-short dash).

nearly identical. The simulated EoS-points are located on top of the EoS-lines and we therefore conclude that the OZ-framework is well able to produce an accurate EoS for this case. We have no simulation results at higher pressures, because these simulations take up increasingly amounts of CPU time without being able to discriminate between the different routes for this case. For $u_{\text{attr}} = -0.5k_B T$ depicted in Fig. 2.7, the differences between the different routes are somewhat larger. The e-MSA and Quasi-Chemical route, indicated by the two lower curves in the figure, are still virtually on top of each other, but the c-PY and c-MSA routes clearly predict higher pressures. The simulation point for the highest packing fraction in Fig. 2.7, $\eta = 0.4041$, seems to indicate that the e-MSA- and Quasi-Chemical route are the most accurate. We have not applied a higher pressure in the simulations because the simulation will not be able to discriminate between the e-MSA and the Quasi-Chemical approximation. Our attention was therefore focussed on Fig. 2.8 for which $u_{\text{attr}} = -0.85k_B T$. The value $u_{\text{attr}} = -0.85k_B T$ is fairly close to the critical value of the 3D nearest neighbor lattice model $u_{\text{attr},c} = -0.88618k_B T$ [26], and it discriminates most strongly between the different EoS because it induces relatively strong correlations between the particles on the lattice. The simulation results clearly indicate that the e-MSA route produces the most accurate EoS. The e-MSA EoS is even more accurate
Figure 2.6: Caption as in Fig. 2.5 for \( u_{\text{attr}} = -0.2k_B T \).

Figure 2.7: Caption as in Fig. 2.5 for \( u_{\text{attr}} = -0.5k_B T \).
Figure 2.8: Caption as in Fig. 2.5 for $u_{attt} = -0.85k_B T$.

than the commonly used Quasi-Chemical approximation. Note from Fig. 2.8 that the EoS based on the Quasi-Chemical approximation shows a Van der Waals loop [33], indicating mechanical instabilities for certain packing fractions, although the simulations show that the system is still homogeneous. The EoS based on the c-PY route still has a fairly large positive slope, indicating that the fluid is nowhere near phase separation. Thus, this route predicts too strong a critical interaction strength. Both EoS based on the MSA-closure show a fairly flat profile. Especially the e-MSA EoS seems close to the critical point. Therefore, we expect that this route produces a fairly accurate critical interaction strength.

Figs. 2.7 and 2.8 clearly indicate that the thermodynamic consistency problem becomes severe for more strongly interacting systems. Close to the critical point we see large differences between the different routes. The MSA-closure seems to produce a more accurate EoS than the PY-closure (compare results for the c-PY- and c-MSA EoS), and the energy route seems to be more accurate than the compressibility route (compare e-MSA and c-MSA EoS). Unfortunately, we do not know of a tractable method to construct an EoS based on the energy route within the PY-closure. The fact that the MSA-closure seems to work better than the PY-closure when the EoS properties are considered is in contradiction with the results for the structural correlations for which the PY-closure was found to be the most accurate.

The thermodynamic inconsistencies in the EoS-behavior observed in strongly
interacting systems have their consequences for the accuracy of the liquid-gas spinodals, because LG-phase separation only occurs at relatively high interaction strengths.

![Figure 2.9: Liquid-Gas spinodals for the 3D nearest neighbor fluid.](image)

This is shown in Fig. 2.9 where the LG-spinodals obtained via the c-PY (dotted line), c-MSA (long dash-short dashed line), e-MSA (full line), and the Quasi-Chemical approximation (long dashed line) are shown. It also shows the binodal based on MC-data for the 3D Ising model (short dashed line). The binodal data for this model are transformed according to the equations of section 2.5.4 [26]. Note that the spinodals and the binodal are plotted as $u_{\text{attr}}$ versus $\eta$. This representation of the spinodal/binodal is more usual, and convertible to the representation in the $pV$-plane that was used in Fig. 2.2 of section 2.2.3. The binodal of Ref. [26] is exact within 0.01% for the region depicted in Fig. 2.9, and it serves to show the deviations of the top of the spinodals from the exact location of the critical point $(\eta_c, u_{\text{attr},c}) = (0.5, -0.886618k_BT)$. The spinodal predicted on the basis of the Bragg-Williams random mixing approximation is not shown in Fig. 2.9, it has a critical point of $(\eta_c, u_{\text{attr},c}) = (0.5, -2/3k_BT)$. In Fig. 2.9 it is seen that the e-MSA spinodal (full lines) is the most accurate
of the spinodals that we have tested. The Quasi-Chemical- (long dash) and c-MSA (long dash-short dashed) spinodals are reasonable, while the c-PY (dotted line) is the least accurate. Note from Fig. 2.9 that thus far we have not been able to locate the critical point predicted by the e-MSA spinodal. This is due to inaccuracies in the numerical differentiation used to solve the spinodal condition $(\partial p/\partial \eta)_{T,N} = 0$ (see section 2.5.3). Nevertheless, as expected on the basis of Fig. 2.8, it is clear from Fig. 2.9 that the e-MSA spinodal is the most accurate of the spinodals tested. Note that, although the location of the e-MSA spinodal is accurate, the compressibility $\kappa_T$ calculated via (see Eq. 2.53)

$$\frac{k_B T}{v_0} \eta \kappa_T = \frac{1}{1 - \eta \sum_{l,m,n} c(l,m,n)}$$

(2.92)

does not diverge at the e-MSA spinodal. The compressibility, when calculated via Eq. 2.92, only diverges on the c-MSA and c-PY spinodals (as seen from Eq. 2.86). However, it does diverge on the e-MSA spinodal when defined via the thermodynamic condition $\kappa_T = \frac{1}{\eta} (\partial \eta / \partial p)_{T,N}$. This is simply another form of the thermodynamic inconsistency problem.

The c-MSA spinodal, defined by Eq. 2.86, is the boundary of the non-solution region. It is the region $(u_{\text{attr}}, T_f)$ for which the OZ-equation combined with the MSA-closure has no solutions. The OZ-MSA-formalism only has solutions outside the region spanned by the c-MSA spinodal, which implies that states within the e-MSA spinodal (in the region between the e-MSA and c-MSA spinodal) do exist. The e-MSA EoS, Eq. 2.85, therefore shows Van der Waals-loops [33] upon entering the region spanned by the e-MSA spinodal [59]. This is in contrast to the c-MSA EoS, Eq. 2.80, which never enters (or even crosses) the region spanned by the c-MSA-spinodal: it simply stops to exist on the border of the c-MSA spinodal.

Let us now consider the c-PY spinodal, which apart from the fact that it is not able to produce a reasonable prediction of the critical point, also displays more fundamental problems: the curve cuts $\eta = 0$ for a finite $u_{\text{attr}}$ which implies that an infinitely dilute gas shows a LG phase transition upon cooling. This can clearly not be the case, because the infinitely large interparticle distances in an ideal gas exclude that the particles interact with each other, although this is an absolute necessity for a LG-phase separation to occur. Further, if we plot the inverse structure factor $S^{-1}(0,0,0)$, which is equal to $(k_B T \kappa_T / v_0)^{-1}$ (see Eq. 2.44), versus $\eta$ at constant interaction energy for the gaseous branch of a LG-separated fluid, another anomaly shows up. The result is depicted in Fig. 2.10. The inverse structure factor $S^{-1}(0,0,0)$ reaches the compressibility-spinodal in a non-functional fashion if it is lowered to 0, e.g., for $\eta = 0.11$ and $u_{\text{attr}} = -1.2 k_B T$ we find from Fig. 2.10 two values of $S^{-1}(0,0,0)$. This is in contradiction with thermodynamics which tells us that the free energy $\mathcal{A}$, of which $S^{-1}(0,0,0)$ is a second derivative, is a state function which can only have a single value for each $\eta$ and $u_{\text{attr}}$. Thus, $S^{-1}(0,0,0)$ can also only have a single value at fixed $\eta$ and $u_{\text{attr}}$, which is in
Figure 2.10: Inverse structure factor of the gaseous branch of a LG separated 3D nearest neighbor fluid as a function of the packing fraction at $u_{attr} = -1.2k_B T$ obtained within the PY-closure. Points are the results of calculation, and the line is to guide the eye.

In contrast to what is observed in Fig. 2.10. The behavior of $S^{-1}(0,0,0)$ as a function of $u_{attr}$ at constant $\eta$ also shows a kink on the gaseous branch of LG-phase separated systems, but this is not shown here. From Fig. 2.10 we conclude that states $(\eta, u_{attr})$ for which two values of $S^{-1}(0,0,0)$ are found must be rejected. The spinodal can therefore not be reached from gaseous states. The $S^{-1}(0,0,0)$ on the liquid branch of the systems shows a normal one-to-one dependence on both $\eta$ and $u_{attr}$ and does not have to be rejected.

A schematic overview of the behavior of $S^{-1}(0,0,0)$ near the c-PY spinodal (full curve) is drawn in Fig. 2.11. If we follow the $S^{-1}(0,0,0)$ of states that are connected via constant-$u_{attr}$ path to the spinodal on the gaseous side of the diagram (horizontal line on the low density side of Fig. 2.11, we first enter the region enclosed by the spinodal from the right until the dashed line is reached, after which we return along the same horizontal line to the spinodal. If $S^{-1}(0,0,0)$ is followed to the spinodal along a constant-$\eta$ path on the gaseous side of the diagram, we find an identical behavior: the spinodal is first passed from above until the dashed curve is reached, after which we return along the same vertical line to the spinodal. On the liquid side of the diagram we never enter the region within the spinodal. The region spanned by the dashed curve and the liquid branch of the spinodal is the non-solution region of the OZ-equation when considered...
Figure 2.11: Schematic overview of LG spinodal obtained within the PY-closure. The full curve indicates the spinodal. The straight horizontal and vertical lines are respectively constant-\(u_{\text{attr}}\) and constant-\(\eta\) paths along which \(S^{-1}(0,0,0)\) drops to 0. If a path reaches the dashed curve a 180° reversal of direction is observed.

within the PY-closure. Notice from Fig. 2.9 that the non-solution regions are different within the OZ-PY- and OZ-MSA formalisms. Similar findings as described in Figs. 2.10 and 2.11 have been reported for continuum models studied within the PY-closure \([9,58]\). Striking is the identical behavior of Baxter's sticky sphere model \([9]\) of which the 3D nearest neighbor model can be considered as the lattice analog. The unphysical behavior is thus not a lattice artifact, but is typically caused by the PY-closure.

The large thermodynamic inconsistencies that are observed near the critical point demand a very careful comparison to numerical data to elucidate what closure-route combination produces the most accurate results. The results for the 3D nearest neighbor model reported here favor the e-MSA route but we do not know whether this is true in general. The close relation between liquid-liquid and liquid-gas phase separation \([60]\) suggests that this is also true near the liquid-liquid spinodal of 3D nearest neighbor fluid mixtures. Careful studies of such mixtures are currently underway \([61]\).

## 2.8 Conclusions

In this work we have investigated how well attractive interactions can be captured by the OZ-formalism within the PY- and MSA-closure. For that purpose we have investigated the 3D nearest neighbor lattice model, in which the attractions between the particles alone determine the structural correlations. This is in contrast to continuum space models in which a liquid-like ordering occurs due to the repulsions between the cores of the particles. The attractions are only of minor influence on the ordering of particles in such continuum space models \([62,63]\). The
use of the simple and extensively studied 3D nearest neighbor model \([24,32,49]\) not only allows to single out the influence of the attractive interactions on the structural correlations, but has the additional advantage that the theoretical equations are relatively easily solved. This allows for a systematic introduction of higher order complexities, e.g., extension of particle size beyond one lattice site (which introduces packing effects on the lattice), extension of the range of the attractive potential, directional attractions, and chain connectivity.

Comparison to \(NpT\)-Monte Carlo data shows that both the MSA- and PY-closure are well able to predict the 2 particle distributions in the nearest neighbor model for not too strongly correlated systems (\(|u_{\text{attr}}| \leq 0.5k_BT\) and \(\eta \geq 0.5\)). The PY-closure is shown to be a little more accurate than the MSA-closure. Equations of state based on the compressibility route within both the PY- and MSA-closure have been obtained as well as the EoS based on the energy route within the MSA-equation. The EoS are compared to \(NpT\)-MC data and to results obtained within the Quasi-Chemical approximation. It is shown that the e-MSA EoS is the most accurate when compared to MC data. It is more accurate than the Quasi-Chemical approximation, even for interactions relatively close to the critical interaction strength \(u_{\text{attr},c} = -0.886618k_BT\). The c-PY and c-MSA route also produce an accurate EoS if \(|u_{\text{attr}}| \leq 0.5\), but show severe deviations from MC data for more strongly interacting systems. We see that the inconsistencies between the different routes become very large for strongly interacting systems, especially near the critical point.

The locations of the critical points (the top of the liquid-gas spinodals) show deviations from the values \(\eta = 0.5\) and \(u_{\text{attr},c} = -0.886618k_BT\) found from MC-simulations [26]. The c-PY and c-MSA routes produce spinodals with a critical point that is further removed from the exact values than the Quasi-Chemical approximation, for which \(u_{\text{attr},c} = -0.81093k_BT\). However, the best spinodal, even better than the spinodal based on the Quasi-Chemical approximation, is produced by the e-MSA route. The c-PY spinodal displays, apart from the relatively large deviations from the semi-exact data, unphysical features that contradict thermodynamic conceptions. Such unphysical behavior has been found previously for continuum models that were considered within the PY-closure [9,58], the observed behavior is therefore not a lattice artifact, but related to the use of the PY-closure.
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Chapter 3

Athermal lattice polymers: A comparison between RISM-theory and Monte Carlo simulations

3.1 Introduction

Equation of state properties of polymeric materials are of great importance in the process industry. They are in principle fully determined by the molecular organization of the material and therefore, a lot of attention has been paid to the development of molecular based equations of state over the years [1-9]. The most simple polymeric molecules consist of a linear sequence of covalently coupled particles (the segments). The ordering of the particles in the material is then determined by three effects: repulsive interactions (packing effects), attractive interactions (cohesion), and covalent bonding between the particles (chain connectivity).

Classical theories that try to explain the thermal properties from the molecular organization [1-5,10-14] all start from the fundamental statistical mechanical equation, $A_{\text{conf}} = -k_B T \ln Q_N$ [15,16]. It relates the configurational Helmholtz free energy $A_{\text{conf}}$, a thermodynamic quantity, to the configurational integral $Q_N$, which probes all molecular configurations that are possible in the polymeric material. Once the Helmholtz free energy is known, all other thermodynamic parameters of the polymeric material follow from well-established thermodynamic relations [17]. Principal difficulty in the approach is the calculation of the configurational integral $Q_N$ from the molecular organization of the material. For that purpose several approximations, that result in a neglect of local structural correlations, are adopted. Often, space is discretized such that a segment is cap-
ured into a cell [1,2] or a lattice site [3,4,10]. This approximation amounts to a complete [3,4,10] or partial [1,2] neglect of the packing effects present in real polymeric liquids. Other approximations regard the effects of the attractive interactions (Bragg-Williams approximation; Quasi-Chemical approximation) [15,16], and the chain-connectivity [11,12] on the structural correlations. Despite these approximations, the models have been quite successful in explaining the thermodynamic behavior of polymeric materials. Comparison to Monte Carlo simulations for the equation of state (EoS) [18], and the liquid-gas- [19], and liquid-liquid phase behavior [20-22] of such models has sometimes lead to an almost quantitative agreement. Relatively recent developments along this line of work comprise the Generalized-Flory theory [6,23], which incorporates packing effects by generalizing the Flory [11] and Huggins [12] theory to continuum space, and Bawendi and Freed's principally exact solution of the polymeric lattice model [24].

Another line of development towards the thermal properties of polymer liquids, originates from liquid state physics [25-31]. It attempts to calculate the structural correlations, i.e., the organization of the molecules in space, as accurately as possible. The EoS- and other macroscopic material properties can then be related to these correlations via formally exact statistical mechanical routes [32]. The models studied within this approach are continuum space models which show liquid-like packing effects caused by the repulsive cores of the particles in the fluid [33,34]. Principal routes to incorporate the effect of attractive interactions [27,33,35-38] and chain-connectivity [30,39-41] have also been developed and comparisons to Monte Carlo simulations have been made [42-44]. Especially the polymer-RISM model of Curro and Schweizer [39] has proven to be a tractable method to accurately reproduce the structural correlations in continuum polymeric fluids.

In this work we have discretized the polymer-RISM model onto a cubic lattice with fraction $\eta_m$ of the available space filled with linear molecules that each consist of $s$ segments. Each segment occupies exactly one lattice site. We do not consider systems with attractive segment-segment interactions, only non-attracting polymer systems are considered here. The objective of our work is twofold. First, in the limit $s = 1$ a simple non-overlapping and non-interacting monatomic lattice fluid, in which structural correlations are completely absent, results [45-47]. This implies that the correlations for $s > 1$ are only due to the covalent bonding between the segments of the molecules. Thus, by comparing to Monte Carlo simulations, we can investigate the abilities of the polymer-RISM theory to incorporate chain-connectivity effects, without an interference of liquid-like packing effects, that largely determine the structural correlations in continuum fluids. The work is complementary to that of the previous chapter [48], in which it was investigated how well the Ornstein-Zernike formalism is able to incorporate the effect of attractions be-
between the fluid particles on the structural correlations, without an interference of packing or connectivity effects. The second objective of the work presented here is to make a direct comparison of the polymer-RISM theory to a classical lattice model. For that purpose the compressibility-EoS that can be obtained within the polymer-RISM approach is compared to the EoS of the compressible lattice fluid obtained within the Huggins approximation [12]. The EoS is also compared to $NpT$-Monte Carlo simulations.

The rest of this chapter is organized as follows. In section 3.2 the lattice formulation of the polymer-RISM theory is presented, the solution method is outlined, and the compressibility-EoS is given. In section 3.3 the $NpT$-simulation method that was employed is briefly described. In section 3.4 results for the intermolecular 2-particle distribution function $g(r_1, r_2)$ of a dimeric fluid and of fluids consisting of linear 16- and 30-mers are presented. For the intramolecular 2-particle distributions, $\omega(r_1, r_2)$, that are needed as an input for the calculation of the intramolecular 2-particle distributions, $g(r_1, r_2)$, we have used the Random Flight (RF)-model [49,50], the Non Reversal Random Walk-model [51], and semi-exact intramolecular distributions obtained from MC-simulations. In section 3.4 the results for the structural correlations are presented and compared to MC-data. The abilities of the polymer-RISM model to incorporate chain connectivity effects are discussed. The results for the compressibility-EoS are presented and compared to the EoS of a compressible fluid obtained within the Huggins approximation [12] and to MC-data. Some concluding remarks are made in section 3.5.

3.2 The discretized polymer-RISM equation

3.2.1 Structural correlations

Consider $N$ chains that are packed in a volume $V$ discretized by a 3D cubic mesh. The chain molecules each consist of $s$ segments, numbered from 1 to $s$, that occupy consecutive nearest neighbor sites on the lattice. The chains are flexible in nature. The overall fraction of filled lattice sites $\eta_m$, the segmental packing fraction, is given by

$$\eta_m = \frac{Ns v_0}{V}$$

(3.1)

where $v_0$ is the volume of a lattice site. The chain packing fraction $\eta$ follows directly from $\eta_m$ by $\eta = \eta_m/s$.

The molecular organization of a lattice fluid, consisting of flexible polymeric molecules at packing fraction $\eta$, is fully quantified if the inter- and intramolecular 2-particle distributions, $g_{ij}(r_1, r_2)$ and $\omega_{ij}(r_1, r_2)$, are known. Here, $i$ and $j$ denote respectively the $i$-th and $j$-th segment in a linear molecule, thus $\{i, j\} \in \{1, s\}$, and $(r_1, r_2)$ denote the positions of respectively segment $i$ and $j$. If $g_{ij}(r_1, r_2)$ is
considered, then \(i\) and \(j\) belong to two arbitrary but different molecules, and if \(\omega_{ij}(r_1, r_2)\) is considered, then \(i\) and \(j\) belong to the same molecule. Physically, \(\eta_j g_{ij}(r_1, r_2)\) is the probability that, if the lattice site at \(r_1\) is occupied by segment \(i\) of a molecule, the lattice site at \(r_2\) is occupied by a \(j\)-th segment of another molecule. The \(\eta_j\) is the packing fraction of \(j\)-th segments on the lattice, it is equal to the chain packing fraction \(\eta\). The \(\omega_{ij}(r_1, r_2)\), on the other hand, is the probability of finding segment \(j\) at position \(r_2\) and segment \(i\), that belongs to the same molecule, at position \(r_1\). Thus, \(\omega(r_1, r_2)\) is a measure of the conformation of a molecule.

Chandler and Andersen [30] have been able to relate the total 2-particle correlation function, \(h_{ij}(r_1, r_2)\), defined by

\[
h_{ij}(r_1, r_2) = g_{ij}(r_1, r_2) - 1
\]  

(3.2)

to the direct 2-particle correlation function \(c_{ij}(r_1, r_2)\) and the intramolecular 2-particle distribution \(\omega_{ij}(r_1, r_2)\) in a manner analogous to the Ornstein-Zernike (OZ) equation for simple fluids [26].

In the case of simple fluids, the OZ-equation can be obtained by realizing that the total 2-particle correlation \(h(r_1, r_2)\) (note that there are no indices because a simple fluid particle does not consist of segments), is an infinite sum of direct correlation paths that involve more and more particles

\[
h(r_1, r_2) = c(r_1, r_2) + \eta \sum_{r_3} c(r_1, r_3)c(r_3, r_2) + \eta^2 \sum_{r_3, r_4} c(r_1, r_3)c(r_3, r_4)c(r_4, r_2) + \ldots
\]

(3.3)

Summation of all terms directly leads to the OZ-equation

\[
h(r_1, r_2) = c(r_1, r_2) + \eta \sum_{r_3} c(r_1, r_3)h(r_3, r_2)
\]

(3.4)

Note that in Eqs. 3.3 and 3.4 we are using a \(\sum\)-sign instead of the more common, \(\int\)-sign, because here we are dealing with a lattice system in which space is discretized. In analogy with Eq. 3.3, the \(h_{ij}(r_1, r_2)\) of a molecular fluid are thought to be built of an infinite sum of paths that consist of direct correlation links between segments belonging to different molecules, and also intramolecular links between segments that belong to the same molecule

\[
h_{ij}(r_1, r_2) = \sum_{r_3, r_4} \omega_{ik}(r_1, r_3)c_{kl}(r_3, r_4)\omega_{lj}(r_4, r_2) + \eta \sum_{r_3, \ldots, r_6} \omega_{ik}(r_1, r_3)c_{kl}(r_3, r_4)\omega_{lm}(r_4, r_5)c_{mn}(r_5, r_6)\omega_{nj}(r_6, r_2) + \ldots
\]

(3.5)
in which \( \{i,j,\ldots,n\} \in \{1,s\} \). On the rhs of Eq. 3.5, summation over repeated indices is assumed. Summation of all terms in Eq. 3.5 directly results in the Reference Interaction Site Model (RISM) equation, which is in matrix notation given by

\[
H(r_1, r_2) = \sum_{r_3,r_4} (\Omega(r_1, r_3)C(r_3, r_4) (\Omega(r_4, r_2) + \eta H(r_4, r_2)))
\]

(3.6)

\( H(r_1, r_2) \), \( C(r_1, r_2) \), and \( \Omega(r_1, r_2) \) are matrices which contain the elements \( h_{ij}(r_1, r_2) \), \( c_{ij}(r_1, r_2) \), and \( \omega_{ij}(r_1, r_2) \). For molecules consisting of \( s \) segments the matrices are of order \( s \times s \)

\[
H(r_1, r_2) = \begin{vmatrix}
    h_{11} & \cdots & h_{1s} \\
    \vdots & \ddots & \vdots \\
    h_{s1} & \cdots & h_{ss}
\end{vmatrix}
\]

(3.7)

where the \((r_1, r_2)\) on the rhs denotes that all elements \( h_{ij} \) depend on \((r_1, r_2)\). For \( C(r_1, r_2) \) and \( \Omega(r_1, r_2) \) we have expressions identical to Eq. 3.7.

Contrary to the Ornstein-Zernike equation, the RISM-equation cannot be derived from a first principles diagrammatic analysis. The equation is approximate because it only includes linear correlation paths consisting of \( \omega- \) and \( c- \) links (see Eq. 3.5). Some important paths that typically occur for long flexible molecules, and that are not included in Eq. 3.6 are discussed in Ref. [52].

A diagrammatically exact set of equations for the structural correlations in molecular fluids is given by the Chandler-Silbey-Ladanyi (CSL) theory [53]. In Ref. [54] it is shown for an athermal dimeric fluid that the 2-particle distributions obtained with the CSL-theory are less satisfactory than the distributions obtained from the RISM approach. This is due to a fortuitous cancellation of errors within the RISM-approach: both the RISM- and the CSL-equations need to be supplemented with an approximate closure equation, and it turns out for the case of athermal dimers that the approximate closure performs better when combined with the approximate RISM-equation than with the exact CSL-equations.

For the cubic lattice model considered here, we must write \( h_{ij}(r_1, r_2) = h_{ij}(r_2 - r_1) = h_{ij}(l, m, n) \) in order to be able to solve Eq. 3.6. We also need to combine the equation with a set of closure equations that operate on the segment-segment level. The Percus-Yevick closure is used here. It is given by [27]

\[
c_{ij}(l, m, n) = g_{ij}(l, m, n) \left( 1 - e^\beta u_{ij}(l,m,n) \right)
\]

(3.8)

in which \( u_{ij}(l, m, n) \) is the segmental interaction potential and \( \beta = 1/k_BT \). For an athermal fluid in which the polymer segments occupy exactly one lattice site, we have the interaction potential

\[
\begin{align*}
  u_{ij}(0,0,0) & \rightarrow \infty \\
  u_{ij}(l, m, n) & = 0 \quad \text{otherwise}
\end{align*}
\]

(3.9)
Thus, Eq. 3.8 can be split in a condition stating that segments cannot overlap

\[ g_{ij}(0, 0, 0) = 0 \]  

and in

\[ c_{ij}(l, m, n) = 0 \quad \text{for } l^2 + m^2 + n^2 \geq 1 \]  

Eqs. 3.2, 3.6, 3.10, and 3.11 form a closed set of equations that can in principle be solved for the \( h_{ij}(l, m, n) \), for known \( \omega_{ij}(l, m, n) \) and packing fraction \( \eta \) (in Eqs. 3.2 and 3.6 we replace \((r_1, r_2)\) by \((l, m, n)\)). Unfortunately, Eq. 3.6 is of order \( s \times s \) and becomes intractable for molecules consisting of many segments. Curro and Schweizer first realized that in the case of ring shaped molecules there is an equivalence of segments within the molecule [39]: the elements of Eq. 3.7 will all be the same. In a later paper they showed that this is also approximately true for long chain-like molecules [55]. Thus, the subscripts of the total- and direct correlations can be dropped in Eq. 3.6. A little reorganization gives

\[
h(l, m, n) = \sum_{l',m',n'} \sum_{l'',m'',n''} \omega(l - l', m - m', n - n') c(l' - l'', m' - m'', n' - n'') \left( \omega(l'', m'', n'') + \eta_m h(l'', m'', n'') \right)
\]  

(3.12)

where \( \eta_m \) is the segmental packing fraction and \( \omega(l, m, n) \) is the averaged intramolecular distribution function given by

\[
\omega(l, m, n) = \frac{1}{s} \sum_{i=1}^{s} \sum_{j=1}^{s} \omega_{ij}(l, m, n)
\]  

(3.13)

Eq. 3.12 is called the polymer-RISM equation. The \( \omega(l, m, n) \) denotes the average number of segments of a chain that will be found on position \((l, m, n)\) from an average segment of the same chain. In going from Eq. 3.6 to Eq. 3.12 Curro and Schweizer reduced the complex \( s \times s \) matrix equation to a single scalar equation that can be relatively easily solved. In Eqs. 3.8-3.11 we can now also drop the indices if ring-shaped or long linear polymer molecules are considered. A set of only four equations, Eqs. 3.10-3.12 and \( h(l, m, n) = g(l, m, n) - 1 \), remains to be solved if \( \omega(l, m, n) \) and \( \eta_m \) are known.

We finally want to mention that an overall 2-particle distribution \( G(l, m, n) \), consisting of an intramolecular and an intermolecular part, can be defined according to

\[
\eta_m G(l, m, n) = \omega(l, m, n) + \eta_m g(l, m, n)
\]  

(3.14)

where \( \eta_m G(l, m, n) \) denotes the total density of particles at position \((l, m, n)\) from a chosen particle. It is an important quantity that is directly related to the EoS-behavior of the athermal polymeric lattice fluid (see section 3.2.4).
3.2.2 Solution method

Solution of Eqs. 3.10-3.12 is most convenient in Fourier space. The 3D-discretized Fourier transform is defined for symmetric functions, \( f(l, m, n) = f(\pm l, \pm m, \pm n) \), as [46]

\[
\hat{f}(u, v, w) = \sum_{l,m,n} f(l, m, n) \cos lu \cos mv \cos nw \tag{3.15}
\]

and its inverse transformation is given by

\[
f(l, m, n) = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{f}(u, v, w) \cos lu \cos mv \cos nw \, du \, dv \, dw \tag{3.16}
\]

Transformation of Eq. 3.12 with help of Eq. 3.15 leads to removal of the double sum present in Eq. 3.12:

\[
\hat{h}(u, v, w) = \hat{\omega}(u, v, w) \hat{c}(u, v, w) \left( \hat{\omega}(u, v, w) + \eta_m \hat{h}(u, v, w) \right) \tag{3.17}
\]

Writing Eq. 3.17 explicitly in terms of \( \hat{h}(u, v, w) \) and using the inverse transform Eq. 3.16, results in

\[
h(l, m, n) = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\hat{\omega}^2(u, v, w) \hat{c}(u, v, w)}{1 - \eta_m \hat{\omega}(u, v, w) \hat{c}(u, v, w)} \cos lu \cos mv \cos nw \, du \, dv \, dw \tag{3.18}
\]

where \( \hat{c}(u, v, w) = c_0 \) for hard athermals, as can be seen from Eqs. 3.11 and 3.15. If it is assumed that we know \( \hat{\omega}(u, v, w) \) (see next subsection), we can obtain the structural correlations in athermal lattice polymer by the construction of a single equation for \( c_0 \) with help of Eq. 3.18 and the non-overlap condition \( h(l, m, n) = -1 \) (Eq. 3.10)

\[
-1 = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\hat{\omega}^2(u, v, w) c_0}{1 - \eta_m \hat{\omega}(u, v, w) c_0} \, du \, dv \, dw \tag{3.19}
\]

Eq. 3.19 can be solved efficiently for \( c_0 \) with a Newton-Raphson scheme combined with a 3D quadrature routine. Once \( c_0 \) is known we obtain \( h(l, m, n) \) from Eq. 3.18. Note that it only takes the solution of one equation in one unknown to determine the structural properties of athermal polymeric lattice fluids. For athermal monomeric fluids we have \( \hat{\omega}(u, v, w) = 1 \) and, from Eq. 3.19, \( c_0 \) is directly found to be \( c_0 = -1/(1 - \eta_m) \). From Eq. 3.18 we then have for \( h(l, m, n) \)

\[
h(l, m, n) = -\left( \frac{\sin \pi l}{\pi l} \right) \left( \frac{\sin \pi m}{\pi m} \right) \left( \frac{\sin \pi n}{\pi n} \right) \tag{3.20}
\]

thus

\[
h(0, 0, 0) = -1
\]

\[
h(l, m, n) = 0 \quad \text{otherwise} \tag{3.21}
\]
Eq. 3.21 illustrates that for athermal monomers all structural correlations disappear if a monomer occupies exactly one lattice site. This is in great contrast to the monomeric continuum fluid, where packing effects determine the (complicated) solution of $h(l, m, n)$ [29]. Thus, the lattice model presented here allows to study the influence of chain-connectivity on the structural correlations without the liquid-like ordering effects that are observed in continuum space models at higher packing fractions.

3.2.3 The intramolecular distribution function

In this subsection, the intramolecular distribution functions $\omega(l, m, n)$ that were used in the calculations are presented.

Generally, $\omega(l, m, n)$ is not known for flexible molecules because the surrounding medium influences the conformation of each molecule: there is an intrinsic coupling of $\omega(l, m, n)$ and $g(l, m, n)$, and, contrary to rigid molecules, $\omega(l, m, n)$ is not obtainable separately. It is thus impossible to use it as an input function for the calculation of $g(l, m, n)$ in the RISM-equation. Curro and Schweizer [39] have solved this problem by invoking Flory's ideality hypothesis [56], which states that for dense polymer melts there is a balance between inter- and intramolecular excluded volume interactions, implying that the mean squared end to end distance $\langle R^2 \rangle$ scales linearly with the number of covalent bonds, $s - 1$, in the chain.

Such scaling behavior is also observed for the Random Flight (RF) model [49, 50] and the Non Reversal Random Walk model (NRRW) [51]. Therefore, Curro and Schweizer argue that such chain models are good candidates for the intramolecular distribution function in the calculation of $g(l, m, n)$. In this chapter we have tested both. Alternative solutions to deal with the intrinsic coupling of $g(l, m, n)$ and $\omega(l, m, n)$ have been presented in the form of fully self-consistent schemes [57-59].

The RF-intramolecular 2-particle distribution can be obtained for cubic lattice systems as follows. We start by expressing the probability $W_i(l, m, n)$ to find a random flight that started at $(0,0,0)$ after $i$ jumps at $(l, m, n)$ in terms of the $i-1$ jump probability $W_{i-1}(l, m, n)$ as [49]

$$W_i(l, m, n) = \sum_{l', m', n'} \tau(l', m', n') W_{i-1}(l-l', m-m', n-n')$$  \hspace{1cm} (3.22)

The $\tau(l, m, n)$ is the 1-jump probability. Only jumps to nearest neighbor sites occur, $\tau(l, m, n)$ is thus given by

$$\tau(l, m, n) = \frac{1}{6} \text{ if } l^2 + m^2 + n^2 = 1$$

$$\tau(l, m, n) = 0 \text{ otherwise}$$  \hspace{1cm} (3.23)
Eq. 3.22 is valid due to the independence of subsequent jumps. Fourier transformation (Eq. 3.15) and iterative use of Eq. 3.22 gives

\[ \hat{W}_i(u,v,w) = \hat{\tau}_i(u,v,w) \]  

(3.24)

with \( \hat{W}_1(u,v,w) = \hat{\tau}(u,v,w) \). In Eq. 3.24, \( \hat{\tau}(u,v,w) = \frac{1}{2}(\cos u + \cos v + \cos w) \) as is seen from Eqs. 3.23 and 3.15.

The intramolecular distribution function of a random flight chain consisting of \( s \) segments, \( \hat{\omega}(u,v,w) \), can now be expressed in terms of the \( i \)-jump probabilities \( \hat{W}_i(u,v,w) \). From Eq. 3.13 it is clear that an \( s \)-mer chain consists of \( 2 \) flights of \( s - 1 \) jumps (\( \omega_{1s} \) and \( \omega_{s1} \)), four \( s - 2 \) flights, six \( s - 3 \) flights, etc. Thus, from Eq. 3.13 we obtain

\[ \hat{\omega}(u,v,w) = 1 + 2 \sum_{i=1}^{s-1} (s-i)\hat{W}_i(u,v,w) \]  

(3.25)

where the 1 accounts for the self-correlation of segments (the \( \omega_{ii} \) contribution in Eq. 3.13), and \( \hat{W}_i(u,v,w) \) is given by Eq. 3.24. Explicit summation in Eq. 3.25 gives

\[ \hat{\omega}_{RF}(u,v,w) = \frac{1 - \frac{2}{5} \hat{\tau}^2 - \frac{2}{5} \hat{\tau} + \frac{2}{5} \hat{\tau}^{s+1}}{(1 - \hat{\tau})^2} \]  

(3.26)

where \( \hat{\tau} = \hat{\tau}(u,v,w) \). Eq. 3.26 is analogous to its continuum version presented in Refs. [55,60].

Apart from the RF-model we have also investigated the NRRW-model for linear chains. In the NRRW-model direct back-folding of the chains, such that segments \( i - 1 \) and \( i + 1 \) will overlap, is forbidden. This leads to an expansion of the chains compared to the RF-case: the RF mean squared end-to-end distance is approximately \( 2/3 \) of the NRRW end-to-end distance (for infinitely long chains the factor \( 2/3 \) is exact). Eq. 3.25 is still valid for calculation of the \( \hat{\omega}_{NRRW}(u,v,w) \) if the jump probabilities \( \hat{W}_i(u,v,w) \) are altered according to the method described in Appendix A.

Finally, we have also used the intramolecular distribution obtained from the Monte Carlo simulations presented in section 3.3, as an input in the discretized RISM-equation Eq. 3.12. This \( \omega(l,m,n) \) does not invoke the ideality assumption, contrary to the intramolecular distributions of the RF- and NRRW-chains, and fully accounts for the excluded volume contributions. Therefore, it serves as a means to check the Flory ideality hypothesis.

### 3.2.4 Equation of State

In this section a compressibility based equation of state for molecular lattice systems is presented.

The quantity \( \eta_m g(r_1, r_2) \) is the average density of segments at position \( r_2 \), on
condition that there is a segment at \( r_1 \) that belongs to a different molecule, and \( \omega(r_1, r_2) \) is the average density of segments at \( r_2 \) on condition that there is a segment of the same molecule at \( r_1 \). The density fluctuation \( \chi(r_1, r_2) \) for a polymeric lattice fluid is then given by

\[
\chi(r_1, r_2) = \eta_m^2 g(r_1, r_2) + \eta_m \omega(r_1, r_2) - \eta_m^2 .
\] (3.27)

The general relation of the isothermal compressibility \( \kappa_T \) to the density fluctuations is then given by [61]

\[
\frac{k_B T \eta_m}{v_0} < N_s > \kappa_T = \sum_{r_1} \sum_{r_2} \chi(r_1, r_2)
\] (3.28)

where \( \sum_{r_2} \) denotes summation over all lattice positions. Thus, the isothermal compressibility can be expressed as

\[
\frac{k_B T}{v_0} \kappa_T = \sum_{l,m,n} (G(l, m, n) - 1)
\] (3.29)

In Eq. 3.29 we have used Eq. 3.14. The \( v_0 \) is the volume of one lattice site, and \( (l, m, n) = r_2 - r_1 \). Note from Eq. 3.29 that the compressibility is determined by the overall 2-particle distribution \( G(l, m, n) \), and not by intermolecular correlations \( g(l, m, n) \) alone. The rhs of Eq. 3.29 is equal to the isotropic structure factor \( S(0,0,0) \) of the fluid at zero wave vector \( k = (u,v,w) \) [47]. The structure factor \( S(u,v,w) \) is generally defined by

\[
S(u,v,w) = \sum_{l,m,n} (\omega(l,m,n) + \eta_m h(l,m,n)) \cos lu \cos mv \cos nw
\] (3.30)

and is experimentally obtainable with Röntgen- or neutron scattering experiments [62,63]. It measures the density fluctuations in the liquid as is seen from Eq. 3.27. If \( \kappa_T = 1/\eta_m (\partial \eta_m / \partial \eta)_{T,V} \) is integrated over \( \eta_m \) we obtain from Eq. 3.29, after substitution of Eq. 3.17

\[
\frac{pv_0}{k_B T} = \int_{0}^{\eta_m} \left( \frac{1}{\hat{\omega}(0,0,0)} - \eta_m \hat{\omega}(0,0,0) \right) d\eta_m
\] (3.31)

Eq. 3.31 is the compressibility-EoS. Note that \( \hat{\omega}(0,0,0) = s \), for \( \omega(0,0,0) = \sum_{l,m,n} \omega(l,m,n) \) effectively counts the segments that belong to a chain. Baxter has analytically performed the integration over the density in the compressibility equation for monomeric continuum fluids within the PY-closure [64]. His expression can be modified for 3D athermal lattice polymers. Eq. 3.31 is then given by
\[ \frac{p \nu_0}{k_B T} = \frac{\eta_m}{s} - \eta_m^2 c(0,0,0) + \]

\[(\frac{1}{2\pi})^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} (\eta_m \hat{\omega}(u,v,w) \hat{c}(u,v,w) + \ln(1 - \eta_m \hat{\omega}(u,v,w) c(u,v,w))) \, du \, dv \, dw \]

(3.32)

where \( c(0,0,0) = \hat{c}(u,v,w) = c_0 \) for athermal systems. For monomeric systems, \( c_0 = -1/(1 - \eta_m) \). Eq. 3.32 then reduces to

\[ \frac{p \nu_0}{k_B T} = -\ln(1 - \eta_m) \]

(3.33)

Eq. 3.33 is, in contrast to its continuum analog, exact as can be verified via exact enumeration.

Honnell, Hall, and Dickman have presented an EoS for continuum polymeric fluids that was derived via the pressure route [65]. This equation is not valid for lattice systems because it contains a derivative of the segment-segment interaction potential with respect to interparticle distance. Such an operation is not well-defined on the lattice, and the equation is therefore not studied here. In a later chapter we have employed a lattice analog of the virial equation, using the depletion profiles of the polymeric fluid at a repulsive wall, to extract an EoS [66].

### 3.3 Monte Carlo simulation

The simulation method used to obtain the 2-particle distributions, \( g(l,m,n) \) and \( \omega(l,m,n) \), and the equation of state for \( s = 2, s = 16 \) and \( s = 30 \) athermal chain fluids is of \( NpT \)-type, and is described in detail elsewhere [18]. It consists of condensing a polymer slab against a wall in a rectangular section of the cubic lattice with 50 sites in the \( l \)-direction, perpendicular to the wall, and 22 sites in the other two directions. Periodic boundary conditions are used in \( m \)- and \( n \)-direction. A finite pressure is exerted by fluctuating the total volume. The volume fluctuations are created by building/destroying a solid piston site-by-site with respect to the solid wall that is located at \( l = 0 \).

The configuration space is sampled by moving the polymer molecules on the lattice with reptation moves [67]. A volume fluctuation move was applied every 200 reptations. Up to \( 1.2 \times 10^9 \) reptation moves were used, from which the first \( 0.4 - 0.6 \times 10^9 \) were used only for equilibration of each state. Averaging of thermodynamic properties took place every 5000 reptations. The particle distributions were only obtained from the last \( 0.1 \times 10^9 \) moves. Averages of
$g(l, m, n)$ and $\omega(l, m, n)$ were collected every 5000 reptations from a middle section of the polymer slab, at least 7 sites away from the solid wall and from the jagged edge of the piston. The $g(l, m, n)$ and $\omega(l, m, n)$ were only obtained for $r = \sqrt{l^2 + m^2 + n^2} \leq 4$.

Each simulation run also produces a density profile of the pressurized polymer near the solid wall. The density profiles that were obtained from the runs performed in this work are used in a subsequent chapter to study the performance of the discretized polymer-RISM equation, modified as in Ref. [68], in describing the adsorption of polymeric lattice fluids near a hard wall.

All runs were performed on a RISC IBM 6000 machine. The longest runs for the highest packing fractions took circa 30 hours of CPU time. Simulation results are available on request via e-mail at tgpken@urc.tue.nl.

### 3.4 Results and discussion

In section 3.4.1 we compare the structural properties of the discretized polymer-RISM model to Monte Carlo data. Comparisons for several intramolecular segment-segment distributions are made. In section 3.4.2 we compare the equation of state properties to $NpT$-simulation data, and to predictions of a compressible version of the Huggins model [12].

#### 3.4.1 Structural correlations

In Fig. 3.1 the intermolecular distribution $g(l, m, n)$ of a non-interacting dimeric fluid is shown as a function of segment-segment separation distance. We have plotted $g(l, m, n)$ as $g(r)$ with $r = \sqrt{l^2 + m^2 + n^2}$. This is not fully correct, as $g(l, m, n)$ is not fully isotropic, e.g., $g(2, 2, 1)$ and $g(3, 0, 0)$ have slightly different values. Plotting as $g = g(r)$ is a necessity, however, in making 2D plots, and the reduction of information is only marginal because $g(2, 2, 1) \approx g(3, 0, 0)$. We have obtained $g(3)$ by numerical averaging of $g(2, 2, 1)$ and $g(3, 0, 0)$. The simulation data in the figures are denoted by symbols and the results of the calculations by the line. The use of a line does not mean that the results of the calculations for $g(r)$ are continuous with $r$, but is merely to distinguish between theory and simulation. The accuracy of the simulations shown in Fig. 3.1 and the other figures is smaller than the size of the symbols. Error bars are therefore omitted.

In Fig. 3.1 it is seen that the polymer-RISM equation is able to accurately reproduce the intermolecular 2-particle distribution of a dimeric lattice fluid with the intramolecular distribution function Eq. 3.13 given by

\[
\begin{align*}
\omega_{11}(0,0,0) & = 1 \\
\omega_{11}(l,m,n) & = 0 \quad \text{for } l^2 + m^2 + n^2 \geq 1 \\
\omega_{12}(l,m,n) & = \frac{1}{6} \quad \text{for } l^2 + m^2 + n^2 = 1
\end{align*}
\]
Figure 3.1: Intermolecular 2-particle distribution in an athermal dimeric fluid at $\eta_m = 0.3014$. Symbols are obtained from MC-simulation and the line is calculated from the discretized polymer-RISM theory.

\[ \omega_{12}(l, m, n) = 0 \quad \text{otherwise} \quad (3.34) \]

and $\omega_{ij}(l, m, n) = \omega_{ji}(l, m, n)$. Note that for dimeric lattice fluids, Eq. 3.34 is exact, as is Curro and Schweizer’s equivalence of segments that lead to Eq. 3.12. The decrease of $g(r)$ for $r = 1$ in Fig. 3.1 is due to the fact that one of the six nearest neighbors of each particle is taken by another particle that belongs to the same molecule (chemical binding). This leaves less room for particles belonging to other molecules and results in a lower probability, $\eta_m g(r)$, of encountering particles belonging to different molecules on the nearest neighbor positions. This decrease of $g(r)$ for smaller $r$ is called the correlation hole effect [69,39].

In Figs. 3.2 and 3.3 that denote $g(r)$ for respectively non-interacting linear $s = 16$-mers and $s = 30$-mers, it is seen that the correlation hole is deeper in polymeric fluids when compared to a dimeric fluid at roughly the same packing fraction. This is because in a polymeric fluid most segments are covalently bonded to two other segments, and not to one as is the case for the dimeric fluid. It is also seen that the correlation hole is present over larger interparticle distances. The flexible molecules extend over large amounts of space: the average separation distance between the chain ends is proportional to $\sqrt{s - 1}$. Notice from Figs. 3.2 and 3.3 that the intermolecular 2-particle distribution, $g(r)$, does not scale monotonically with $r$: $g(\sqrt{3}) \approx g(2)$. This illustrates that cubic lattice fluids are not isotropic. Two particles at distance $(2,0,0)$ are relatively strongly correlated,
Figure 3.2: Intermolecular 2-particle distribution in an athermal fluid of $s = 16$-mers at $\eta_m = 0.3198$. Symbols are obtained from MC-simulation, lines from theory. The dotted line is obtained for Random Flight chains, the full line for NRRW-chains, and the dashed line is calculated with the intramolecular distribution function obtained from the simulations.

because there are only two nearest neighbor contacts for which correlation-loss occurs on the shortest path between the particles. For two particles at distance (1,1,1), the minimum number of nearest neighbor contacts is three, although the particles are closer than the particles at (2,0,0). It is only because there are more shortest distance paths between two particles at (1,1,1), while there is only one between the particles at (2,0,0), that the particles at (1,1,1) are not more weakly correlated than the particles at (2,0,0).

In Figs. 3.2 and 3.3 we have tested several intramolecular segment-segment distributions, $\omega(l, m, n)$, on their ability to reproduce $g(l, m, n)$ via the polymer-RISM equation, Eq. 3.12. Note first that the results for $g(l, m, n)$ are satisfying, when compared to the simulations (symbols), for all cases tested. The dotted lines in both figures are obtained for the Random Flight intramolecular distribution of Eq. 3.26. Note that the Random Flight distribution is a little more accurate for the $s = 30$-mer indicating that the polymer-RISM equation is more accurate for longer chains. This is obviously due to the equivalence of segments approximation underlying Eq. 3.12. The NRRW-chain model of Appendix A is also shown in Figs. 3.2 and 3.3 by the full line. A little improvement, when compared to the RF-model, especially for $s = 16$, is observed in both figures, but the influ-
ence of an improved intramolecular distribution clearly is marginal. Finally, the results obtained by inserting the \( \omega(l, m, n) \), monitored from the MC-simulations, in Eq. 3.12 are also shown in the figures by the long dashed lines. In the case of \( s = 16 \) virtually no improvement is seen when compared to the NRRW-chain case, and for \( s = 30 \) we observe a less accurate description of \( g(l, m, n) \), when compared to the RF- or NRRW-chain model. This is due to the fact that only \( \omega(l, m, n) \) for \( r = \sqrt{l^2 + m^2 + n^2} \leq 4 \) was extracted from the simulations, and fed into the polymer-RISM equation. The tail-contribution of \( \omega(l, m, n) \) for \( r > 4 \) was simply set to zero. This procedure to which we have resorted to reduce the CPU-times needed in the simulations, is obviously not correct, but does illustrate that the values of \( \omega(l, m, n) \) for the small separation distances \( r \leq 4 \) largely determine the behavior of \( g(l, m, n) \): in both figures we still get reasonable results if we use \( \omega(l, m, n) \) for \( r \leq 4 \) only. The structural properties have also been investigated at other packing fractions than the ones shown in Figs. 3.1-3.3, and almost identical results are obtained. Therefore, they are not shown here. It should be realized that it took the solution of only one equation in the unknown \( c(0, 0, 0) \) to calculate the \( g(l, m, n) \)'s shown here.

### 3.4.2 Equation of state

In Fig. 3.4 an overview of the Monte Carlo data for the EoS of non-interacting \( s = 1, s = 2, s = 16, \) and \( s = 30 \)-mers is shown. It is seen that a fluid consisting of
longer chains needs lower pressures to attain the same packing fraction as a fluid consisting of shorter chains. Thus, covalent bonding between particles lowers the pressure [70]. It is seen from the marginal differences between the EoS of \( s = 16 \) and \( s = 30 \)-mers that the influence of chain length decreases for longer chains.

In Fig. 3.5 the EoS of the athermal dimeric lattice fluid is shown. The state points indicated by the symbols are obtained from MC-simulations and the full line is obtained within the polymer-RISM framework from Eq. 3.32. The results are excellent, although the dotted line is still marginally better. The dotted line is calculated from the Huggins approximation for a compressible lattice fluid. It is given by [10,12]

\[
\frac{p v_0}{\eta k_B T} = s - \frac{1}{c} \ln(1 - c \eta_m) - \frac{s}{\eta_m} \ln(1 - \eta_m) \tag{3.35}
\]

with

\[
c = \frac{2}{s} \left( 1 - \frac{1}{s} \right) \tag{3.36}
\]

In Figs. 3.6 and 3.7 the EoS of respectively \( s = 16 \)-mer chains and \( s = 30 \)-mer chains are shown. It is seen that the EoS calculated on the basis of Eq. 3.35 (dotted line) is reasonably accurate when compared to the MC-data. The other curves shown in the figures are based on the compressibility-EoS, Eq. 3.32, for respectively the Random Flight intramolecular distribution (full curve), the NRRW-
intramolecular distribution of Appendix A (short dash), and the intramolecular distribution function extracted from MC simulations (long dash). The intramolecular distribution function extracted from the simulations was again only considered for $r \leq 4$ lattice spacings, and set to zero for $r > 4$. It is seen from the figures for $s = 16$ and $s = 30$ that the Random Flight chains produce an equation that is far off when compared to the MC-data. Subsequent improvements are obtained by using the intramolecular distribution of a NRRW-chain, and the average $\omega(l, m, n)$ obtained from the simulations, but for all three cases a significant underestimation of the actual values of the pressure occurs. The results obtained thus far are nowhere near the agreement obtained with the Huggins-EoS. The compressibility-EoS for monomers, Eq. 3.33, is exact, and the compressibility-EoS for dimers is very accurate. Therefore, we believe that the results shown in Figs. 3.6 and 3.7 are typically caused by the inexactitude of the intramolecular distributions of flexible chains, and not by an intrinsic unsuitability of the compressibility route to produce an accurate EoS. This is understood as follows. Due to the inexact incorporation of excluded volume in $\omega(l, m, n)$, segments of the same molecule occasionally overlap. Thus, such a fluid can more easily be compressed than a fluid in which the segments never show any overlap. As a result, the dependence of the pressure on $\eta_m$ is not strong enough. In Figs. 3.6
Figure 3.6: EoS of athermal $s = 16$-mers. Symbols indicate simulation results, and the lines are obtained for the Random Flight- (full line), the NRRW- (short dash), and Monte Carlo (long dash) intramolecular 2-particle distributions. The dotted line is obtained from Eq. 3.35.

Figure 3.7: Caption as in Fig. 3.6 but for $s = 30$-mers.
and 3.7 it is seen that the $\omega(l, m, n)$ extracted from the MC-simulations produces the best results. This is simply because it most accurately incorporates the excluded chain volume. A better EoS could have been obtained if $\omega(l, m, n)$ had been extracted from the simulations up to larger distances, but such a procedure would have been computationally intensive.

Let's now look at the consequences of an incorrect $\omega(l, m, n)$ for the EoS at $\eta_m \rightarrow 1$. Physically, we know that all correlations between the segments disappear at full packing, thus $G(l, m, n) = g(l, m, n) + \omega(l, m, n) \rightarrow 1$. In Fig. 3.8, the total 2-particle distribution $G(l, m, n)$ is shown for $s = 16$-mers for both the RF- and NRRW-chain at $\eta_m = 1$. Due to the intramolecular particle-particle overlaps that occur, it is seen that at $\eta_m \rightarrow 1$, $G(l, m, n) = g(l, m, n) + \omega(l, m, n) \neq 1$ for all $(l, m, n)$. Hence, the compressibility $\kappa_T$ is not zero at $\eta_m \rightarrow 1$ (see Eq. 3.29), and the pressure does not increase to infinity at full packing. It is seen in Fig. 3.8 that for the RF-chain the "rest-correlation", i.e., the deviation from $G(r) = 1$, is larger than for the NRRW-chain, which does incorporate the excluded chain volume up to some extent. Therefore, the EoS of the NRRW-chain is a lot better than the EoS of the RF-chain.

From Eq. 3.29 it is seen that the compressibility-EoS is dependent on the total 2-particle distribution $G(l, m, n)$, an accurate prediction of the intermolecular 2-particle distribution $g(l, m, n)$ alone is not sufficient in obtaining an accurate EoS.
via the compressibility route, because the EoS is also highly sensitive to the accuracy of $\omega(l,m,n)$. Fig. 3.9 is an illustration of this. It shows the intermolecular-

Figure 3.9: Total- and intermolecular 2-particle distribution of an athermal $s = 16$-mer at $\eta_m = 0.526$. The symbols indicate simulation results for $G(l,m,n)$ (•) and $g(l,m,n)$ (■). The lines result from calculation. The upper curves indicate the total distributions, and the lower curves the intermolecular distributions. Results are obtained for a Random Flight chain (full line), a NRRW-chain (dashed lines), and the intramolecular distribution obtained from MC-simulations (dotted lines).

(lower symbols and curves) and the total 2-particle distribution (upper symbols and curves) of a $s = 16$-mer for the three intramolecular distributions that we have tested. It is clearly shown that the $g(l,m,n)$'s, calculated from Eq. 3.12, are not very sensitive to the exact nature of $\omega(l,m,n)$, in contrast with the total 2-particle distribution $G(l,m,n)$, which is highly sensitive on $\omega(l,m,n)$. Unfortunately, it is $G(l,m,n)$ and not $g(l,m,n)$ that determines the EoS-behavior. Therefore, the EoS also shows a strong sensitivity on $\omega(l,m,n)$. Thus far no intramolecular distribution exists that produces an EoS for athermal flexible molecules comparable to Eq. 3.35. Even $\omega(l,m,n)$ taken from simulation work might not be appropriate unless the whole long-range contribution is simulated accurately. This will take very high CPU-time demands. A better option is offered in Ref. [71], where Curro, Blatz, and Pings present an approximate scheme to calculate an intramolecular distribution that does incorporate the excluded chain volume. In Ref. [72] it is shown that such a scheme produces very good results for the structural correlations and the EoS of the athermal polymeric lat-
tice fluids considered within the polymer-RISM approach. Note finally that the introduction of a cubic lattice which leads to the removal of all liquid-like ordering effects, has made it particularly easy to demonstrate the origin of the failure of the polymer-RISM theory to produce an accurate compressibility-EoS. The results obtained here are also valid for continuum models. The compressibility-EoS of continuum models obtained within the RISM-framework suffers from the same $\omega(l, m, n)$ sensitivity, as do the EoS obtained from other routes: an accurate intramolecular distribution function is also a necessity in obtaining an accurate EoS within the continuum polymer-RISM equation. Such an intramolecular distribution might well be obtained from the approach based on the Curro, Blatz and Pings scheme [71,72]. Another option is to use a self-consistent scheme [57-59], in which an intrinsic coupling of $\omega(l, m, n)$ and $g(l, m, n)$ is established. However, such a scheme is not guaranteed to produce an accurate EoS, unless it incorporates the excluded chain volume up to a high degree.

3.5 Conclusions

In this work we have presented a cubic lattice model of an athermal, i.e., $u_{\text{attr}} = 0$, polymer system that allows to study both the structural and the thermodynamic properties of polymer fluids. The model is a discretized version of the polymer-RISM model of Curro and Schweizer [39]. The results for the structural correlations and the equation of state properties have been compared to $NpT$-Monte Carlo simulation results. The EoS properties are also compared to a classic EoS based on the Huggins approximation. The intermolecular 2-particle distribution compares favorably with simulation results, but the EoS-behavior does not. The EoS obtained thus far are far worse than the EoS obtained on the basis of the Huggins approximation for the same model system. The molecular origin of this failure of the polymer-RISM approach, i.e., the complete (RF) or partial (NRRW) absence of excluded volume in the intramolecular distribution functions, has been detected. This was particularly easy for the lattice model used here, due to the absence of liquid-like packing effects. However, our conclusions remain for the continuum version of the model. The use of a lattice, not only allowed to compare the polymer-RISM theory to a classical lattice polymer theory, but was also convenient from the computational point of view: the structural correlations of the segments on the lattice are very easy to obtain numerically.
References


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Chapter 4

Lattice polymers with nearest neighbor interactions: A comparison between RISM-theory and Monte Carlo simulations

4.1 Introduction

The thermal behavior of fluids, e.g., the equation of state, and the liquid-gas- and liquid-liquid phase behavior, is highly important in the process industry. It can be fully explained from the molecular organization of the fluids, and many molecular theories that predict or describe the thermal behavior of fluids have been constructed [1-3]. In this work we focus on properties of polymeric fluids consisting of molecules that are modelled as a linear sequence of covalently coupled particles (segments). The molecular organization in such fluids can be attributed to three effects among the segments: covalent bonding, and attractive and repulsive interactions.

Integral equation based theories of polymeric fluids offer [4-7], contrary to the more classical cell- [1,8], lattice- [9-12], and hole theories [13-15], the possibility to systematically incorporate the influence of repulsive and attractive interactions and chain-connectivity on the structural correlations present in the fluid. Once the structural correlations between the particles have been calculated from the integral equation framework, the equation of state (EoS) and phase separation properties are obtained from these structural correlations via well established statistical mechanical routes [16]. It is well known that the overall fluid structure, i.e., the sum of the inter- and intramolecular contributions, is largely determined
by the repulsive interactions between the particle cores (packing effects), and that the effects of the attractive interactions and chain-connectivity only appear as perturbations on the structure caused by the repulsions [17]. Fortunately, it is possible to capture the packing effects within an integral equation approach to a high degree of accuracy, as is seen from our knowledge of the structural and equation of state properties [18-21] of the hard sphere model, for which the repulsion between the particle cores is the sole factor that determines the fluid structure. Although of less importance for the overall fluid structure, it is nevertheless very desirable to also incorporate the effects of the attractive interactions and chain-connectivity in a polymer theory, because of the decisive importance of these factors in understanding phase separation phenomena on the basis of the fluid structure. Phase separation phenomena are very important in polymeric fluids, and believed to be dominated by a subtle balance of attractive interactions and chain connectivity effects [22,23], although more recent work has shown that packing effects may also be a contributing factor in the phase separation of polymer fluids [24-27].

The objective of the work in this chapter was to single out the influence of the attractive interactions and chain-connectivity on the structural and thermal properties by removing the effect of the repulsive cores (the packing effect), of which we know that it can be incorporated accurately in integral equation approaches [17,20]. This is possible by discretizing the space available to the fluid on a cubic mesh [28]. In previous chapters it was shown that such a discretization of space provides very clearcut tests of the abilities of the Ornstein-Zernike integral equation [29] to incorporate attractive interparticle interactions [30] and of the polymer-RISM integral equation [4] to incorporate chain-connectivity effects [31]. Here, we extend the work presented in the previous chapter by including attractive interactions in the polymer-RISM formalism. We have calculated the structural correlations, the EoS, and the liquid-gas spinodal from a discretized version of the polymer-RISM model. Thus far, the very important liquid-liquid miscibility behavior is not considered. Liquid-liquid phase separation can certainly be studied within the polymer-RISM equation [32,33], but here we have chosen to consider the closely linked [34] but simpler case of liquid-gas equilibrium first.

Apart from the possibility to study the performance of the polymer-RISM equation without the predominant interference of packing effects, the discretization of space allows to compare the polymer-RISM model with the vast body of existing polymer lattice results [9-12], and simplifies the solution procedure of the polymer-RISM equation significantly. We also mention that it is less CPU-time consuming to perform Monte Carlo simulations, to which we compare the polymer-RISM model, for lattice models.

The contents of the rest of this chapter is as follows. In section 4.2.1 we will
briefly present the polymer-RISM theory for lattice polymers subject to nearest neighbor interactions. We have tested both the Mean Spherical Approximation (MSA) [35] and Percus-Yevick (PY) [36] closure. The solution procedure of the polymer-RISM equation is also briefly outlined in section 4.2.1. Equations of state based on respectively the energy-MSA (e-MSA) [37] and the compressibility-PY (c-PY) [38] route are given in section 4.2.2. Liquid-gas spinodal conditions are briefly recapitulated [34,39] in section 4.2.3. In section 4.3, the \( NpT \)-MC simulations, from which the EoS- and structural properties are extracted, are outlined. The results are presented in section 4.4. Results for the intermolecular 2-particle distribution of Random Flight 30-mers with segmental interaction energies of \( U_{\text{attr}} = 0.0k_B T, -0.05k_B T, \) and \( -0.2k_B T \) are calculated within the MSA- and PY-closure, and comparisons to MC simulations at varying packing fractions \( \eta_m \) are made. Results for the e-MSA and c-PY EoS are compared to \( NpT \)-simulation results, and to the EoS predicted by a Non-Random Mixing polymer theory based on the Quasi-Chemical approximation [12]. Liquid-gas spinodals based on the c-MSA and c-PY route are calculated and compared to the LG-spinodal obtained from the Non-Random Mixing theory [12]. We also present results for the intermolecular 2-particle distribution and the EoS obtained with a somewhat modified intramolecular distribution function. Concluding remarks are drawn in the final section 4.5.

4.2 Polymer-RISM lattice theory

4.2.1 Structural correlations

Consider a cubic lattice fluid consisting of flexible linear molecules that each consist of \( s \) covalently coupled segments. Each segment occupies exactly one lattice site and is subject to a nearest neighbor potential given by

\[
\begin{align*}
  u(0,0,0) & \rightarrow \infty \\
  u(l,m,n) & = u_{\text{attr}} \quad \text{if } l^2 + m^2 + n^2 = 1 \\
  u(l,m,n) & = 0 \quad \text{otherwise} \\
\end{align*}
\]

(4.1)

The structural correlations in the nearest neighbor polymeric lattice fluid can, for long chain molecules \([4,40]\), be characterized by two quantities: a total intermolecular 2-particle correlation, \( h(l,m,n) \), and an intramolecular 2-particle distribution, \( \omega(l,m,n) \). They both are a function of the distance \( (l,m,n) \) between the two particles (segments) under consideration. The total intermolecular correlation can be expressed in terms of the intramolecular distribution function via the polymer-RISM equation \([4]\). In discretized form, it reads

\[
\hat{h}(u,v,w) = \hat{\omega}(u,v,w)\hat{c}(u,v,w)(\hat{\omega}(u,v,w) + \eta_m\hat{h}(u,v,w))
\]

(4.2)
where $\eta_m$ is the packing fraction of the segments. Eq. 4.2 is written in 3D-Fourier space. A Fourier transformation on a 3D cubic lattice is for symmetric functions $f(l, m, n) = f(\pm l, \pm m, \pm n)$ defined by [28]

$$\hat{f}(u, v, w) = \sum_{l,m,n} f(l, m, n) \cos lu \cos mv \cos nw \quad (4.3)$$

The complementary real space quantity $f(l, m, n)$ is then obtained from $\hat{f}(u, v, w)$ by the inverse transformation

$$f(l, m, n) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{f}(u, v, w) \cos lu \cos mv \cos nw dudvdw \quad (4.4)$$

where $f$ can be $h$, $c$, or $\omega$. Thus, $\hat{h}(u, v, w)$ and $\hat{\omega}(u, v, w)$ in Eq. 4.2 are respectively the Fourier transformed intermolecular correlation function and the intramolecular segment-segment distribution. The $\hat{c}(u, v, w)$ is the Fourier transformed direct correlation function.

In a dense polymer melt, the distribution of the segments in a polymer molecule is in a first approximation given by a Random Flight [41]. The $\hat{\omega}(u, v, w)$ is then given by [31,42]

$$\hat{\omega}_{RF}(u, v, w) = \frac{1 - \tilde{\tau}^2 - \frac{1}{2} \tilde{\tau} + \frac{2}{3} \tilde{\tau}^{+1}}{(1 - \tilde{\tau})^2} \quad (4.5)$$

where $\tilde{\tau}(u, v, w) = \frac{1}{3}(\cos u + \cos v + \cos w)$ is the 1-jump probability [42]. In Eq. 4.5 it is enclosed that the positions of the segments of a chain are only dependent on the position of the previous segment. Thus, the RF-chain is not subject to excluded volume interactions. The validity of Eq. 4.5 as a model for the intramolecular structure of linear chains is confirmed experimentally for dense homopolymer melts [43], but is doubted for polymer mixtures [44], and can certainly not be used in polymer solutions [45].

The total real space intermolecular 2-particle distribution $h(l, m, n)$ is obtained from Eq. 4.2 by inverse transformation of $\hat{h}(u, v, w)$ according to Eq. 4.4

$$h(l, m, n) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\hat{\omega}^2(u, v, w) \hat{c}(u, v, w)}{1 - \eta_m \hat{\omega}(u, v, w) \hat{c}(u, v, w)} \cos lu \cos mv \cos nw dudvdw \quad (4.6)$$

It is seen from Eq. 4.6 that $h(l, m, n)$ can be obtained for a Random Flight chain fluid, Eq. 4.5, for known $\eta_m$ and $\hat{c}(u, v, w)$. The real space direct correlation function, $c(l, m, n)$, from which $\hat{c}(u, v, w)$ can be constructed via Eq. 4.3, is given by a closure relation that supplements the discretized polymer-RISM equation. Here, we study the MSA-closure, which reads for the nearest neighbor model of Eq. 4.1 [35]

$$g(0, 0, 0) = 0$$
$$c(l, m, n) = -\beta u_{attr} \quad \text{if } l^2 + m^2 + n^2 = 1$$
$$c(l, m, n) = 0 \quad \text{otherwise} \quad (4.7)$$
and the PY-closure [36]

\[
\begin{align*}
  g(0, 0, 0) &= 0 \\
  c(l, m, n) &= g(l, m, n) \left(1 - e^{\beta u_{\text{attr}}} \right) \quad \text{if } l^2 + m^2 + n^2 = 1 \\
  c(l, m, n) &= 0 \quad \text{otherwise}
\end{align*}
\] (4.8)

where the intermolecular 2-particle distribution, \( g(l, m, n) \), is related to the intermolecular 2-particle correlation, \( h(l, m, n) \), by

\[
  h(l, m, n) = g(l, m, n) - 1
\] (4.9)

The first equation of both closures, the non-overlap condition \( g(0, 0, 0) = 0 \), is physically exact, and assures that segments can not occupy the same lattice site. The second equation in the two closures represents the effect of the attractive interactions on the correlations. We term it the contact relation. The third relation, \( c(0, 0, 0) = 0 \), illustrates that the direct correlation has the same reach as the segment-segment interactions. Note that the attractive interactions are incorporated directly into the RISM-framework via the closure equations. Eqs. 4.5, 4.6, 4.7 or 4.8, and 4.9 form a complete set of equations from which the 2-particle distributions of the nearest neighbor RF-polymer model can be obtained.

The set of equations is solved in the following way. First, \( c(u, v, w) \) is constructed from the closure equation with help of Eq. 4.3. For the MSA-closure we have

\[
  c(u, v, w) = c_0 - 2c_{\text{attr}}(\cos u + \cos v + \cos w)
\]

with \( c_0 = c(0, 0, 0) \). The unknown \( c_0 \) is then found by combining Eq. 4.6 with the non-overlap condition. This gives

\[
-1 = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\hat{\omega}^2(u, v, w) \hat{c}(u, v, w)}{1 - \eta_m \hat{\omega}(u, v, w) \hat{c}(u, v, w)} \, du \, dv \, dw
\] (4.10)

Eq. 4.10 is solved iteratively by a Newton-Raphson procedure combined with a 3D-quadrature routine. Thus, determining the direct correlation function of the nearest neighbor lattice fluid within the MSA-closure amounts to solving only one equation in one unknown. Once \( c_0 \) is known, the total correlation \( h(l, m, n) \) is found from Eq. 4.6.

For the PY-closure, \( c(u, v, w) = c_0 + 2c_1(\cos u + \cos v + \cos w) \) with \( c_0 = c(0, 0, 0) \) and \( c_1 = c(\pm 1, 0, 0) = c(0, \pm 1, 0) = c(0, 0, \pm 1) \). The unknowns \( c_0 \) and \( c_1 \) are found from equations that are constructed by combining Eq. 4.6 with the non-overlap condition and the contact relation

\[
-1 = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\hat{\omega}^2(u, v, w) \hat{c}(u, v, w)}{1 - \eta_m \hat{\omega}(u, v, w) \hat{c}(u, v, w)} \, du \, dv \, dw
\]
Thus, the direct correlation function of the nearest neighbor lattice polymer fluid is found within the PY-closure from solving two equations in two unknowns. The $h(l, m, n)$ is again obtained from Eq. 4.6. Note that the PY- and MSA-closures are identical for athermal systems ($u_{attr} = 0.0k_BT$).

### 4.2.2 Equation of state

In this section we present two ways of obtaining the equation of state of the polymeric lattice fluid. Both routes express the pressure in terms of a single thermodynamic state. They are the compressibility route if the PY-closure is considered, and the energy route if the MSA-closure is considered [37,38].

Let us start by considering the general form of the pressure derived from the lattice compressibility-EoS. It is given by

$$pV_0 = \int_0^{\eta_m} \left( \frac{1}{\hat{\omega}(0, 0, 0)} - \eta_m \hat{c}(0, 0, 0) \right) d\eta_m$$

as was outlined in the previous chapter.

Baxter has shown that it is possible to analytically integrate the equation over the packing fraction if the PY-closure is used to calculate the fluid structure. His expression can also be applied to the nearest neighbor polymer lattice fluid, and is given by

$$pV_0 = \frac{\eta_m}{s} + \frac{\eta_m^2}{2} \left( -2c(0, 0, 0) + 6c(1, 0, 0) \left( \frac{c(1, 0, 0)}{1 - e^{\beta u_{attr}}} - 2 \right) \right) +$$

$$\left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left( \eta_m \hat{\omega}(u, v, w) \hat{c}(u, v, w) + \ln(1 - \eta_m \hat{\omega}(u, v, w) \hat{c}(u, v, w)) \right) dudvdw$$

where $V_0$ is the volume of one lattice site. Eq. 4.13 is more convenient than Eq. 4.12, because in Eq. 4.12 the direct correlation $\hat{c}(0, 0, 0)$ has to be known for all fluid states with packing fractions in between 0 and $\eta_m$, whereas in Eq. 4.13, $\hat{c}(0, 0, 0)$ only has to be known for a single packing fraction $\eta_m$.

Stell and Hoyer [37] have derived an analytical expression for the pressure $p = -(\partial E/\partial V)_{S,N}$ obtained from the energy equation for a monomeric fluid that is
considered within the MSA-equation. Their expression has been generalized to molecular fluids, see e.g., Ref. [46]. For the nearest neighbor polymer fluid the result is given by

\[
\frac{p v_0}{k_B \eta} \left| \frac{p v_0}{k_B \eta} \right|_0 = -\frac{1}{2} s^2 \eta (\bar{c}(0,0,0) - \bar{c}_0(0,0,0)) + \\
- \frac{s}{2(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left( \frac{1}{\eta_m} \ln(1 - \eta_m \hat{\omega}(u,v,w) \bar{c}(u,v,w)) + \right. \\
\left. \frac{\hat{\omega}(u,v,w) \bar{c}(u,v,w)}{1 - \eta_m \hat{\omega}(u,v,w) \bar{c}(u,v,w)} \right) du dv dw + \\
+ \frac{s}{2(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left( \frac{1}{\eta_m} \ln(1 - \eta_m \hat{\omega}(u,v,w) \bar{c}_0(u,v,w)) + \right. \\
\left. \frac{\hat{\omega}(u,v,w) \bar{c}_0(u,v,w)}{1 - \eta_m \hat{\omega}(u,v,w) \bar{c}_0(u,v,w)} \right) du dv dw 
\]  
(4.14)

In Eq. 4.14 \( \eta = \eta_m/s \) is the molecular packing fraction. Quantities which carry a subscript 0 are obtained from the athermal random flight lattice fluid, considered in the previous chapter. It serves as a reference fluid in Eq. 4.14.

The different routes to the EoS of a fluid only produce equivalent answers if the structural correlations are known exactly. Generally, the results obtained from Eqs. 4.13 and 4.14 will be different, due to the approximate nature of the polymer-RISM equation and the closure equations. The size of this thermodynamic inconsistency can be judged from the results presented in section 4.4.

### 4.2.3 Liquid-gas spinodal

Polymeric fluids in principle exhibit a liquid-gas (LG) transition under the appropriate thermodynamic conditions, although in practice the molecules tend to degrade before the temperature is raised high enough for a LG-transition to occur. In this chapter we nevertheless do calculate the LG-spinodal of a 30-mer, because we have a general interest in the accuracy of the thermodynamic properties that can be obtained from the polymer-RISM framework, and also because the liquid-gas phase separation phenomenon in a 1-component fluid is closely related to liquid/liquid miscibility phenomena [34], which are of great importance in polymer mixtures [22,23].

The LG-spinodal is defined by [1]

\[
\left( \frac{\partial^2 A}{\partial V^2} \right)_{N,T} = - \left( \frac{\partial p}{\partial V} \right)_{N,T} = 0 
\]  
(4.15)

It should not be confused with the binodal, which is the line that connects all thermodynamic equilibrium states. The spinodal is the line that separates the
thermodynamic regions in which the fluid is metastable and unstable [1]. Although a fluid with conditions located in the metastable or unstable region will ultimately always phase separate, the distinction between the metastable and unstable region is not purely formal: the phase separation mechanisms of the fluid into a liquid and a gas are noticeably different in the metastable and unstable region [47]. The spinodal and binodal share the critical point, which is the top $(\partial^2 A/\partial V^2)_{N,T} = 0$ of both curves [1]. The temperature $T_c$ belonging to the critical point is the highest temperature for which a LG-transition occurs.

From Eq. 4.15 and the thermodynamic definition for the isothermal compressibility, $\kappa_T = -1/V (\partial V/\partial p)_{N,T}$, we see that $\kappa_T \rightarrow \infty$ at the spinodal. The isothermal compressibility is defined in the RISM-framework by [31]

$$k_B T \eta_m \kappa_T = \left( \frac{1}{\omega(0,0,0)} - \eta_m \bar{c}(0,0,0) \right)^{-1} \quad (4.16)$$

Thus, the compressibility-spinodal condition is given by

$$\frac{1}{\omega(0,0,0)} - \eta_m \bar{c}(0,0,0) = 0 \quad (4.17)$$

Eq. 4.17 is used to obtain the spinodals of nearest neighbor lattice polymers within the MSA- and PY-closures. Due to the approximate nature of the polymer-RISM- and closure-equations, both spinodals will be different.

4.3 Monte Carlo simulation

An $NpT$-simulation method described previously [12] was used for obtaining the inter- and intramolecular 2-particle distributions and the EoS for interacting 30-mers with $u_{\text{attr}} = -0.05 k_B T$ and $-0.2 k_B T$ at varying packing fractions. The simulation details are as described in chapter 3 for the athermal 30-mers [31]. The error bars on the simulation results were generally smaller than the symbols to depict the results. They are therefore omitted in the figures of the next section. The CPU-times needed to equilibrate a melt at a certain pressure were generally longer than for athermal systems. The longest CPU-times for the highest densities ($\eta_m = 0.7$) took up to 30 hours on a RISC IBM 6000 machine. The increase of CPU-time, when compared to athermal systems, is mostly due to the higher packing fractions that interacting systems attain at comparable pressures. The simulation results are available on request via e-mail at tgpken@urc.tue.nl.

4.4 Results and discussion

4.4.1 Structural correlations

In Figs. 4.1-4.4 the 2-particle distributions of interacting $s = 30$-mers are presented for $u_{\text{attr}} = -0.05 k_B T$ at $\eta_m = 0.2885$ (Fig. 4.1) and $\eta_m = 0.5301$ (Fig. 4.2),
Figure 4.1: Intermolecular 2-particle distribution of a $s = 30$-mer at $\eta_m = 0.2885$. The segmental interaction strength is $u_{attr} = -0.05k_BT$. The symbols represent results from MC simulation data. The full- and the dashed line denote respectively the solution obtained with the PY- and MSA-closures for the RF-intramolecular distribution of Eq. 4.5. The long dash-short dash- and dotted lines denote respectively the result obtained with the PY- and MSA-closures for the corrected intramolecular chain distribution of Eq. 4.18.

Table 4.1: Values of the elements in the terms of the corrected intramolecular distribution function of a 30-mer given by Eq. 4.18

<table>
<thead>
<tr>
<th>$\omega_{RF}(l, m, n)$</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{RF}(0, 0, 0)$</td>
<td>1.618743160</td>
</tr>
<tr>
<td>$\omega_{RF}(1, 0, 0)$</td>
<td>0.645332143</td>
</tr>
<tr>
<td>$\omega_{RF}(1, 1, 0)$</td>
<td>0.305167785</td>
</tr>
<tr>
<td>$\omega_{NRRW}(1, 0, 0)$</td>
<td>0.476023356</td>
</tr>
<tr>
<td>$\omega_{NRRW}(1, 1, 0)$</td>
<td>0.239736684</td>
</tr>
</tbody>
</table>

and $u_{attr} = -0.2k_BT$ at $\eta_m = 0.2940$ (Fig. 4.3) and $\eta_m = 0.5681$ (Fig. 4.4). The intermolecular distribution, $g(l, m, n)$, obtained from the simulations are denoted by the symbols ($\bullet$). The calculated $g(l, m, n)$ are indicated by the lines. All $g(l, m, n)$ are plotted as $g(r)$ with $r = \sqrt{l^2 + m^2 + n^2}$ for notational convenience [31]. Notice that the non-isotropic character of the cubic lattice shows up in the simulations and calculations of Figs. 4.1-4.4 as $g(\sqrt{3}) \approx g(2)$ [31]. In Figs. 4.1-
4.4 the PY- and MSA-closures are denoted by respectively the full and dashed line. The intramolecular distribution that was used to calculate both lines is the Random Flight distribution given by Eq. 4.5. Results obtained with a somewhat modified intramolecular distribution function, presented in Eq. 4.18, are also depicted. As a first approximation to improve upon the RF-intramolecular distribution function, we subjected $\hat{\omega}_{RF}(u,v,w)$ to a correction of its first few terms, viz.

$$
\dot{\omega}_{corr}(u,v,w) = (1 - \omega_{RF}(0,0,0)) + \\
2(\omega_{NRRW}(1,0,0) - \omega_{RF}(1,0,0)) (\cos u + \cos v + \cos w) + \\
4(\omega_{NRRW}(1,1,0) - \omega_{RF}(1,1,0)) (\cos u \cos v + \cos u \cos w + \cos v \cos w) + \hat{\omega}_{RF}(u,v,w)
$$

From $\hat{\omega}_{RF}(u,v,w) = \sum_{l,m,n} \omega_{RF}(l,m,n) \cos lu \cos mv \cos nw$ (see Eq. 4.3 for $f = \omega$) it is seen that the first term in Eq. 4.18, $(1 - \omega_{RF}(0,0,0))$, corrects for the particle overlaps that are inherent in the full RF-intramolecular distribution $\hat{\omega}_{RF}(u,v,w)$. The other two terms have the effect that $\omega_{RF}(1,0,0)$ and $\omega_{RF}(1,1,0)$ are replaced by respectively $\omega_{NRRW}(1,0,0)$ and $\omega_{NRRW}(1,1,0)$, which are the values of the intramolecular distribution of a Non Reversal Random Walk [41]. These values are more realistic than those given by $\omega_{RF}(1,0,0)$ and $\omega_{RF}(1,1,0)$ for, the unphysical, back-folding of segment $i + 1$ on segment $i - 1$ is excluded in a NRRW- and not in a RF-chain. The values of the terms that appear
Figure 4.3: Caption as in Fig. 4.1 but for $\eta_m = 0.2940$ and $u_{attr} = -0.2k_B T$.

Figure 4.4: Caption as in Fig. 4.1 but for $\eta_m = 0.5681$ and $u_{attr} = -0.2k_B T$. 
in Eq. 4.18 are obtained by enumeration of all possible chain conformations as is briefly outlined in Appendix A. Their numerical values are given in Table 4.1.

Note from Eq. 4.18 that \( w_{corr}(u, v, w) \) is not correctly normalized to the length of the molecules under consideration, i.e., \( w_{corr}(0,0,0) \neq 30 \). It would have been more correct to renormalize the tail contribution of \( w_{corr}(0,0,0) \) such that \( w_{corr}(0,0,0) = 30 \). We have not undertaken such a normalization, for the results obtained with the corrected intramolecular distribution are only meant as a first indication of the influence of the intramolecular distribution function on the structural and thermodynamic properties. We have studied higher order corrections than given in Eq. 4.18, but their influence on the structural- and EoS-properties were marginal, indicating that the lower order terms of the intramolecular distribution function, which correspond to the smallest interparticle distances, are most influential. This was also found in previous work on athermal polymers [31], in which a complete neglect of all terms of the intramolecular distribution function for \( \sqrt{r^2 + m^2 + n^2} > 4 \) still lead to reasonably accurate predictions for the intermolecular 2-particle distributions. The results for the intermolecular distribution function obtained with the corrected intramolecular distribution function of Eq. 4.18 are indicated in Figs. 4.1-4.4 by the dotted line (MSA-closure) and the long dash-short dashed line (PY-closure).

By comparing to the MC simulation data (●) in Figs. 4.1-4.4, we see that the intermolecular distributions predicted by the polymer-RISM equation for the RF-intramolecular distribution of Eq. 4.5 are far from accurate (full and dashed line) for both closures that were studied. Especially in the fluid with stronger attractions between the segments, \( u_{attr} = -0.2k_BT \), it is seen that the calculated and simulated intermolecular distributions differ greatly (see Figs. 4.3 and 4.4). For the weakly interacting systems, \( u_{attr} = -0.05k_BT \), the difference between the simulations and calculations is smaller, although significant disparities are still observed at the lower density (see Fig. 4.1).

If the corrected intramolecular distribution is inserted in the polymer-RISM equation, Eq. 4.2, we see by comparing the intermolecular distributions obtained with \( \omega_{RF}(u,v,w) \) and \( \omega_{corr}(u,v,w) \), that there is a very strong influence of the precise form of the intramolecular 2-particle distribution on the intermolecular 2-particle distribution, especially for \( u_{attr} = -0.2k_BT \). In the case of the MSA-closure, the use of \( \omega_{corr}(u,v,w) \) results in an improvement of the calculated intermolecular distribution function (compare dashed and dotted lines in Figs. 4.1-4.4). In the case of the PY-closure there is a shift from a too high to a too low contact value \( g(l,O,O) \) upon changing from \( \omega_{RF}(u,v,w) \) to \( \omega_{corr}(u,v,w) \), and no real improvement is observed (compare full and long dash-short dashed lines in Figs. 4.1-4.4).

In chapter 3 it was shown for athermal lattice fluids that the exact type of intramolecular distribution function used in the polymer-RISM equation is of little influence on the intermolecular distribution. The three different intramolecular distributions that were tested in that chapter, all produced an accurate intermolecular distribution upon insertion in the polymer-RISM equation [31]. But,
from Figs. 4.1-4.4 it is seen that the intermolecular distribution shows an increased sensitivity for the exact form of the intramolecular distribution upon the introduction of attractive interactions: the sensitivity of $g(l, m, n)$ on $\omega(l, m, n)$ grows with increasing segmental interaction strength. We observe a gradual deterioration of the intermolecular distribution for increasing segmental interaction strength for both $\hat{\omega}_{RF}(u, v, w)$ and $\hat{\omega}_{corr}(u, v, w)$. Clearly, for interacting systems, it is an absolute necessity to have an accurate intramolecular distribution function if one wants to calculate the intermolecular distribution function. From the results presented in this section it is seen that especially the lower order terms of the intramolecular distribution function need to be precise. An accurate intramolecular distribution may be partially extracted from MC-simulations, or can be obtained from a self-consistent scheme [48,49], although such a scheme is less likely to produce accurate results because it is not yet possible to construct an intramolecular distribution function from a theoretical analysis that fully accounts for the excluded volume interaction of polymer molecules.

Before we turn to the equation of state behavior, we want to mention that even if we succeed in obtaining an accurate description of the intramolecular distribution function of an interacting polymeric lattice fluid, there is still doubt about the applicability of the RISM approach to such relatively strongly interacting systems in which the correlations are more pronounced: the very primitive RISM equation was originally devised to study the structure of weakly correlated systems [50].

4.4.2 Equation of state

In Fig. 4.5-4.7 the equations of state for 30-mers with segment-segment interactions of respectively $u_{attr} = -0.0k_BT$, $-0.05k_BT$, and $-0.2k_BT$ are shown. The symbols are obtained from $NpT$-simulations, and the dotted line in the figures is obtained from Eq. 16 of Ref. [12]. It is a Non-Random Mixing equation of state based on the Quasi-Chemical approximation [51]. It is seen in the figures that the NRM equation performs well in the three cases considered here. The full- and short dashed-line in Fig. 4.5 are reproduced from previous work [31], and show the EoS that are obtained for respectively the RF- and NRRW-intramolecular distribution. The NRRW-intramolecular 2-particle distribution produces an improved compressibility-EoS when compared to the RF-intramolecular 2-particle distribution, because excluded volume is partially taken into account in the NRRW-chain, in contrast with the RF-chain. In the previous chapter this was shown to be very important for the EoS-behavior [31]. The RF- and NRRW-EoS are reproduced in Fig. 4.5, because we want to compare them to the EoS based on $\hat{\omega}_{corr}(u, v, w)$ of Eq. 4.18 (long dashed line in Fig. 4.5). Note that $\hat{\omega}_{corr}(u, v, w)$ produces a more accurate EoS than the NRRW-intramolecular distribution, although $\hat{\omega}_{NRRW}(u, v, w)$ is only different from the RF-distribution in the first three terms (see Eq. 4.18). This is because in Eq. 4.18, we have set the first term of the corrected intramolecular distribution function to the physically correct value
Figure 4.5: Equation of state of athermal $s = 30$-mers. The symbols are obtained from MC-simulation, and the dotted line is obtained from Eq. 16 of Ref. [12]. The full-, short dashed-, and long dashed-lines are obtained from Eq. 4.13 for respectively the RF-, NRRW-, and corrected RF-intra molecular chain distribution.

of $\omega_{\text{corr}}(0,0,0) = 1$, while $\omega_{\text{NRRW}}(0,0,0) > 1$ (a NRRW-chain is subject to intramolecular particle overlaps). This illustrates the importance of an accurate intramolecular distribution function for small segmental distances in predicting an EoS. Note that for each intramolecular distribution function we only show one line in Fig. 4.5: the PY- and MSA-closures are identical in case of athermal fluids, and the e-MSA EoS reduces to the c-PY EoS. In Fig. 4.6, the EoS of a weakly interacting ($u_{\text{attr}} = -0.05k_B T$) 30-mer is shown. Clearly, the use of the corrected intramolecular distribution function of Eq. 4.18 results for both the c-PY and the e-MSA route in a significant improvement of the predicted EoS. Note the strong sensitivity of the EoS on the intramolecular 2-particle distributions: changing the first three terms of $\omega_{RF}(u,v,w)$ according to Eq. 4.18 results in a dramatic improvement of the EoS. In Fig. 4.7, the EoS for a more strongly interacting ($u_{\text{attr}} = -0.2k_B T$) 30-mer fluid is depicted. Note first from Fig. 4.7 (although this is also true for Figs. 4.5 and 4.6), that the pressures calculated with $\hat{\omega}_{RF}(u,v,w)$ do not rise to infinity at $\eta_m \rightarrow 1$. This is due to the absence of excluded volume in $\hat{\omega}_{RF}(u,v,w)$ [31], and is also true for pressures obtained with the corrected intramolecular distribution function, $\hat{\omega}_{\text{corr}}(u,v,w)$, in which excluded chain volume is only very crudely taken into account. In spite of the crude incorporation of the excluded chain volume, the use of the corrected intramolecular
Figure 4.6: Equation of state of a 30-meric cubic lattice fluid for a segmental interaction energy $u_{\text{attr}} = -0.05k_B T$. The symbols are obtained from MC-simulation, and the dotted line is governed by Eq. 16 of Ref [12]. The full- and dash-dot line are obtained from Eq. 4.13 (c-PY route) for respectively the RF- and corrected RF-intramolecular chain distribution. The dashed and long dashed lines are obtained from Eq. 4.14 (e-MSA route), again for respectively the RF- and corrected RF-distribution.

distribution of Eq. 4.18 results in a large improvement of the EoS in Fig. 4.7 and Figs. 4.5 and 4.6, which illustrates the importance of the incorporation of excluded volume in the intramolecular distribution function for the prediction of an accurate EoS. Although the EoS is largely improved upon using the corrected intramolecular distribution function, it is seen by comparing Fig. 4.7 to Figs. 4.5 and 4.6 that the overall consistency of the calculated EoS deteriorates with increasing segmental interaction strength, $u_{\text{attr}}$: the size of the thermodynamic consistency problem is huge for interacting polymer systems. The sensitivity of the e-MSA and c-PY-EoS on the intramolecular distribution is such strong for interacting polymer systems that it must be doubted whether the polymer-RISM theory in the form used here will ever produce an accurate EoS for interacting lattice systems, even for a very accurate intramolecular distribution function. The results presented here strongly suggest the need for closures that reduce the sensitivity of the structural correlations and the EoS on the intramolecular distribution function. The molecular closures presented in Refs. [52,53] might be good candidates to accomplish this, but thus far, we have not tested the merits of these closures on the lattice.
We think that the above mentioned problems also apply to the continuum space version of the polymer-RISM theory: although the situation might be a little better in continuum space because in such systems liquid-like ordering effects, that are absent on the lattice, largely determine the EoS- and structural properties, we expect it to be difficult to construct an accurate continuum space EoS, for excluded volume effects and interactions are not treated differently in the continuum version of the polymer-RISM model.

4.4.3 Liquid-Gas spinodal

In Fig. 4.8 we show the compressibility-MSA and c-PY liquid-gas spinodals for 30-mers calculated along the lines outlined in section 4.2.3. Both curves were obtained with the RF-intramolecular chain distribution given by Eq. 4.5. Thus far, we have not calculated the spinodals with the corrected intramolecular distribution given by Eq. 4.18. The c-MSA and c-PY spinodals are compared to the LG-spinodal calculated with the Non-Random mixing (NRM) theory of Ref. [12]. This theory produces (see Figs. 4.5-4.7) an accurate EoS for polymeric lattice fluids. Thus far, the LG-phase separation data of the NRM theory of Ref. [12] are not compared to MC-simulation results. In Ref. [54] it is shown that the LG-binodal data of a slightly different model based on the NRM-theory compare reasonably well to MC-data. In Ref. [55] it is shown by comparison to semi-grand canonical MC simulations that the NRM model of Ref. [12] does reasonably accu-
Figure 4.8: Liquid-gas spinodals for a cubic lattice fluid consisting of 30-mers. The dotted line is obtained from the Non-Random mixing theory of Ref. [12]. The full- and dashed lines are obtained within the polymer-RISM framework via respectively the compressibility-PY and compressibility-MSA route. Both the c-PY and c-MSA spinodals are calculated with help of the RF-intramolecular distribution.

rately reproduce the binodal for the closely linked liquid-liquid mixing/demixing phenomenon. Hence, we have reasons to believe that the LG-spinodal of the NRM-theory in Fig. 4.8 is reasonably accurate.

Apart from the fact the locations of the c-PY- and c-MSA-spinodal are quite far from the NRM-spinodal, the c-PY spinodal (full curve) and the c-MSA spinodal (dashed curve) also display more severe problems. The c-MSA spinodal cuts \( \eta_m = 1 \) at finite \( u_{\text{attr}} \), indicating that there is a spinodal point at a finite segmental interaction strength on a fully packed lattice. This is clearly unphysical, because the isothermal compressibility should be zero for such an incompressible situation and not infinite, which is the value needed to find a spinodal point (see Eqs. 4.16 and 4.17). The anomaly is caused by the absence of excluded volume in the RF-intramolecular distribution used to calculate the c-MSA spinodal: due to the intramolecular segmental overlaps that are present if \( \hat{\omega}_{RF}(u, v, w) \) is used, empty- and doubly occupied sites occur at \( \eta_m \rightarrow 1 \), resulting in a non-zero compressibility. Improvements can certainly be expected for intramolecular 2-particle distributions which do include the intramolecular excluded volume up to some extent.

The c-PY closure also cuts \( \eta_m = 1 \) at finite segmental interaction strength. The
same reasoning applies, and improvements will certainly be obtained for improved intramolecular distribution functions. The c-PY spinodal also cuts $\eta_m = 0$ at finite segmental interaction strength. This is also an anomaly, for interactions between molecules do not occur in such an infinitely diluted gas, the infinitely large distances between the molecules prevent the molecules to interact with each other, which makes a LG-transition impossible. This anomaly is linked to the use of the PY-closure [56], and is not related to the use of a primitive intramolecular 2-particle distribution, as is clear from the fact that the phenomenon is also observed in monatomic simple lattice- [30] and continuum fluids [57]. Hence, the PY-closure is fundamentally not suitable to investigate liquid-gas separation (and the closely related phenomenon of liquid-liquid phase separation [58]). The inappropriateness of the PY-closure to calculate the LG-spinodal via the compressibility route is illustrated in Fig. 4.9, where the inverse structure factor at zero wave vector, defined by $S^{-1}(0,0,0) = (\sum_{l,m,n} \omega(l,m,n) + \eta_m h(l,m,n))^{-1}$, is plotted versus $\eta_m$ at constant $u_{\text{attr}}$. As is seen from its definition and Eqs. 4.2 and 4.16, $S^{-1}(0,0,0)$ is directly proportional to $\kappa_T^{-1}$. Thus, a spinodal point corresponds to $S^{-1}(0,0,0) = 0$. The curve that can be drawn through the open circles in Fig. 4.9 forms a trace of subsequent thermodynamic states, taken at fixed $u_{\text{attr}}$, with a decreasing value of $S^{-1}(0,0,0)$, that ultimately ends, as can be checked from Fig. 4.8, on the gaseous branch of the spinodal if $S^{-1}(0,0,0) = 0$. 

![Figure 4.9: Dependence of the inverse structure factor at zero wave vector on the packing fraction $\eta_m$ of a 30-mer lattice fluid at $u_{\text{attr}} = -0.32k_BT$. The $S^{-1}(0,0,0)$ is calculated within the PY-closure.](image-url)
In Fig. 4.9 it is seen that if $S^{-1}(0,0,0)$ is plotted versus packing fraction $\eta_m$ at fixed $u_{attr}$, a non-functional form is obtained (note that we have partially plotted $S^{-1}(0,0,0)$ at negative $\eta_m$, which is necessary because the gaseous branch of the spinodal in Fig. 4.8 cuts $\eta_m = 0$). Thus, the result of Fig. 4.9 contradicts thermodynamics, which states that the free energy, $A(\eta_m; u_{attr})$, and its derivatives with respect to $\eta_m$ and $u_{attr}$, e.g., $S^{-1}(0,0,0)$, are state-functions [1]. Hence, Fig. 4.9 indicates that the gaseous branch of the LG-spinodal obtained via the c-PY route has no physical meaning. If an $S^{-1}(0,0,0)$-trace that ends at the liquid branch is followed at $u_{attr} = \text{const}$, no anomalies are observed. Results for the liquid branch of the spinodal can thus not be rejected on physical grounds.

4.5 Conclusions

In this work we have extended the discretized polymer-RISM model of Ref. [31] to incorporate attractive nearest neighbor interactions between the segments of flexible, linear polymeric molecules on a cubic lattice. As intramolecular 2-particle distribution, $\omega(l, m, n)$, an input quantity in the polymer-RISM model, we have chosen the distribution belonging to a Random Flight chain. The results for the intermolecular 2-particle distribution, $g(l, m, n)$, obtained within the PY- and MSA-closures, are shown to gradually worsen with increasing interparticle attraction, $u_{attr}$, when compared to $NpT$-MC simulation results. It was also shown that small changes of that part of the intramolecular distribution function that is determined by the small interparticle distances, $r = \sqrt{l^2 + m^2 + n^2} \leq 2$, have a tremendous effect on the intermolecular 2-particle distribution. The effect increases with $u_{attr}$, indicating a strong sensitivity of $g(l, m, n)$ on $\omega(l, m, n)$ for nearest neighbor lattice fluids. This sensitivity requires the input of a very accurate $\omega(l, m, n)$ in the polymer-RISM equation. Such an intramolecular distribution can, most probably, only be obtained with help of Monte Carlo simulation.

Equations of state, calculated from the compressibility-PY- and energy-MSA-route have also been presented. They are also shown to be very sensitive to the exact form of $\omega(l, m, n)$. We again observe that the sensitivity increases with attractive interaction energy.

We have also presented some results for the liquid-gas spinodal of 30-mer cubic lattice fluids. Although LG-phase separation is not of vital importance in polymeric fluids, it is worthwhile to investigate, because of its close relation with the very important liquid-liquid miscibility behavior of polymeric fluids. The spinodals that we have obtained were based on the compressibility-PY- and compressibility-MSA route. Both routes produce different spinodals, due to the thermodynamic inconsistency that is inherent to the polymer-RISM approach. The c-MSA and c-PY closures both show unphysical effects. In case of the c-MSA spinodal the problems are related to the absence of excluded volume in the
intramolecular distribution. In case of the c-PY spinodal the problems are more fundamental, and linked to the use of the closure itself [30,56,57].

In conclusion, the polymer-RISM theory as used in the form presented here, is not able to incorporate attractive interactions between the molecule-segments, and produces an EoS that can not meet the comparison with conventional work on lattices [12]. The strong sensitivity of the structural and thermodynamic properties on the intramolecular distribution function is a very serious problem of which we expect that it can not easily be cured: more accurate intramolecular distribution functions that might be obtained with help of MC-simulations or a self consistent scheme [48,49], are certainly important, but do not cure the sensitivity of the polymer-RISM theory on \( \omega(l,m,n) \). A better approach seems to try to find closures which reduce the sensitivity of \( g(l,m,n) \) and the thermodynamic properties on \( \omega(l,m,n) \). The molecular closures of Refs. [52,53] should be tested for this.
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Chapter 5

Polymeric lattice fluids near hard and interacting walls:
A comparison of discretized polymer-RISM theory and Monte Carlo simulations

5.1 Introduction

Polymer adsorption is an interesting phenomenon with wide applications in e.g., composite- and coatings industry. An understanding of the molecular origins of the adsorption phenomenon is therefore beneficial in optimizing processes in these industries.

Classical approaches to study polymer adsorption build on work performed on bulk lattice-[1,2] and continuum fluids [3,4]. Well known lattice theories to study the adsorption of a polymeric fluid at a solid wall are the theories of Helfand [5,6], and Scheutjens and Fleer [7-9]. An important aspect of these theories is that they account for the changes in conformational entropy of the molecules in the interfacial region, that occur due to the presence of the wall. Well known theories that consider the adsorption of a continuum space polymeric fluid at a solid wall are the theories of Helfand [10], and Hong and Noolandi [11]. These continuum approaches use Gaussian Random Walk (GRW) chain statistics to describe the polymer chain conformations in the interfacial region. GRW-chain statistics applies in the bulk of dense 1-component fluids [12], but is not suited for situations that deviate strongly from the bulk circumstances. Hence, the theories of Refs. [10,11] are less suited in case strong wall-fluid interactions cause the interfacial region to be very different from the bulk of the fluid.
In this chapter we investigate an approach to the polymer adsorption phenomenon that does not build on the work of Refs. [1-4]. It is based on integral equations that describe the correlations of the fluid particles with the adsorbing wall. Several of such approaches have been presented [13-17]. They mostly consider the adsorption of monatomic spherical particles [13-16], only the study of Yethiraj and Hall considered the adsorption of large flexible polymeric molecules [17]. Their method to calculate the adsorption profiles of a polymeric fluid near a solid impenetrable wall is an extension of the polymer-RISM theory, that considers the correlations between the molecules in the bulk of a polymeric fluid [18]. The adsorption version of the polymer-RISM theory uses the concept of an intramolecular distribution, \( \omega(r_1, r_2) \), to describe the conformations of the polymer molecules near the solid wall [19]. As is the case in the continuum theories of Refs. [10,11], the effects of the wall on the chain conformation are not taken into account. Therefore, it is expected that the theory will deteriorate with increasing wall-segment interaction.

The study of Yethiraj and Hall in Ref. [17] is concerned with the adsorption of a continuum fluid. Here, we want to study the adsorption from a cubic lattice fluid with the same method. This allows for comparison with a classical lattice model, the Scheutjens-Fleer theory [7]. The calculated adsorption profiles are also compared against \( NpT \)-Monte Carlo simulation data that provide us with exact reference material. The results for the adsorption profiles presented here, only concern non-interacting impenetrable walls. Further, the adsorption profiles are employed to obtain an equation of state (EoS) of the bulk fluid via the method of Dickman [20]. The results for the EoS are also compared to the simulation data.

The outline of the rest of this chapter is as follows. In section 5.2.1 the method of Henderson, Abraham, and Barker [13] for introducing a solid wall in an integral equation formalism, is applied to a discretized version of the polymer-RISM equation, employed previously to study the structural properties of bulk lattice fluids [21,22]. It will become clear that the method is particularly easy to employ in the case of a cubic lattice fluid. The principal results of section 5.2.1 are expressions for the adsorption profiles and isotherms of a polymeric lattice fluid consisting of linear chains. Attention is focussed on the adsorption of a 1-component fluid consisting of linear molecules, but is is briefly outlined how competitive adsorption, e.g., of a mixture of ring and chain molecules, or of a mixture of chain molecules of different size, can be studied. In section 5.2.2 the solution procedure is outlined. It is demonstrated that the solution method is particularly easy, it only takes the solution of two equations in two unknowns to obtain the adsorption profile. In section 5.2.3 we will briefly recapitulate the method used by Dickman to extract an EoS of the bulk fluid from the adsorption profiles. In section 5.3 the MC-simulation is outlined. Thus far, we have only performed \( NpT \)-simulations for 30-mers at a non-interacting wall. Chains with segmental interaction energies of \( u_{\text{attr}} = -0.0k_BT, -0.05k_BT, \) and \(-0.2k_BT\) have
been tested. In section 5.4 we present the results for the calculated adsorption profiles, and compare them to the simulation results and the adsorption profiles calculated from the Scheutjens-Fleer theory. We also present results for the EoS of the bulk fluid. Conclusions are collected in section 5.5.

5.2 Polymer-RISM theory for lattice fluids near a solid wall

5.2.1 Outline of the method

In this section the discretized version of the polymer-RISM equation [21-23] is modified to enable the calculation of the adsorption profiles of polymeric lattice fluids at an impenetrable wall. The method [13] was originally used to study the behavior of a simple fluid near an impenetrable wall, and was later applied to study adsorption within the polymer-RISM theory [17]. The general principle of the method is as follows. First, the polymer-RISM equation for a mixture of two molecule types, simple monatomic particles and polymeric molecules, is written down. Secondly, the concentration of the simple fluid particles is reduced to zero to ensure that these particles do not influence each other. In a last step, the simple particles are extended in two directions such that they turn into a wall. Then, construction of the adsorption profile of the polymer molecules at the wall amounts to calculating the correlations between the wall and an average polymer segment. From the adsorption profile the amount of adsorbed material can be quantified by construction of an adsorption isotherm.

Consider a mixture of two particle types, simple monatomic particles that occupy exactly one lattice site, and linear polymer chains. The chains consist of $s$ covalently bonded segments that occupy consecutive nearest neighbor sites on the lattice. The monatomic particles and the segments of the polymer molecules interact via nearest neighbor potentials given by

\[
\begin{align*}
    u_{ij}(0,0,0) & \rightarrow \infty \\
    u_{ij}(l,m,n) & = u_{\text{attr},ij} \quad \text{if } l^2 + m^2 + n^2 = 1 \\
    u_{ij}(l,m,n) & = 0 \quad \text{otherwise}
\end{align*}
\]

(5.1)

where \(\{i,j\} \in \{1,2\}\) denote the particle type: \(i = 1\) corresponds to a monatomic particle, and \(i = 2\) to a segment of a polymer chain.

The structural correlations present in such a mixture of particles can be studied with the polymer-RISM equation for mixtures. It can conveniently be written down in matrix form [18], and is given by

\[
\tilde{H}(u,v,w) = \tilde{\Omega}(u,v,w)\tilde{C}(u,v,w) \left( \tilde{\Omega}(u,v,w) + \tilde{H}(u,v,w) \right)
\]

(5.2)
in which $\mathbf{H}$, $\mathbf{Q}$, and $\mathbf{C}$ are $2 \times 2$ matrices with elements $\eta_{mi} \eta_{mj} \hat{h}_{ij}(u,v,w)$, $\eta_{mi} \eta_{mj} \hat{c}_{ij}(u,v,w)$ and $\hat{c}_{ij}(u,v,w)$. The symbols $\eta_{m1}$ and $\eta_{m2}$ denote respectively the packing fractions of monatomic particles, and of the segments of the polymeric molecules. The Kronecker delta, $\delta_{ij}$, has a value 1 if $i = j$ and 0 otherwise. The $\hat{h}_{ij}(u,v,w)$, $\hat{c}_{ij}(u,v,w)$ and $\hat{c}_{ij}(u,v,w)$ represent respectively the total intermolecular 2-particle correlation function, the intramolecular 2-particle distribution, and the direct correlation function. The $\hat{h}_{ij}(u,v,w)$, $\hat{c}_{ij}(u,v,w)$, and $\hat{c}_{ij}(u,v,w)$ are written in 3D Fourier space, defined by

$$\hat{f}(u,v,w) = \sum_{l,m,n} f(l,m,n) \cos lu \cos mv \cos nw$$

with $f = h, \omega$, or $c$. Eq. 5.3 is only valid if the symmetry conditions $f(l,m,n) = f(\pm l, \pm m, \pm n)$ apply. The real space analogs of $\hat{h}_{ij}(u,v,w)$, $\hat{c}_{ij}(u,v,w)$, and $\hat{c}_{ij}(u,v,w)$ can then be found from the inverse transformation

$$f(l,m,n) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{f}(u,v,w) \cos lu \cos mv \cos nw \ du \ dv \ dw$$

The meaning of the real space direct correlation function, $c_{ij}(l,m,n)$, is merely mathematical, in contrast with $h_{ij}(l,m,n)$ and $\omega_i(l,m,n)$. The $h_{ij}(l,m,n)$ is the total intermolecular correlation function. It is related to the probability $P_{ij}(l,m,n)$ of finding a particle $j$ at distance $(l,m,n)$ from another particle $i$ that is part of a different molecule, via $P_{ij}(l,m,n) = \eta_{mj}(h_{ij}(l,m,n) + 1)$. The $\omega_i(l,m,n)$ is the intramolecular 2-particle distribution function. For the monatomic particles the only non-zero term is $\omega_1(0,0,0) = 1$, but in case of flexible polymer molecules $\omega_2(l,m,n)$ gives the packing fraction of segments located at $(l,m,n)$ from a segment that belongs to the same molecule. If the polymer molecules are considered to be Random Flights, which is a reasonable first approximation [12,23], then $\hat{\omega}_2(u,v,w)$ is given by [21,25,26]

$$\hat{\omega}_{2,RF}(u,v,w) = \frac{1 - \hat{\tau}^2 - \frac{2}{3} \hat{\tau} + \frac{2}{3} \hat{\tau}^2 + 1}{(1 - \hat{\tau})^2}$$

in which $\hat{\tau}(u,v,w) = (\cos u + \cos v + \cos w)/3$ is the Fourier transform, Eq. 5.3, of the 1-jump probability given by

$$\tau(l,m,n) = \begin{cases} 1/6 & \text{if } l^2 + m^2 + n^2 = 1 \\ 0 & \text{otherwise} \end{cases}$$

From Eq. 5.6 it is clear that only polymer conformations that consist of a sequence of jumps between nearest neighbor sites are allowed. If we are interested in the adsorption of ring-shaped molecules, Eq. 5.5 has to be replaced by

$$\hat{\omega}_{2,ring}(u,v,w) = \frac{1 + \hat{\tau}^2 - \frac{2}{3} \hat{\tau} + \frac{2}{3} \hat{\tau}^2 + 1}{1 - \hat{\tau}}$$

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as can be derived from the analysis presented in chapter 3. Note that Eq. 5.2 can be used to study the structural properties of polymer mixtures, if we replace the monatomic particles 1 by a second type of polymer molecules. Studies of polymer mixtures based on Eq. 5.2 have been presented in Refs. [18,27-30]. In this work we only use Eq. 5.2 to study the adsorption of a polymeric lattice fluid. For that purpose we perform the matrix multiplications in Eq. 5.2 and take the limit $\eta_{m1} \to 0$. A set of 4 equations results. It is given by

$$
\hat{h}_{11}(u,v,w) = \omega_1(u,v,w)\hat{c}_{11}(u,v,w)\omega_1(u,v,w) + \\
\eta_{m2}\omega_1(u,v,w)\hat{c}_{12}(u,v,w)\hat{h}_{21}(u,v,w) \\
\hat{h}_{12}(u,v,w) = \omega_2(u,v,w)\hat{c}_{12}(u,v,w)\omega_2(u,v,w) + \\
\eta_{m2}\omega_1(u,v,w)\hat{c}_{12}(u,v,w)\hat{h}_{22}(u,v,w) \\
\hat{h}_{21}(u,v,w) = \omega_2(u,v,w)\hat{c}_{21}(u,v,w)\omega_2(u,v,w) + \\
\eta_{m2}\omega_2(u,v,w)\hat{c}_{22}(u,v,w)\hat{h}_{21}(u,v,w) \\
\hat{h}_{22}(u,v,w) = \omega_2(u,v,w)\hat{c}_{22}(u,v,w)\omega_2(u,v,w) + \\
\eta_{m2}\omega_2(u,v,w)\hat{c}_{22}(u,v,w)\hat{h}_{22}(u,v,w)
$$

The particles of type 1 are monomers, thus, from $\omega_1(0,0,0) = 1$ and Eq. 5.3, we have $\hat{\omega}_1(u,v,w) = 1$. The first equation of the set Eq. 5.8 describes the correlations between the simple fluid particles in the mixture. It is of no interest to us here: the concentration of simple fluid particles $\eta_{m1}$ was reduced to zero to exclude encounters of such particles, which guarantees that the other correlations in the mixture are independent of the correlations between the simple fluid particles. The second and third equation in Eq. 5.8 both denote the correlations between a simple fluid particle and a polymer segment, and the fourth equation governs the correlations occurring between two average segments of two different polymer molecules. Note that the fourth equation is identical to the polymer-RISM equation [23] that was studied in the previous chapters for the athermal polymeric lattice fluid [21] and the nearest neighbor lattice fluid [22]. This equation determines the bulk structural properties of the polymeric molecules of type 2, and can be solved separately from the three other equations in Eq. 5.8 with the method outlined in the previous chapters. The results for the bulk structural quantities of the polymeric fluid, $\hat{h}_{22}$, $\hat{c}_{22}$ and $\hat{\omega}_2$, are subsequently used as input quantities in the calculation of the adsorption profile of the polymeric fluid from the second equation of Eq. 5.8. Instead of the second equation we can also take the third equation of Eq. 5.8 to accomplish this, because both equations produce equivalent answers for symmetry reasons. Here, we choose to use the second. Before the adsorption profiles can be calculated from $\hat{h}_{12}(u,v,w)$, some rearrangements have to be made. First, it is written in real space form as

$$
\hat{h}_{12}(l,m,n) = \sum_{l',m',n'} (\omega_1(l',m',n')+\eta_{m2}\hat{h}_{22}(l',m',n'))c_{12}(l-l',m-m',n-n')
$$
The monatomic particle 1 can then effectively be extended in \(m\)– and \(n\)–direction by removing the \(m\)– and \(n\)–coordinates in \(h_{12}(l, m, n)\) and \(c_{12}(l, m, n)\): only the \(l\)–distance to particle 1 remains to be a positional parameter, and therefore, the particle turns into a wall [13]. Hence, from Eq. 5.9 we obtain

\[
h_{12}(l) = \sum_{l', m', n'} (\omega_2(l', m', n') + \eta_{m2} h_{22}(l', m', n')) c_{12}(l - l')
\]

(5.10)

In Eq. 5.10, it is particle 1 and not the segment of the polymer molecule, 2, that is transformed into a wall, as is seen from \(\omega_{22}\) and \(h_{22}\) which are still dependent on three coordinates \(l\), \(m\), and \(n\). Note that the creation of a wall, in going from Eq. 5.9 to Eq. 5.10, is particularly easy on the cubic lattice, which is due to the independence of \(l\), \(m\), and \(n\). This is in contrast to the continuum space analog of the fluid presented here, in which, due to the use of the particle-particle distance \(r = \sqrt{l^2 + m^2 + n^2}\) as an independent coordinate, bipolar coordinates have to be involved in the extension of the simple fluid particle.

Eq. 5.10 is the discretized version of the polymer-RISM equation that was used in Ref. [17] to study the adsorption behavior of continuum space polymeric fluids. To obtain the distribution of an average polymer segment with respect to the wall, Eq. 5.10 has to be combined with a closure equation. We have chosen to employ the Percus-Yevick closure. In 1D-form it is given by [31]

\[
\begin{align*}
g_{12}(0) & = 0 \\
c_{12}(l) & = g_{12}(l)(1 - e^{\beta u_{12}(l)}) & l \geq 1
\end{align*}
\]

(5.11)

where \(u_{12}(l)\) is the wall-fluid interaction potential. It is given by Eq. 5.1 for \(i = 1\) and \(j = 2\) upon removal of the \(m\)– and \(n\)–dependence in that equation. The \(g_{12}(l)\) denotes the segmental distribution with respect to the wall, and is the objective of the work presented here. The \(g_{12}(l)\) and \(h_{12}(l)\) are related as

\[
h_{12}(l) = g_{12}(l) - 1
\]

(5.12)

From \(g_{12}(l)\), the adsorption profile of the polymeric fluids directly follows via multiplication of \(g_{12}(l)\) with the bulk packing fraction of the polymer fluid, \(\eta_{m2}\). From the adsorption profile, \(\eta_{m2} g_{12}(l)\), an adsorption isotherm, \(\Gamma(\eta_{m2})\), is constructed as

\[
\Gamma(\eta_{m2}) = \sum_{l=1}^{l_{\text{bulk}}} \eta_{m2} h_{12}(l)
\]

(5.13)

where \(l_{\text{bulk}}\) is taken sufficiently large for the simulation to reach into the bulk region of the polymeric fluid. Note that \(h_{12}(l) = g_{12}(l) - 1\) is the excess amount of adsorbed material relative to the bulk.

Note that the method presented in this section is suitable to study competitive
adsorption for two or more molecule types. In that case the number of molecule types in the matrix equation Eq. 5.2 has to be extended, but the general procedure is not changed. Competitive adsorption [32] of ring- and linear polymeric molecules or of a mixture of linear molecules of different lengths might be studied in this way. Here we are only interested in a first test of the formalism, and therefore, we have only tested 1-component fluids consisting of linear polymer chains.

### 5.2.2 Solution procedure

Eqs. 5.10, 5.11 and 5.12 form a complete set of equations from which the adsorption profile, \( \eta_{m2g12}(l) \), and adsorption isotherm, \( \Gamma(\eta_{m2}) \), can be constructed if the bulk structural properties of the polymeric fluid, i.e., \( \tilde{h}_{22}(u, v, w) \) and \( \tilde{\omega}_2(u, v, w) \), are known. These bulk properties can be obtained with methods outlined previously in this thesis [21,22].

The set Eqs. 5.10-5.12 are solved in 1D-Fourier space, defined by

\[
\tilde{f}(u) = \sum_l f(l) \cos lu
\]  

(5.14)

and the inverse

\[
f(l) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \tilde{f}(u) \cos lu \, du
\]  

(5.15)

With help of Eq. 5.14 we can write Eq. 5.10 as

\[
\tilde{h}_{12}(u) = (\tilde{\omega}_2(u, 0, 0) + \eta_{m2} \tilde{h}_{22}(u, 0, 0)) \tilde{c}_{12}(u)
\]  

(5.16)

where \( \tilde{h}_{22}(u, 0, 0) \) and \( \tilde{\omega}_2(u, 0, 0) \) are 3D Fourier series, given by Eq. 5.3 for \( v = w = 0 \). We do not have to take Fourier sine terms into account in Eq. 5.14, because blowing up particle 1 does not violate the symmetry relation \( \tilde{h}_{12}(l) = \tilde{h}_{12}(-l) \). In Eq. 5.16 the replacement \( \tilde{\omega}_2(u, 0, 0) + \eta_{m2} \tilde{h}_{22}(u, 0, 0) = \tilde{\omega}_2(u, 0, 0)/(1 - \eta_{m2} \tilde{\omega}_2(u, 0, 0) \tilde{c}_{22}(u, 0, 0)) \) is allowed according to the fourth equation of Eq. 5.8. This replacement is convenient due to the short ranged character of the direct correlation function \( \tilde{c}_{22}(u, v, w) \) when compared to the total correlation function \( \tilde{h}_{22}(u, v, w) \). Combination of Eq. 5.16 with the 1D-PY closure Eq. 5.11 then results in two equations in the unknowns \( \tilde{c}_{12}(0) \) and \( \tilde{c}_{12}(1) \)

\[
-1 = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\tilde{\omega}_2(u, 0, 0)}{1 - \eta_{m2} \tilde{\omega}_2(u, 0, 0) \tilde{c}_{22}(u, 0, 0)} \tilde{c}_{12}(u) du
\]

\[
\frac{\tilde{c}_{12}(1)}{1 - e^{\beta \tilde{h}_{12}(1)}} - 1 = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\tilde{\omega}_2(u, 0, 0)}{1 - \eta_{m2} \tilde{\omega}_2(u, 0, 0) \tilde{c}_{22}(u, 0, 0)} \tilde{c}_{12}(u) \cos u du
\]

(5.17)
where from Eqs. 5.11 and 5.14, \( \tilde{c}_{12}(u) = c_{12}(0) + 2c_{12}(1) \cos u \). Eq. 5.17 is numerically solved with a combined Newton-Raphson - 1D-quadrature routine. Once \( c_{12}(0) \) and \( c_{12}(1) \) are found, the wall-segment correlations are obtained from

\[
h_{12}(l) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\tilde{\omega}_2(u,0,0)}{1 - \eta_{m2}\tilde{\omega}_2(u,0,0)\tilde{\epsilon}_{22}(u,0,0)} \tilde{c}_{12}(u) \cos l d\phi \tag{5.18}
\]
as is seen from Eqs. 5.15 and 5.16. Note that Eq. 5.17 can easily be solved analytically if the adsorption of an athermal monomeric fluid is considered. For such a fluid we have \( \tilde{\omega}_2(u,0,0) = 1 \) and \( \tilde{\epsilon}_{22}(u,0,0) = -1/(1 - \eta_{m2}) \), and from Eqs. 5.17 and 5.18 it is then found that the adsorption profile is given by

\[
\begin{align*}
h_{12}(0) &= -1 \\
h_{12}(1) &= -\left(\frac{(\eta_{m2} - 1)(1 - e^{\beta u_{12}(1)})}{1 + (\eta_{m2} - 1)(1 - e^{\beta u_{12}(1)})}\right) \\
h_{12}(l) &= 0 \quad \text{if } l \geq 2
\end{align*}
\tag{5.19}
\]

From Eq. 5.19 we see that in case of a monomeric lattice fluid, the influence of the wall reaches only one layer deep into the fluid. The reason that this is not the case for a polymeric lattice fluid, is the chain connectivity constraint that propagates via \( \tilde{\omega}_2(u,0,0) \) in Eq. 5.18.

The result of Eq. 5.19 for monomer adsorption is exact. This is seen by equilibrating the chemical potential of the athermal monomeric bulk fluid and the chemical potential of the same fluid in the layer closest to the wall. The bulk chemical potential is given by

\[
\mu_{\text{bulk}} = \ln \left(\frac{\eta_{m2}}{1 - \eta_{m2}}\right) \tag{5.20}
\]

which follows directly from exact enumeration [1]. For the layer closest to the wall, the canonical partition function is given by

\[
Q(N(1), M, T) = \frac{M!}{N(1)!(M-N(1))!} \left(e^{-\beta u_{12}(1)}\right)^{N(1)} \tag{5.21}
\]

if there are \( M \) lattice sites and \( N(1) \) particles in the layer closest to the wall. The chemical potential in the layer closest to the wall is then given by \( \mu_1 = -k_BT (\partial \ln Q/\partial N(1))_{M,T} \). Thus

\[
\frac{\mu_1}{k_BT} = \ln \left(\frac{\eta_{m2}g_{12}(1)}{(1 - \eta_{m2}g_{12}(1))e^{-\beta u_{12}(1)}}\right) \tag{5.22}
\]

with \( N(1)/M = \eta(1) = \eta_{m2}g_{12}(1) \) being the site occupancy fraction in layer 1, the layer closest to the wall. Equilibration of Eqs. 5.20 and 5.22 results in Eq. 5.19.
5.2.3 The wall-equation of state

Dickman [20,33] has presented a method to calculate the equation of state of a polymeric lattice fluid from its adsorption profile at a repulsive wall. It is intuitively clear that such an EoS exists because higher pressures "push" the fluid to the wall, and thus effect the adsorption profiles. Dickman pointed out that the pressure route, that is commonly used to obtain the EoS of simple- [34] and polymeric continuum fluids [35], is not valid for lattice fluids, because it contains a derivative of the interaction potential with respect to the interparticle distance. Such a derivative is not well defined for lattice systems.

The lattice wall-EoS has the form of a charging formula [34]. It reads

\[ \frac{p\nu_0}{k_BT} = \int_{\phi=0}^{1} \frac{\eta(1)}{\phi} d\phi \]  \hspace{1cm} (5.23)

where \( \nu_0 \) is the volume of one lattice site. In the derivation of Eq. 5.23, the overall potential energy of the system is divided in a bulk part that contains the restrictions which define the chain structure and prohibit segmental overlaps, and in a part \( U_{12} \) caused by the wall-fluid interactions. If \( U_{12} \) is further decomposed (which is possible without approximation) into separate nearest neighbor wall-segment interactions \( u_{12}(1) \), Eq. 5.23 results. The derivation of Eq. 5.23 has been presented in chapter 2. The integration limits (\( \phi = 0 \) and \( \phi = 1 \)) in Eq. 5.23 correspond respectively to a wall with an infinitely strong repulsive nearest neighbor interaction, and to a non-interacting wall. Eq. 5.23 was originally used to extract the equation of state of a lattice fluid from NVT-MC simulation data, but here we use it to obtain an alternative route to the EoS within the polymer-RISM theory presented in section 5.2.1. Results for the wall-EoS obtained from the adsorption profiles will be presented in section 5.4.

5.3 Monte Carlo simulations

In previous chapters we have reported \( NpT \)-MC simulations from which the bulk 2-particle distributions, \( h_{22}(l,m,n) \) and \( \omega_2(l,m,n) \), and the thermodynamic properties of 1-component 30-meric cubic lattice fluids with segmental interaction energies of \( u_{\text{attr}} = -0.0k_BT, -0.05k_BT, \) and \( -0.2k_BT \) were obtained [21,22]. The simulation method is based on work by Madden [36]. Apart from the bulk properties, the method also produces the adsorption profiles of the fluids at an impenetrable and non-interacting wall. Here, we use these profiles as a reference for comparison to the adsorption profiles calculated with the polymer-RISM- and Scheutjens-Fleer theory. The results for the adsorption profiles presented in this chapter are available on request via e-mail at tgpken@urc.tue.nl.
5.4 Results and Discussion

In section 5.4.1 we compare the adsorption profiles of 30-meric cubic lattice fluids with segment-segment interactions $u_{\text{attr}} = -0.0k_BT$, $-0.05k_BT$, and $-0.2k_BT$ to profiles obtained from MC-simulations and the classical Scheutjens-Fleer model [7,37]. Only adsorption profiles at a non-interacting wall are considered. In section 5.4.2 results for the EoS of the bulk of the adsorbing fluid obtained via the wall-EoS, Eq. 5.23, are compared to MC-simulation data, and to results obtained previously within the polymer-RISM framework via the compressibility-PY- and energy-MSA route [21,22].

5.4.1 Adsorption profiles

Before the actual results for the adsorption profiles are presented we first make a few general remarks about the Scheutjens-Fleer (SF) theory. The SF-theory is an extension of the Flory-Huggins Mean Field lattice theory [1]. In the SF-theory, a pre-averaging of polymer concentrations in the layers parallel to the adsorbing wall takes place. All possible molecule conformations are accounted for by a matrix method that calculates the probability of all conformations of the polymer molecules near the wall. The matrix-method accounts for compositional differences between the layers that occur due to the presence of the wall and that propagate via the chain-connectivity and segmental interaction energies [7]. Thus, the Mean Field (MF) SF-theory does account, contrary to the method of section 5.2.1, for conformational changes of the adsorbing molecules [38]. The method is called self-consistent for the distribution of the molecules over the layers is found by a minimization of the overall free energy of the adsorbing fluid. The MF-approximation is physically plausible at higher bulk packing fractions, but seems invalid at lower packing fractions. Therefore, it is interesting to compare the SF-theory to the approach of section 5.2.1, in which such an averaging of properties over the layers does not take place. Another reason for us to compare the abilities of the approach of section 5.2.1 to the SF-formalism is its simplicity: it only takes one (in case of a non-attracting wall) or two (in case of an attracting wall) equations, see Eq. 5.17, to find the unknowns that are needed to calculate $g_{12}(l)$ via Eq. 5.18, where in the SF-formalism there is a coupling of equations, there are several equations for each layer, that makes the numerical solution of these equations more complicated.

In this chapter, we compare the results of section 5.2.1 to the simplest version of the SF-formalism. More sophisticated versions, that use a different discretization of space or partially account for the intramolecular excluded chain volume via a Rotational Isomeric State (RIS) scheme [39,40] do exist, but since the polymer-RISM formalism as presented in section 5.2.1 uses a cubic lattice and does not account for intramolecular excluded volume (due to the use of a Random Flight intramolecular distribution), we have chosen to compare it to the simplest ver-
sion of the SF-formalism. Note that comparison to the SF-formalism that uses a RIS-scheme would be more appropriate if the RF-intramolecular distribution of Eq. 5.5 is replaced by a Non Reversal Random Walk (NRRW) intramolecular distribution (see Appendix A).

In Figs. 5.1-5.4, some adsorption profiles of the linear 30-mer lattice polymeric chains at a non-interacting wall are shown. In Figs. 5.1 and 5.2, \( u_{\text{attr}} = -0.0k_B T \) and \( \eta_{m2} \) is respectively 0.2074 and 0.6865. In Figs. 5.3 and 5.4, \( u_{\text{attr}} = -0.2k_B T \) and \( \eta_{m2} \) is respectively 0.2940 and 0.7262. We do not show any adsorption profiles for the fluid with \( u_{\text{attr}} = -0.05k_B T \), for which we have also performed MC-simulations, because the qualitative behavior of these profiles is identical to those of the athermal lattice fluid. The symbols in Figs. 5.1-5.4 are obtained from MC-simulations, the dashed line is obtained with the SF-theory, and the full line is obtained with the method outlined in section 5.2.1. The full- and dashed lines in the figures suggest that the theories predict a continuous profile. This is not the case, the lines are only drawn to distinguish theoretical and simulation data. The MC-points in the Figs. 5.1-5.4 show that there is a depletion of polymeric molecules near the non-interacting wall in all cases studied. In Figs. 5.1 and 5.2, where results for an athermal fluid near a non-interacting wall are depicted, the depletion is of purely entropic origin: an average segment of a polymeric molecule has a reduced probability of being close to the wall, due to chain-connectivity constraints. In Figs. 5.3 and 5.4 the depletion is increased when compared to Figs. 5.1 and 5.2, due to the cohesive energy of the bulk fluid considered in Figs. 5.3 and 5.4: apart from the entropic restrictions that the molecules experience in the vicinity of the wall, there is an additional depletion because the wall prevents the molecular segments close to the non-interacting wall to form energetically favorable \( (u_{\text{attr}} = -0.2k_B T) \) segmental interactions. Note from Figs. 5.1-5.4 that the depletion hole is also deeper at lower bulk packing fractions: at higher packing fractions the polymeric material is pushed harder to the wall, and in the limit \( \eta_{m2} \rightarrow 1 \), the simulations will show a completely flat adsorption profile, \( g_{12}(l) = 1 \) for all \( l \), which corresponds to a complete absence of wall-fluid correlations. From the figures it is seen that the SF-theory performs best at high packing fractions, which was to be expected for the MF-approximation is most appropriate at these high packing fractions. The polymer-RISM theory performs far from well at high packing fractions: from Figs. 5.2 and 5.4, it is seen that for both the athermal fluid and the fluid with \( u_{\text{attr}} = -0.2k_B T \), the depletion at the wall is severely overestimated. The absence of possibilities to change the form of the molecules in the interfacial region will certainly be of influence on this failure, but, as will become apparent soon, the absence of excluded volume in the RF-intramolecular distribution \( \hat{\omega}_{2,RF}(u,v,w) \) that is used in the calculations is more important. At lower packing fractions, see Figs. 5.1 and 5.3, it is seen that the polymer-RISM- and SF-theory are of comparable accuracy. Both theories severely underestimate the depth of the depletion hole. For the SF-formalism
Figure 5.1: Adsorption profile of an athermal 30-mer linear chain fluid at a non-interacting wall. The bulk packing fraction is \( \eta_{m2} = 0.2074 \). The wall is located at \( l = 0 \). The symbols are obtained from the simulations, the dashed line from the Scheutjens-Fleer theory, and the full line from the polymer-RISM theory of section 5.2.1.

Figure 5.2: Caption as in Fig. 5.1, but for \( \eta_{m2} = 0.6865 \).
Figure 5.3: Caption as in Fig. 5.1, but for $u_{\text{attr}} = -0.2k_BT$ and $\eta_m^2 = 0.2940$.

Figure 5.4: Caption as in Fig. 5.1, but for $u_{\text{attr}} = -0.2k_BT$ and $\eta_m^2 = 0.7262$. 
this is not surprising, for the MF-approximation that is adopted is physically less plausible at lower packing fractions. Despite this fact, the polymer-RISM theory performs only a little better at lower packing fractions. The main reason is again the complete absence of excluded volume in the RF-intramolecular distribution, but before such is discussed we first present an overview of the behavior of the polymer-RISM- and Scheutjens-Fleer theory in Fig. 5.5.

![Figure 5.5](image.png)

**Figure 5.5:** Bulk density dependence of the wall-fluid distribution in the layer closest to the wall. Full lines are obtained within the polymer-RISM theory, and the dotted lines within the SF-formalism of Ref. [7]. The symbols are obtained from MC-simulation. The (●) represent an athermal 30-mer fluid, and (■) a 30-mer fluid with segmental interaction strengths of $u_{\text{attr}} = -0.2k_BT$. Lower full- and dotted lines are for the interacting fluid, and upper lines are for the athermal fluid.

In Fig. 5.5, we have plotted the normalized packing fraction in the layer closest to the wall, $g_{12}(1)$, versus the bulk packing fraction, $\eta_{m2}$, of an athermal (●) and interacting (■, $u_{\text{attr}} = -0.2k_BT$) 30-mer lattice fluid for both the polymer-RISM- (full lines), and the SF-formalism (dotted lines). The symbols are the results of Monte Carlo simulations. The upper full- and dotted line are for the athermal fluid, and the lower full- and dotted line are for the interacting fluid. First, we mention a few things about the lines obtained within the SF-formalism. It is seen that the $\eta_{m2}$-dependence of $g_{12}(1)$ displayed by the dotted lines is reasonably accurate for $\eta > 0.25$. The predictions for $g_{12}(1)$ are best at high packing fractions, but in case of the interacting fluid there is a deterioration for lower val-
ues of $\eta_m$. Although we have not performed any simulations for $\eta_m > 0.75$, because the CPU-time demands increase strongly with $\eta_m$, it is seen that the SF-formalism is fairly accurate at these packing fractions: the SF-theory shows the correct limiting value $g_{12}(1) = 1$ at $\eta_m = 1$. This limit is correct, for in a system that is fully packed with polymeric molecules, there can simply be no space to create a depletion hole. At low packing fraction ($\eta_m < 0.25$) the SF-theory seems not correct: the lines for the interacting and non-interacting fluids cross, while such is not observed from the simulations (unfortunately we can not guarantee that the lines obtained from the simulations do not cross for very low packing fractions, because it it not possible to perform accurate simulations for such low $\eta_m$). As stated before, it is not surprising that the SF-theory does not work well at low packing fractions, because the MF-approximation that is adopted in the SF-theory is not valid at low packing fractions.

The full lines predicted by the polymer-RISM theory of section 5.2.1 are, although the SF-formalism is far from accurate, certainly not closer to the simulation results than the dotted lines in Fig. 5.5. The full lines clearly show that the dependence of $g_{12}(1)$ on $\eta_m$, predicted by the polymer-RISM theory, is too weak: the $g_{12}(1)$ is overestimated at low $\eta_m$, as was also observed from Figs. 5.1 and 5.3, and underestimated at high $\eta_m$ (see Figs. 5.2 and 5.4). Although both the high and low density limits of $g_{12}(1)$ are incorrect, the lines predicted by the polymer-RISM theory do not show a crossing of lines at low $\eta_m$, which seems to be in agreement with the simulation results.

The problems associated with the polymer-RISM theory are mainly due to the use of the Random Flight intramolecular distribution function, $\hat{\omega}_{2,RF}(u, v, w)$, in which there is a complete absence of intramolecular excluded volume. At high packing fraction this is seen most easily. Due to the fact that intramolecular segmental overlaps occur, there are unoccupied and doubly occupied sites, even if the lattice is fully packed with polymeric molecules. Hence, the sum of the inter- and intramolecular correlations in the bulk of the fluid, $\omega_2(l, m, n) + \eta_m h_22(l, m, n)$, is not equal to zero, although zero is the physically correct value for a fully packed lattice [21]. As a result, there still is a depletion at the wall for $\eta_m = 1$: it is seen from Eq. 5.10 that the physically correct adsorption profile $h_{12}(l) = 0$ is only obtained if $\omega_2(l, m, n) + \eta_m h_22(l, m, n) = 0$. In chapter 3, it is shown that these "rest-correlations", the deviations of $\omega_2(l, m, n) + \eta_m h_22(l, m, n)$ from 0, at $\eta_m = 1$ can only be reduced by using an intramolecular distribution function, $\hat{\omega}_2(u, v, w)$, that forbids intramolecular segment-segment overlaps [21]. A first candidate that does incorporate the excluded chain volume up to some extent would thus be the intramolecular distribution function of a NRRW-chain which excludes direct back-folding within a polymer chain (see Appendix A).

At lower packing fractions it is somewhat harder to see that the absence of excluded volume in $\hat{\omega}_{2,RF}(u, v, w)$ is responsible for the inaccuracy of the polymer-RISM theory. To clarify the low density limit of $g_{12}(1)$ that is observed in Fig. 5.5, we consider a lattice fluid at bulk packing fraction $\eta_m \to 0$ near a non attracting
wall. For that case, $g_{12}(1)$ can be expressed with help of Eqs. 5.10 and 5.11 as

$$g_{12}(1) = 1 - \frac{\sum_{m,n} \omega_{2,RF}(1,m,n)}{\sum_{m,n} \omega_{2,RF}(0,m,n)}$$

(5.24)

From Eq. 5.24 it is seen that in the theory of section 5.2.1, $g_{12}(1)$ is fully determined by parts of the bulk intramolecular distribution function. The equation also shows that the athermal and interacting fluid display the same limiting value of $g_{12}(1)$ (see full lines in Fig. 5.5), because we have taken the same $\hat{\omega}_{2,RF}(u,v,w)$ in the calculation of the adsorption profiles of both fluids. From Fig. 5.5, it is seen that the limiting values of $g_{12}(1)$ observed for the simulated fluids are also fairly close together. This is rather surprising, and can not be fully explained with Eq. 5.24, because Eq. 5.24 is approximate (it expresses $g_{12}(1)$ in terms of bulk quantities, and does not take distortions of the chain conformations in the interfacial region into account), and even if we assume that it holds, it is still expected to give different values of $g_{12}(1)$ for athermal and interacting fluids, because the average conformations (and thus $\omega_{2}(l,m,n)$) of isolated interacting and athermal chains are expected to be different in the simulations. Nevertheless, despite the objections to Eq. 5.24, it gives an indication why the $g_{12}(1)$ of the simulated fluids tend to meet at $\eta_{m2} \rightarrow 0$.

If we replace the Random Flight intramolecular distribution results $\omega_{2,RF}(0,m,n)$ and $\omega_{2,RF}(1,m,n)$ by $\omega_{2,NRRW}(0,m,n)$ and $\omega_{2,NRRW}(1,m,n)$ in Eq. 5.24 (see Appendix A for the calculation procedure of the $\omega_{2,NRRW}$-terms), we see a lowering of the calculated value of $g_{12}(1)$ from 0.39922 to 0.26872, which is a significant improvement, as is seen in Fig. 5.5.

Usage of a NRRW-intramolecular distribution function instead of a RF-intramolecular distribution does not only lower $g_{12}(1)$ at $\eta_{m2} \rightarrow 0$, it also increases $g_{12}(1)$ at $\eta_{m2} = 1$, as already discussed. Therefore, the average slope of the full lines shown in Fig. 5.5 will also be closer to the slope of the lines that can be drawn through the simulation results. Thus, improvements of the results obtained with the method of section 5.2.1 must be expected, but thus far we have not undertaken calculations with an improved intramolecular distribution function. In a later stage, it might also be necessary to incorporate the effects of the wall on the average conformation of the molecules, but for now it seems most important and straightforward to improve along the lines outlined above. Note finally that it may also be interesting to obtain the adsorption isotherm $\Gamma(\eta_{m2})$ via Eq. 5.13, especially for fluids with an improved intramolecular distribution function. Thus far, we have not calculated such isotherms.

### 5.4.2 Equation of state

In this section some results obtained with the wall-EoS, Eq. 5.23 are presented. The wall-EoS is compared to MC-simulations, and to the EoS obtained previously.
from the compressibility-PY- (c-PY) and energy-MSA (e-MSA) route [21,22].

In Fig. 5.6, the symbols represent an overview of the simulation results for

30-mer cubic lattice fluids with nearest neighbor segmental interaction strengths of \( u_{\text{attr}} = -0.0k_BT \) (\( \bullet \)), \(-0.05k_BT \) (\( \triangle \)), and \(-0.2k_BT \) (\( \square \)). These simulation results were shown previously in chapters 3 and 4. The lines in the figure are obtained from the theory of section 5.2.1 via Eq. 5.23. The integration over \( \phi \) in Eq. 5.23 was performed numerically and interpolates between the values of \( \bar{\eta}(1) = \bar{\eta}_{m2} g_{12}(1) \) that are calculated for fifteen wall-fluid interaction strengths varying from \( u_{12}(1) \rightarrow \infty (\phi = 0) \) to \( u_{12}(1) = +0.0k_BT (\phi = 1) \). From Fig. 5.6 it is seen that the absolute values of the pressures are in the range of the simulation results. The dependence of the calculated pressures on the segmental interaction strengths seems in reasonable agreement with the simulation results. The curvatures of the calculated lines displayed in Fig. 5.6 is nevertheless different from the curvatures of the lines that can be drawn through the simulation results. Therefore, in Figs. 5.7-5.9 we have redrawn the EoS shown in Fig. 5.6 in terms of the compressibility factor, \( pv_0s/k_BT\eta_{m2} \). In Figs. 5.7-5.9 we have plotted the MC-results (\( \bullet \)), the wall-EoS (full line), the c-PY EoS (dotted line), and the EoS obtained via the e-MSA route (dashed line). In Fig. 5.7, the e-MSA EoS is not shown, because it reduces to the c-PY EoS in case of athermal fluids. The
Figure 5.7: Compressibility factor of an athermal cubic lattice fluid consisting of 30-meric RF-chains. The (●) indicate simulation results. The dotted line has been obtained previously via the compressibility-PY route [21], and the full line indicates the result obtained via the wall-method of section 5.2.3.

The c-PY- and e-MSA EoS have been discussed in detail elsewhere [21,22]. There it was found that these EoS are extremely sensitive to the exact form of the intramolecular distribution function that is used. It was concluded that it is an absolute necessity (but not a guarantee) in obtaining an improved EoS for interacting fluids, to use an intramolecular distribution function that incorporates the excluded chain volume as accurately as possible. Note that the c-PY- and e-MSA EoS do show the correct ideal gas limit, \( p v_0 s / k_B T \eta_{m2} = 1 \) for \( \eta_{m2} \to 0 \). This is in contrast to the wall-EoS which, not surprisingly, does not show this limit. This is not due to Eq. 5.23, as is seen in Fig. 2 of Ref. [33] where EoS extracted from simulations based on Eq. 5.23 are presented, but is a result of the absence of excluded chain volume in \( \hat{\omega}_{2,RF}(u,v,w) \). It was shown in the previous subsection that if \( \hat{\omega}_{2,RF}(u,v,w) \) is used, then \( g_{12}(1) \) is overestimated at \( \eta_{m2} \to 0 \) (see Fig. 5.5). Such will most probably also be the case for a repulsive wall, and hence, the compressibility factor calculated from \( g_{12}(1) \) via Eq. 5.23 will be overestimated at \( \eta_{m2} \to 0 \). Therefore, improvement of the calculated adsorption profiles via an improved intramolecular distribution function will certainly lead
Figure 5.8: Compressibility factor of a cubic lattice fluid consisting of 30-mer RF-chains with segmental interactions of \( u_{\text{attr}} = -0.05k_B T \). The (●) is obtained from simulations. The dashed- and dotted lines indicate results obtained previously via respectively the energy-MSA- and compressibility-PY route, and the full line indicates the wall-EoS obtained via Eq. 5.23.

to an improved compressibility factor at \( \eta_{m2} \rightarrow 0 \). The physically correct ideal gas limit will not be obtained easily, because in that case \( g_{12}(1) \) has to be calculated exactly. Such seems only possible with help of very accurate simulations. Note from Eq. 5.19 that in case of a monomeric fluid, \( g_{12}(1) \) attains the value \( g_{12}(1) = e^{-\beta u_{12}(1)} \) in the limit \( \eta_{m2} \rightarrow 0 \). Thus, insertion of \( g_{12}(1) \) in the wall-EoS does, in case of a monomeric fluid, indeed produce the correct ideal gas limit \( p v_0/(k_B T \eta_{m2}) = 1 \). This obviously illustrates that there is nothing fundamentally wrong with the wall-route to the EoS, the incorrect low density limit observed in case of polymeric fluids, is thus simply caused by an incorrect intramolecular distribution function.

From Figs. 5.6-5.9 it is also seen that the pressure calculated from the wall-EoS does not rise to infinity at \( \eta_{m2} \rightarrow 1 \). This is again caused by an absence of intramolecular excluded volume in \( \hat{\omega}_{2,RF}(u,v,w) \): the physically correct adsorption profile \( g_{12}(1) = 1 \), for which the compressibility factor does go to infinity (see Eq. 5.23), will only be obtained if there are no "rest-correlations" at \( \eta_{m2} \rightarrow 1 \), thus if \( \omega_2(l,m,n) + \eta_{m2} h_{22}(l,m,n) = 0 \) for all \( (l,m,n) \) (see Eq. 5.10). As shown previously [21], reductions of the "rest-correlations", and thus improvements of the high density limit of the EoS, are obtained if \( \hat{\omega}_{2,RF}(u,v,w) \) is replaced by
\[ \omega_{2,NRWW}(u,v,w) \]. Note from Eq. 5.19 that monomeric fluids do again behave correctly at a fully packed lattice: \( g_{12}(1) = 1 \), and from Eq. 5.23 it is then seen that the pressure does rise to infinity for a fully packed monomeric lattice fluid. Finally, note that the wall-method is sufficiently general to obtain an EoS for a bulk lattice fluid from the SF-formalism. Here, we have not considered such an EoS.

5.5 Conclusions

In this work we have presented a method [13], based on the polymer-RISM equation [23], to obtain the adsorption profiles of polymeric lattice fluids near an impenetrable wall. Here, we only show adsorption profiles for fluids near a non-interacting wall, but wall-fluid interactions can easily be taken into account, as is shown from the calculation of the equation of state for the bulk of a lattice fluid that is adsorbed at a repulsive wall [20]. The calculated adsorption profiles are compared to the Scheutjens-Fleer theory [7] and to \( NpT \)-Monte Carlo simulations. The EoS are also compared to the simulation results.

Results of the comparison of both theories to the simulation results were as follows. At higher bulk packing fractions (\( \eta_{m2} > 0.5 \)), the adsorption profiles obtained from the polymer-RISM approach cannot compete yet with the profiles obtained from the SF-formalism: the SF-profiles are closer to the simulation re-
sults. At lower packing fractions, for which the SF-theory is less accurate due to its Mean Field approximation, the profiles of both theories are shown to be of comparable quality when compared to the simulation results. The polymer-RISM based theory predicts depletion holes that are severely overestimated at high- and underestimated at low bulk packing fraction. As a result, the wall-EoS does also not show the correct high and low density limits.

The reason for the observed deficiencies of the polymer-RISM adsorption theory can be largely attributed to the absence of excluded volume in the average conformation of the polymer chains. It is made plausible that an improved average chain conformation, e.g., conformations that use a NRRW-scheme, will result in improved adsorption profiles and EoS. Such improvements are well possible, and since the adsorption profiles obtained from the SF-formalism are certainly not perfect (we must admit that thus far we have not compared to more advanced versions of the SF-formalism [39]), we think that it is worthwhile to further investigate the method presented here, the more so because it is numerically very simple when compared to the SF-formalism.
References


[22] R.H.C. Janssen, PhD-thesis (Eindhoven University of Technology - The Netherlands, 1996); chapter 4


Chapter 6

Lattice fluid of associating particles with one directional attractive force: Dimer formation

6.1 Introduction

Many fluids exhibit directional attractive forces. Most of the remarkable properties of for instance water (e.g., the very high boiling point and the density maximum at $T=276.984K$) can be explained in terms of such directional (dipolar) forces. The chemical bonding (covalent) forces between atoms that are responsible for the formation of molecules are also (very strong) directional forces.

A simple model for a fluid with directional attractive forces is a fluid of hard particles with an off-center spot that is the origin of an attractive potential. Two particles can form an attractive interaction if the particles are oriented towards each other in such a way that the attractive potentials are within each others reach. If the origin of the attractive potential is located near the edge of the spherical particle, and if the potentials are short ranged enough to prevent bonding of more than one particle per spot (steric saturation), then the directional attractions will have the character of a bond between two particles. Depending on the strength and nature of the attractive potential, the chemical character of these bonds can be dipolar or covalent.

In this chapter a new cubic lattice model of an associating fluid consisting of non-overlapping particles that occupy exactly one lattice site is developed and its structural properties are compared to Monte Carlo simulations. Each particle is allowed to form one directional attractive bond with a neighboring particle. A schematic picture of the model is drawn in Fig. 6.1. The formalism that we have
used in constructing the lattice model is due to Wertheim. He has developed a
general statistical mechanical framework for fluids of particles that exhibit direc­tional and saturable attractions. His work originally focused on particles that
have only one off-center attractive spot [1,2] and was later generalized to include
more off-center spots per particle [3-6]. The method, the multiple density formal­
ism, which reduces to a 2-density formalism for singly associating fluids, is based
on a separation of the interparticle potential in a purely repulsive isotropic part
and an attractive potential that is a function of the particle orientation. This
separation allows to divide the overall particle density in a density of non-bonded
particles, and in a density of particles that have formed a bond with another
particle. Wertheim has arrived at an Ornstein-Zernike-like matrix equation for
the 2-particle distributions in such a fluid in terms of the densities of the bonded
and non-bonded particles. The 2-particle distributions can thus be obtained by
combining the OZ-like matrix equation with a closure equation if the bonded and
non-bonded particle densities are known. These are now provided by a mass­
balance equation that determines how the overall particle density is divided in
a density of bonded and non-bonded particles on the basis of the 2-particle dis­
tributions that appear in the OZ-matrix equation. A fully self-consistent scheme
thus appears.
Once the 2-particle distributions are known they can be used to obtain the ther­
modynamics, e.g., the equation of state [1,2,7], but in this and later chapters

Figure 6.1: Fragment of a 3D associating fluid in which four nearest neighbor bonds
are visible.
of the thesis we have only been interested in the structural properties of fluids with directional attractive forces. Wertheim has also provided a perturbational approach [2] within the 2-density formalism to directly obtain the excess thermodynamic functions of the fluid with respect to a fluid of hard non-interacting particles without focusing on the structural properties. The perturbational route has been studied extensively [8-12] and compared to MC data for fluids with one or more attractive spots per particle. The OZ-matrix route has received less attention [7,13] and is the focus of this work. We are interested in using the attractions between the particles as a model for covalent bonding. Especially the case of two attractive spots per particle is interesting, because these particles are able to cluster into chains if the attractive potential is strong and of sufficiently short range. The fluid of chains that results can serve as a model of a polydisperse chain fluid [5,14-16]. Such a system will be investigated in the next chapter, here we start by considering the structural properties of the lattice fluid [17-19] that consists of particles with one attractive spot. The reason for adopting a cubic lattice is twofold. First, as mentioned above, we are interested in applying the multiple density formalism to polymerizing fluids. Adopting a lattice then allows to compare the results of the multiple density approach to the large body of polymer lattice models that have been developed over the years (see next chapter and references cited therein). A second reason to study the lattice model of Fig. 6.1 is the absence of all liquid-like ordering effects in the model. The ordering of the particles on the lattice is purely caused by the directional attractions, whereas in a continuum model, the ordering is largely caused by the repulsive cores of the particles. Therefore, the lattice model stringently tests how well the effects of the directional attractive forces on the structure are captured by the OZ-matrix formalism, without the liquid-like ordering effects that are pre-dominant in the continuum model.

The outline of the rest of this chapter is as follows. In section 6.2.1 we will briefly sketch the derivation of the 2-density formalism as presented in Refs. [1,2]. In section 6.2.2 we outline the basic equations of the formalism for 1-component lattice systems and indicate how we have performed the calculations for very strongly associating fluids. In section 6.2.3 the 2-density formalism is applied to binary mixtures, and we show how the total 2-particle distribution can be divided in an inter- and intramolecular part. Such a division allows to obtain both parts separately, in contrast to the RISM-equation for dimers [20] in which the intramolecular 2-particle distribution is an input for the calculation of the intermolecular distribution. In section 6.3 a Monte Carlo simulation of the associating cubic lattice fluid, from which structural correlation data are extracted for comparison to the theory, is presented. In section 6.4 theoretical and simulation results are presented, compared and discussed. Finally, conclusions are presented in section 6.5.
6.2 Lattice formulation of the 2-density formalism

6.2.1 Wertheim’s derivation

Here, we briefly recapitulate Wertheim’s work which forms the foundation for our model. An extensive derivation can be found in Refs. [1,2]. In the approach taken by Wertheim, the overall density of the particles in the fluid is split in parts. For a fluid consisting of particles with one attractive spot the formalism is in terms of two densities: the overall particle density $\rho$ is divided in a density $\rho_0$ of non-bonded particles, and in a density $\rho_1$ of particles that did form an attractive bond with another particle

$$\rho = \rho_0 + \rho_1$$  \hspace{1cm} (6.1)

In a fluid of particles with only one attractive spot we can thus recognize non-bonded and bonded particles. The total 2-particle distribution function $G(1,2)$, which is the objective of our calculations, can therefore be constituted from contributions arising from the correlations between two particles which have not formed an attraction bond $g_{00}(1,2)$, two particles of which one has formed an attraction bond $g_{10}(1,2)$ and $g_{01}(1,2)$, and two particles that both have formed an attraction bond $g_{11}(1,2)$. For instance, the $g_{10}(1,2)$ denotes the contribution to the total 2-particle distribution function of particle 1 that is bonded (denoted by the subscript 1) to a non-bonded (denoted by the subscript 0) particle 2. The coordinates of particles 1 and 2 are given by $1 \equiv (r_1, \Omega_1)$ and $2 \equiv (r_2, \Omega_2)$, where $r_i$ denotes the position and $\Omega_i$ the orientation of particle $i$.

To arrive at a multiple density approach, the pair interaction potential $u(1,2)$ (which depends on the orientations of particle 1 and 2) must be split in two parts, an isotropic repulsive part $u_R(r_1, r_2)$ (isotropic i.e., independent of $\Omega_1$ and $\Omega_2$) and a directional attractive part $u_{attr}(1,2)$. It is then possible to divide the Mayer function $f(1,2) = e^{-\beta u(1,2)} - 1$ in an attractive $F(1,2)$ and a purely repulsive part $f_R(r_1, r_2)$,

$$f(1,2) = f_R(r_1, r_2) + F(1,2)$$  \hspace{1cm} (6.2)

where

$$f_R(r_1, r_2) = e_R(r_1, r_2) - 1 = e^{-\beta u_R(r_1, r_2)} - 1$$  \hspace{1cm} (6.3)

and

$$F(1,2) = e_R(r_1, r_2) f_A(1,2) = e^{-\beta u_R(r_1, r_2)} (e^{-\beta u_{attr}(1,2)} - 1)$$  \hspace{1cm} (6.4)

It has proven possible for this division of the Mayer function to arrive at an exact (diagrammatic) expansion of $\rho$ in terms of the activity $z$, $f_R(r_i, r_j)$— and $F(i,j)$—bonds, after which the overall density $\rho$ can be split in densities of bonded and non-bonded particles. The $\rho_0$ and $\rho_1$ are then both classified by a different part of the set of diagrams that constitutes $\rho$. Starting from the grand canonical partition function $\Xi(\mu, V, T)$ and using these expansions of $\rho_0$ and $\rho_1$, Wertheim...
arrived at exact diagrammatic expansions of the structural correlations \( g_{00}(1,2), g_{10}(1,2) = g_{01}(1,2) \) and \( g_{11}(1,2) \) in terms of \( \rho_0 \) and \( \rho_1 , f_R(\mathbf{r}_1, \mathbf{r}_2) \) and \( F(1,2) \)-bonds. He then defined, along the same lines as the direct correlation function is defined for simple fluids, partial direct correlation functions \( c_{00}(1,2), c_{10}(1,2) = c_{01}(1,2) \) and \( c_{11}(1,2) \), and obtained their diagrammatic expansions in terms of \( \rho_0, \rho_1, f_R(\mathbf{r}_1, \mathbf{r}_2), \) and \( F(1,2) \). The partial correlations could then be related to the direct correlations via an OZ-matrix equation. This procedure of obtaining an OZ-matrix equation bears strong resemblance to the derivation of the OZ-equation for simple fluids \[21-23\].

To obtain the fluid structure, the OZ-matrix equation has to be combined with an appropriate closure equation and with a so called self-consistency relation based on Eq. 6.1. The self-consistency relation appears naturally in the case of the directional attractive fluid system and is a mass balance equation that determines division in bonded and non-bonded particles. Its physical relevance can be seen as follows. For a simple fluid without directional attractions it is clear that the OZ-equation and a closure determine the fluid structure \( g(1,2) \) in terms of the particle density \( \rho \). In the same way, we have for the fluid with directional forces that the OZ-matrix equation and a closure equation determine the correlations \( g_{00}(1,2), g_{10}(1,2) \) and \( g_{11}(1,2) \) in terms of \( \rho_0 \) and \( \rho_1 \). These correlations in turn, determine how the particles are distributed over bonded and non-bonded particles. This is not the case for a simple fluid where we only have one "type" of particles. Thus, for the fluid with directional attractive forces, the \( \rho_0 \) and \( \rho_1 \) determine \( g_{00}(1,2), g_{10}(1,2) \) and \( g_{11}(1,2) \) via the OZ-equation, and on the other hand we have \( g_{00}(1,2), g_{10}(1,2) \) and \( g_{11}(1,2) \) that determine the values of \( \rho_0 \) and \( \rho_1 \). This last step is necessary for internal consistency and is provided by the self-consistency relation. The formalism thus comprises three ingredients, an Ornstein-Zernike matrix equation, a closure relation, and a self-consistent mass balance equation.

### 6.2.2 1-Component systems

In this subsection the basic equations of the multiple density formalism are applied to a cubic lattice fluid of particles with one directional attractive spot. The particles occupy exactly one lattice site and do not overlap. The attractive spot is replaced by an attractive edge of a filled lattice site. Two particles located on nearest neighbor lattice sites will form a bond if the attractive sides of the two particles point towards each other (Fig. 6.1). The overall packing fraction \( \eta \) of the particles on the lattice can then be split in a fraction \( \eta_0 \) of non-bonded and a fraction \( \eta_1 \) of bonded particles, according to

\[
\eta = \eta_0 + \eta_1
\]

On the cubic lattice we can identify six orientations for a particle \( i \) with an attractive edge. These are characterized by an orientation number \( \Omega_i \): If the site
is oriented in $+l$-direction: $\Omega_i = 1$; $-l$-direction: $\Omega_i = -1$; $+m$-direction: $\Omega_i = 2$; $-m$-direction: $\Omega_i = -2$; $+n$-direction: $\Omega_i = 3$; $-n$-direction: $\Omega_i = -3$. Two particles at distance $r_2 - r_1 = (l, m, n)$ can thus form a bond if they are nearest neighbors ($\sqrt{l^2 + m^2 + n^2} = 1$) and if their attractive sides point towards each other. The orientation dependent interaction potential is therefore given by

$$u(0, 0, 0, \Omega_1, \Omega_2) \rightarrow \infty$$

$$u(l, m, n, \Omega_1, \Omega_2) = \begin{cases} u_{\text{attr}} & \text{if } \Omega_1 = -\Omega_2 \text{ and } l^2 + m^2 + n^2 = 1 \text{ and } \\ sgn(l + m + n) (l^2 + 2m^2 + 3n^2) = \Omega_1 & \text{otherwise} \end{cases}$$

$$(6.6)$$

in which $sgn(l + m + n)$ denotes the sign of $(l + m + n)$. The conditions $\Omega_1 = -\Omega_2$, $l^2 + m^2 + n^2 = 1$ and $sgn(l + m + n) (l^2 + 2m^2 + 3n^2) = \Omega_1$ guarantee that the interacting particles are nearest neighbors whose attractive sides point towards each other. If $|u_{\text{attr}}| < k_B T$, the attractive forces have the character of temporary bonds, because the thermal motion of the particles will frequently break the bonds. If $|u_{\text{attr}}| \gg k_B T$, the bonds have the character of real covalent bonds. Therefore, the model can serve as an associating fluid model for small $u_{\text{attr}}$ and as a molecular fluid model for $u_{\text{attr}} \gg k_B T$.

For the application of the multiple density formalism it is necessary to decompose $f(1,2)$ in $f_R(1,2) = f_R(r_1, r_2)$ and $F(1,2)$ (see sec. 6.2.1). As mentioned in the introduction, this is possible if $u(1,2) = u_R(r_1, r_2) + u_{\text{attr}}(1,2)$ where we make the identifications

$$u_R(0, 0, 0, \Omega_1, \Omega_2) \rightarrow \infty$$

$$u_R(l, m, n, \Omega_1, \Omega_2) = 0 \text{ if } \sqrt{l^2 + m^2 + n^2} \neq 0$$

$$(6.7)$$

and

$$u_{\text{attr}}(0, 0, 0, \Omega_1, \Omega_2) = 0$$

$$u_{\text{attr}}(l, m, n, \Omega_1, \Omega_2) = u_{\text{attr}}$$

if $\Omega_1 = -\Omega_2$ and $l^2 + m^2 + n^2 = 1$ and

$$sgn(l + m + n) (l^2 + 2m^2 + 3n^2) = \Omega_1$$

$$u_{\text{attr}}(l, m, n, \Omega_1, \Omega_2) = 0 \text{ otherwise}$$

$$(6.8)$$

Note that the value of $u_R(l, m, n, \Omega_1, \Omega_2)$ is independent of the values of $\Omega_1$ and $\Omega_2$ (orientation independent) and we can thus write $u_R(1,2) = u_R(l, m, n, \Omega_1, \Omega_2) = u_R(l, m, n) = u_R(r_1, r_2)$.

Our final aim is to obtain the orientation averaged 2-particle distribution function $G(l, m, n)$ for the model presented above. The orientation averaged distribution function is obtained from

$$G(l, m, n) = \frac{1}{36} \sum_{\Omega_1} \sum_{\Omega_2} G(l, m, n, \Omega_1, \Omega_2)$$

$$(6.9)$$

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Note that the total 2-particle distribution function is written as capital $G$, the lower case character is reserved for the intermolecular 2-particle distribution function (see section 6.2.3). The total orientation averaged 2-particle correlation $H(l, m, n)$ is related to $G(l, m, n)$ by

$$H(l, m, n) = G(l, m, n) - 1 \quad (6.10)$$

Before the orientation independent 2-particle distributions can be calculated we have to consider the orientation dependent equations of the 2-density formalism. We start by considering the total 2-particle correlation function $H(1, 2)$. It consists of elements $h_{ij}(l, m, n, \Omega_1, \Omega_2)$ (with $\{i, j\} \in \{0, 1\}$) that involve bonded and non-bonded particles [1]

$$\eta^2 H(1, 2) = \eta^2 h_{00}(1, 2) + \eta_0 \eta_1 h_{10}(1, 2) + \eta_1 \eta_0 h_{01}(1, 2) + \eta_0^2 h_{11}(1, 2) \quad (6.11)$$

where e.g., $h_{01}(1, 2)$ denotes that part of the total 2-particle distribution for which an non-bonded particle 1 and a bonded particle 2 are responsible. For $G(1, 2)$ we have an expression identical to Eq. 6.11. The OZ-matrix analog for the partial correlations in the 3D lattice fluid is given by [1]

$$h_{00}(1, 2) \begin{bmatrix} c_{00}(1, 2) & c_{01}(1, 2) \\ c_{10}(1, 2) & c_{11}(1, 2) \end{bmatrix} + \frac{1}{6} \sum_{r_3, \Omega_3} \begin{bmatrix} c_{00}(1, 3) & c_{01}(1, 3) \\ c_{10}(1, 3) & c_{11}(1, 3) \end{bmatrix} \begin{bmatrix} \eta & \eta_0 \\ \eta_0 & 0 \end{bmatrix} \begin{bmatrix} h_{00}(3, 2) & h_{01}(3, 2) \\ h_{10}(3, 2) & h_{11}(3, 2) \end{bmatrix} \quad (6.12)$$

Eq. 6.12 is supplemented with a Percus-Yevick (PY)-like closure [1]

$$y_{ij}(1, 2) = g_{ij}(1, 2) - c_{ij}(1, 2) \quad (6.13)$$

and the exact relations

$$g_{ij}(1, 2) = e_R(1, 2) (y_{ij}(1, 2) + \delta_{i1} \delta_{j1} f_A(1, 2) y_{00}(1, 2)) \quad (6.14)$$

where $e_R(1, 2) = e^{-\beta u_R(1, 2)}$, $f_A(1, 2) = e^{-\beta u_{attr}(1, 2)} - 1$ and $\delta_{ij}$ is the Kronecker delta. The $y_{ij}(1, 2)$ are the partial cavity distribution functions from which the cavity distribution function $y(1, 2)$ can be constructed in a fashion analogous to Eq. 6.11. Note that the closure equations Eqs. 6.13 and 6.14 have the appearance of the Percus-Yevick equation for isotropic systems, apart from the second term of Eq. 6.14 which accounts for the possibility of the formation of a directional bond between particles 1 and 2. It can be seen from Eq. 6.10 and Eq. 6.11 that the relation between $h_{ij}(1, 2)$ and $g_{ij}(1, 2)$ is defined by

$$h_{ij}(1, 2) = g_{ij}(1, 2) - \delta_{i0} \delta_{j0} \quad (6.15)$$
In the case of no attractive interaction, \( u_{\text{attr}} \rightarrow 0 \), no dimer formation occurs \((\eta_1 \rightarrow 0)\) and we can then identify \( h_{00}(1,2) \) with \( H(1,2) \). It is immediately clear that Eq. 6.12 thus reduces to the familiar OZ-equation of a simple monatomic fluid if we identify \( c_{00}(1,2) \) with \( c(1,2) \).

It is important to realize that the \( g_{ij}(1,2) \) do not have physical significance. Only their sum \( G(1,2) \) has physical significance as a 2-particle distribution. The division of the total 2-particle distribution in parts (Eq. 6.11) is necessary to arrive at a useful diagrammatic expansion of the \( G(l,m,n) \) of an associating fluid, and is thus purely a mathematical procedure to enable the calculation of the correlations in an associating fluid.

Eqs. 6.12-6.15 form a complete set of equations if they are supplemented with the mass balance equation [1]

\[
\eta = \eta_0 + \frac{\eta_0^2}{6} \sum_{r_1,\Omega_2} g_{00}(1,2) e_{R}(1,2) f_A(1,2) 
\] (6.16)

The last term of this equation gives \( \eta_1 \) (see Eq. 6.5) in terms of the correlations that follow from Eqs. 6.12-6.15. Thus, the OZ-matrix equation and its closure determine the correlations in terms of \( \eta_0 \) and \( \eta_1 \), and the mass balance equation is then needed for self-consistent determination of \( \eta_0 \) and \( \eta_1 \) from the correlations. Solving the set Eqs. 6.12-6.16 for the \( h_{ij}(1,2) \) then gives the total 2-particle distribution \( G(l,m,n) \) via Eqs. 6.9-6.11.

The direct correlation function \( c(1,2) \) cannot be constructed from the partial direct correlations \( c_{00}(1,2), c_{10}(1,2), c_{01}(1,2) \) and \( c_{11}(1,2) \). There is no direct correlation function analog of Eq. 6.11. In the multiple density formalism is never dealt with a full direct correlation function, but only with a matrix that contains the elements \( c_{00}(1,2), c_{01}(1,2), c_{10}(1,2) \) and \( c_{11}(1,2) \) (Eq. 6.12). This causes no problems because the concept of a direct correlation function is, even for simple fluids, mainly mathematical and only serves to facilitate the calculation of the total correlation \( h(1,2) \). A solution procedure for the equations outlined here is presented in Appendix B.

Ott Weist and Glandt [7] have presented a model for continuum associating fluids with a saturable isotropic potential. If it is translated in terms of a lattice model it differs in one aspect from the model presented above: the attractive potentials cannot be assigned a direction, but operate on all six nearest neighbor lattice sites.

Particles subject to such a non-directional nearest neighbor potential can form a bond with one of the particles that occupy a nearest neighbor site on condition that both particles are still non-bonded. Once a bond is formed the attractive potential of both particles that form the bond is switched off (saturation of the potential) and no further bonds can be formed. Ott Weist and Glandt argue that the saturation of the nearest neighbor potential is fully taken care of by
the 2-density OZ-matrix equation (Eq. 6.12), because it only allows formation of one bond per particle ($\eta_2$ does not appear in Eq. 6.12). In their view, the directionality of the attractive potential is an unnecessary and complicating factor in the model. The equations that govern their model are identical to Eqs. 6.12-6.16 with orientation independent particle coordinates. It can be shown from the self-consistency relations of both the orientation dependent Wertheim model and the orientation independent Ott Weist - Glandt model, that the orientation averaged 2-particle distribution $G(l, m, n)$ is exactly the same for both models if

$$\frac{a_W - 1}{a_{OWG} - 1} = 36 \quad (6.17)$$

where $a_W = e^{-\beta u_{attr}(1,2)}$ for the orientation dependent model, and $a_{OWG}$ is the same quantity for the orientation independent model. This direct analogy does also exist for the continuum versions of both models [13]. Note from Eq. 6.17 that in order to obtain the same distribution $G(l, m, n)$ in both models, a much higher attractive interaction potential $u_{attr}(1, 2)$ is needed in the directional fluid case. This difference is clearly caused by the fact that bond formation is more restricted in the fluid with orientation dependent potentials.

We have chosen to employ the fluid with orientation dependent interactions because the application of the 2-density formalism ($\eta, \eta_0$) is not correct for an orientation independent potential [6]. For full correctness, one should adjust the number of densities involved in the OZ-matrix to the maximum number of attractive bonds that a particle can form. Thus, one should not use the OZ-matrix as a tool to limit the number of bonds per particle.

Finally, for strongly associating particles ($|u_{attr}| >> k_BT$) it is necessary to combine the total- and direct correlations with the non-bonded particle packing fraction $\eta_0$. The new variables $H_{ij}(l, m, n)$ read

$$\begin{align*}
\mathcal{H}_{00}(l, m, n) &= h_{00}(l, m, n) \\
\mathcal{H}_{01}(l, m, n) &= \eta_0 h_{01}(l, m, n) \\
\mathcal{H}_{10}(l, m, n) &= \eta_0 h_{10}(l, m, n) \\
\mathcal{H}_{11}(l, m, n) &= \eta_0^2 h_{11}(l, m, n)
\end{align*} \quad (6.18)$$

An identical replacement is made for the direct correlation matrix elements. The replacements are necessary for the solution scheme of Appendix B diverges for strongly associating fluids. For such fluids $\eta_0 \to 0$, and Eq. B.5 diverges. We have applied Eq. 6.18 in all cases that considered strong association, even if this is not mentioned explicitly. Special interest was paid to infinitely strong associating particles ($a \to \infty$). In that case no non-bonded particles are left ($\eta_0 \to 0$) and a pure dimer lattice fluid which can also be modelled with the RISM-equation [20] is obtained. In section 6.4 we have compared both theories to Monte Carlo simulations.

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6.2.3 Binary mixtures

In this section we will apply the 2-density formalism to a mixture of singly associating A and B particles, that can only form a bond with particles of their own type. The total 2-particle distributions \( G^{AA}(l, m, n) \), \( G^{AB}(l, m, n) \) and \( G^{BB}(l, m, n) \) of two A-, A- and B-, and two B-particles will be calculated. These distributions are directly related to the concentration fluctuations in the mixture [24] and can be split in inter- and intramolecular contributions \( g(l, m, n) \) and \( \omega(l, m, n) \) as will be shown further on.

The interaction potentials present in the A and B mixture are given by

\[
\begin{align*}
  u^{AA}(0, 0, 0, \Omega_1, \Omega_2) & \to \infty \\
  u^{AA}(l, m, n, \Omega_1, \Omega_2) & = u^{attr} \\
  & \text{if } \Omega_1 = -\Omega_2 \text{ and } l^2 + m^2 + n^2 = 1 \text{ and } \\
  & \text{sgn}(l + m + n) \left( l^2 + 2m^2 + 3n^2 \right) = \Omega_1 \\
  u^{AA}(l, m, n, \Omega_1, \Omega_2) & = 0 \quad \text{otherwise} \quad (6.19)
\end{align*}
\]

with \( u^{BB}(l, m, n, \Omega_1, \Omega_2) = u^{AA}(l, m, n, \Omega_1, \Omega_2) \) and

\[
\begin{align*}
  u^{AB}(0, 0, 0, \Omega_1, \Omega_2) & \to \infty \\
  u^{AB}(l, m, n, \Omega_1, \Omega_2) & = 0 \text{ if } \sqrt{l^2 + m^2 + n^2} \geq 1 \quad (6.20)
\end{align*}
\]

Thus, A and B particles never form an attractive bond, only AA and BB dimers are formed.

The OZ-matrix for the mixture reads

\[
H(1, 2) = C(1, 2) + \frac{1}{6} \sum_{r_3, r_5} C(1, 3) \sigma H(3, 2) \quad (6.21)
\]

The matrix \( H(1, 2) \) is given by

\[
H(1, 2) = \begin{bmatrix}
  h^{AA}_{00} & h^{AA}_{01} & h^{AB}_{00} & h^{AB}_{01} \\
  h^{AA}_{10} & h^{AA}_{11} & h^{AB}_{10} & h^{AB}_{11} \\
  h^{BA}_{00} & h^{BA}_{01} & h^{BB}_{00} & h^{BB}_{01} \\
  h^{BA}_{10} & h^{BA}_{11} & h^{BB}_{10} & h^{BB}_{11}
\end{bmatrix} (1, 2) \quad (6.22)
\]

where the \((1, 2)\) on the rhs denotes that all elements of the matrix are dependent on this quantity. The matrix for \( C(1, 2) \) is identical in form. The density matrix is given by

\[
\sigma = \begin{bmatrix}
  \eta^A & \eta^B & 0 & 0 \\
  \eta^A & \eta^B & 0 & 0 \\
  0 & 0 & \eta^B & \eta^B \\
  0 & 0 & \eta^B & 0
\end{bmatrix} \quad (6.23)
\]
In Eq. 6.23, \( \eta^A \) and \( \eta^B \) are the overall densities of A and B particles and \( \eta_0^A \) and \( \eta_0^B \) are the densities of non-bonded A and B particles. In Eq. 6.22, the element \( h_{01}^{AB}(1,2) \) denotes the contribution of an non-bonded (denoted by the 0 in the subscript) particle 1 of type A (denoted by the A in the superscript) and a bonded particle B (to another B particle) to the total correlation \( H^{AB}(1,2) \). The total correlations \( H^{AA}(1,2), H^{AB}(1,2) \) and \( H^{BB}(1,2) \) can be constructed from the partial correlations as

\[
(\eta^A)^2 H^{AA}(1,2) = (\eta^A)^2 h_{00}^{AA}(1,2) + \eta^A \eta_0^A h_{10}^{AA}(1,2) + \eta^A \eta_0^A h_{01}^{AA}(1,2) + (\eta_0^A)^2 h_{11}^{AA}(1,2)
\]

where we can replace the A's with B's to obtain the expression for \( H^{BB}(1,2) \), and

\[
\eta^A \eta^B H^{AB}(1,2) = \eta^A \eta_0^B h_{01}^{AB}(1,2) + \eta_0^A \eta^B h_{10}^{AB}(1,2) + \eta^A \eta_0^B h_{11}^{AB}(1,2)
\]

The total correlations are printed in capitals to distinguish them from the partial AA-, AB-, and BB-correlations \( h_{ij}^{AA}(1,2), h_{ij}^{AB}(1,2) \) and \( h_{ij}^{BB}(1,2) \). From a physical point of view it is clear that \( H^{AB}(1,2) = H^{BA}(1,2) \), and we can therefore also identify symmetry relations between partial correlations: \( h_{00}^{AB}(1,2) = h_{00}^{BA}(1,2), h_{01}^{AB}(1,2) = h_{01}^{BA}(1,2), h_{10}^{AB}(1,2) = h_{10}^{BA}(1,2), h_{11}^{AB}(1,2) = h_{11}^{BA}(1,2) \). Clearly, we also have \( h_{00}^{AA}(1,2) = h_{10}^{AA}(1,2), h_{00}^{BB}(1,2) = h_{10}^{BB}(1,2) \).

The closures that were used are again of PY-type and are given by

\[
y_{ij}^{AA}(1,2) = g_{ij}^{AA}(1,2) - c_{ij}^{AA}(1,2)
\]

and

\[
g_{ij}^{AA}(1,2) = e_R(1,2) (y_{ij}^{AA}(1,2) + \delta_{i1} \delta_{j1} f_A(1,2) y_{00}^{AA}(1,2))
\]

where we can replace all A’s by B’s to obtain the closures for the BB correlations. The closures for the AB correlations have no orientational dependence, due to the absence of attractive forces between A and B particles, and are given by

\[
y_{ij}^{AB}(1,2) = g_{ij}^{AB}(1,2) - c_{ij}^{AB}(1,2)
\]

and

\[
g_{ij}^{AB}(1,2) = e_R(1,2) y_{ij}^{AB}(1,2)
\]

For the \( y_{ij}^{IJ}(1,2) \)'s we have the same symmetries as for the \( h_{ij}^{IJ}(1,2) \)'s. The relations between the partial correlations \( h_{ij}^{IJ}(1,2) \) and \( g_{ij}^{IJ}(1,2) \), with \( \{i,j\} \in \{0,1\} \) and \( \{I, J\} \in \{A, B\} \), are given by

\[
h_{ij}^{IJ}(1,2) = g_{ij}^{IJ}(1,2) - \delta_{ij} \delta_{i0}
\]

Finally, we have two self-consistency relations for the mixture

\[
\eta^A = \eta_0^A + \frac{(\eta_0^A)^2}{6} \sum_{r_2, \Omega_2} y_{00}^{AA}(1,2) e_R(1,2) f_A(1,2)
\]

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where we can again replace the A-label by B to obtain the self consistency relation for the B particles in the fluid. The set, Eqs. 6.19-6.31, fully determines the structure of the binary mixture. The method of solving the set and determining the orientation averaged 2-particle distributions $G^{AA}(l, m, n)$, $G^{AB}(l, m, n)$ and $G^{BB}(l, m, n)$ from it, is outlined in the second part of appendix B.

It is clear that $G^{AA}(l, m, n)$ and $G^{BB}(l, m, n)$ consist of an intermolecular and an intramolecular part, due to the possibility of covalent bonding. On the other hand, $G^{AB}(l, m, n)$ only consists of an intermolecular part by the absence of AB covalent bonds. Therefore

$$\eta^I G^{IJ}(l, m, n) = \delta_{JJ} (\omega^{IJ}(l, m, n) - \delta_{00} \delta_{m0} \delta_{n0}) + \eta^I g^{IJ}(l, m, n)$$

(6.32)

where $\omega^{IJ}(l, m, n)$ is the intramolecular 2-particle distribution function and $g^{IJ}(l, m, n)$ the intermolecular 2-particle distribution function. The $\delta_{00} \delta_{m0} \delta_{n0}$ corrects for the self correlation that is not included in the $G^{IJ}(l, m, n)$. For mixtures of equimolar quantities A and B, $\eta^A = \eta^B$, we have $g^{AA}(l, m, n) = g^{BB}(l, m, n) = g^{AB}(l, m, n) = g^{BA}(l, m, n)$, for the only difference between A and B particles is the label. Thus, from Eq. 6.32 we see for $\eta^A = \eta^B$

$$\omega^{AA}(l, m, n) = \delta_{00} \delta_{m0} \delta_{n0} + \eta^A (G^{AA}(l, m, n) - G^{AB}(l, m, n))$$

$$g^{AA}(l, m, n) = G^{AB}(l, m, n)$$

(6.33)

This labelling method, which is analogous to labelling techniques used to obtain contrast in neutron scattering experiments [25], offers a method to extract molecular conformations $\omega(l, m, n)$ from the calculations. In contrast, the RISM-approach is critically dependent on the input of an intramolecular distribution function, as was shown in chapters 3-5.

### 6.3 MC simulation

To test the calculated structural correlations, we have simulated the 1-component lattice fluid with the interaction potential given by Eq. 6.6 in the canonical (NVT) ensemble using the Metropolis Monte Carlo (MC) method [26,27]. The system was tested at two overall packing fractions: $\eta = 0.5$ with 864 particles in a 12 x 12 x 12 box and $\eta = 0.3015$ with 1235 particles in a 16 x 16 x 16 box. The boxes had periodic boundaries in all directions. It is important to average over a large amount of particles in an NVT ensemble because the limiting value of $G(l, m, n) = G(r_1, r_2)$ at large separation distances $|r_1 - r_2| \to \infty$ depends on the number of particles $N$ in the box as in [27]

$$\lim_{|r_1 - r_2| \to \infty} G(r_1, r_2) = \frac{\rho^{(2)}(r_1, r_2)}{\rho^2} = 1 - \frac{1}{N}$$

(6.34)
Only for $N \to \infty$ we have $G(l, m, n) \to 1$ as is the case for the calculated $G(l, m, n)$ of section 6.2.2, that is obtained from the grand canonical ensemble [1,2].

New configurations were obtained by randomly and simultaneously generating a lattice position and an orientation (six options) for a randomly chosen particle. Each run consisted of at least $50 \times 10^6$ equilibration moves. Averages were calculated over at least $35 \times 10^6$ configurations.

Averages were updated for the internal energy $E$, the packing fractions $\eta_0$ and $\eta_1$ of non-bonded and bonded particles, and the orientation independent 2-particle distribution function $G(l, m, n)$. Simulations were performed for bond strengths varying from $u_{\text{attr}} = -0.5k_B T$ to $u_{\text{attr}} = -7.0k_B T$ in steps of $0.5k_B T$. In the case of $u_{\text{attr}} = -7.0k_B T$, the acceptance probability for a move had decreased to roughly 5%. The statistical errors in the average values of the quantities were estimated by doing runs for the same system with different initial configurations, by dividing runs in 20 parts and comparing the averages for each part, and by blocking of data [28].

The obtained standard deviations for the simulations performed in this work lead to error bars in the figures of the next section that are smaller than the symbols. The error bars are therefore omitted. It will be shown in section 6.4 that $u_{\text{attr}} = -7.0k_B T$ is sufficient to bind $85\% - 90\%$ of the particles into dimers. The full association limit that corresponds to the pure dimeric fluid, can also be simulated with a different method that simply consists of moving dimers through the box. The results of this simulation have already been presented in chapter 3 of this thesis, and we are thus able to cover the full range of pure monomers to pure dimers.

All simulations were performed on a fourteen MIPS R8000 processor Silicon Graphics Power Challenge XL with an IRIX 6.0 operating system in non-parallel runs. The runs for the systems with the strongest interactions took up to two CPU-hours. The simulation results are available on request via e-mail tgpken@urc.tue.nl.

### 6.4 Results and discussion

#### 6.4.1 1-Component systems

The structural correlations on the lattice and the percentage of bonded particles are fully determined by two parameters, the filling fraction of the lattice $\eta$ and the strength of the directional particle-particle attraction $u_{\text{attr}}$.

Fig. 6.2 shows the fraction $\eta_1/\eta$ of particles bonded into dimers as a function of $u_{\text{attr}}$ at two overall particle densities $\eta$. The comparison of theoretical and simulation results is in good agreement at both packing fractions for $|u_{\text{attr}}| \geq 3k_B T$. At lower attractive energies there is a disagreement that worsens if $|u_{\text{attr}}| \to 0$. 135
Figure 6.2: MC-simulation and theory results for the fraction of bonded particles at $\eta = 0.5$ (■) and $\eta = 0.301514$ (●). Lines are theoretical results.

This disagreement was found previously for a continuum associating fluid model [9], and can be attributed to the fact that we are forced to use different definitions of $\eta_{0}$ and $\eta_{1}$ in the theory and the simulations. The disagreement does not mean that the 2-particle distribution $G(l, m, n)$ that is obtained from the theory is incorrect for $|u_{\text{attr}}| \to 0$: theory and simulations both show the correct limit $G(l, m, n) \to 1$ for $|u_{\text{attr}}| \to 0$.

In the theory, $\eta_{1}$ is defined in terms of the partial correlation $g_{00}(l, m, n, \Omega_{1}, \Omega_{2})$ as (see Eq. 6.16)

$$\eta_{1} = \frac{\eta_{0}^{2}}{6} \sum_{l, m, n} \sum_{\Omega_{2}} g_{00}(l, m, n, \Omega_{1}, \Omega_{2}) f_{A}(l, m, n, \Omega_{1}, \Omega_{2})$$  \hspace{1cm} (6.35)

If the limit $|u_{\text{attr}}| \to 0$ is taken it is seen from Eq. 6.35 that $\eta_{1}/\eta \to 0$: no bonds are formed and the non-associating hard cubic lattice fluid results. In the simulations we can not use definition Eq. 6.35, for $g_{00}(l, m, n, \Omega_{1}, \Omega_{2})$ is a non-physical quantity that can not be obtained from the simulations. Instead, in the simulations, we analyze $\eta_{1}$ by counting contacts that occur between the marked edges, i.e., the attractive sites, of nearest neighbor particles. The $|u_{\text{attr}}| \to 0$-limit of $\eta_{1}$ observed from the simulations is then given by

$$\eta_{1} = \eta \cdot \frac{\eta}{6}$$ \hspace{1cm} (6.36)
in which $\eta/6$ is the probability that a marked edge of a particle forms a bond (with strength $|u_{\text{attr}}| \to 0$) with the marked edge of another (neighboring) particle. Thus, in the simulations we have a hard cubic lattice fluid of particles on which the marked edges are always present, even for $|u_{\text{attr}}| \to 0$.

The definitions, Eqs. 6.35 and 6.36, coincide at high interaction strength, as seen in Fig. 6.2 but differ for low attractive energies. Note that the structure of the theoretical and simulated fluids both reduce to the hard cubic lattice fluid structure for $|u_{\text{attr}}| \to 0$.

The structural correlations that are obtained for the associating fluid model are depicted in Figs. 6.3 and 6.4. In the figures we show the total 2-particle distribution as $G = G(r)$ with $r = \sqrt{l^2 + m^2 + n^2}$). The representation as $G(r)$ does not allow to distinguish between distances (2,2,1) and (3,0,0) or (4,3,0) and (5,0,0) which can in principle have different values for $G(l, m, n)$. From the results of the calculations we have seen that the differences in $G(2, 2, 1)$ and $G(3, 0, 0)$ are sufficiently close to justify simple averaging of these values in drawing the pictures. Note that the total 2-particle distribution is a discrete quantity. The lines are drawn through the calculated points in the figures to get a clear distinction between calculated (lines) and simulated (symbols) values of $G(l, m, n)$. Input parameters for the simulations are $\eta$ and $u_{\text{attr}}$. Input parameters for the theory

Figure 6.3: Calculated (lines) and simulated (symbols) total 2-particle distribution at $\eta = 0.301514$. The upper curve corresponds to $\eta_0 = 0.037340$ and the lower curve to $\eta_0 = 0.131740$ (see text).
are $\eta$ and $\eta_0$, from which we can then calculate $u_{\text{attr}}$ via Eq. 6.16. Therefore, comparisons between theory and simulations in Figs. 6.3 and 6.4 are made at fixed values of $\eta$ and $\eta_0$ obtained from the simulations, and not for fixed values of $\eta$ and $u_{\text{attr}}$. Fig. 6.2 indicates that for $|u_{\text{attr}}| > 3.0k_B T$, there will virtually be no difference between a comparison at fixed $(\eta, u_{\text{attr}})$ or at fixed $(\eta, \eta_0)$. In Figs. 6.3 and 6.4, $u_{\text{attr}} = -4.0k_B T$ (lower curves) and $u_{\text{attr}} = -7.0k_B T$ (upper curves), the comparison at fixed $\eta$ and $\eta_0$ is therefore unambiguous.

The agreement between theory and simulation is good in all cases but seems to worsen a little for increasing association strength (upper curves in Figs. 6.3 and 6.4). Therefore, we have also performed a simulation of a fully associated, i.e., dimeric, fluid in which the particle-particle bond is infinitely strong. The simulation of the dimeric fluid, performed in the $NpT$-ensemble by moving the dimers through the box with the reptation move [29], is described in detail elsewhere [30,31]. The results are depicted in Fig. 6.5. They indicate a slight underestimation of the structural correlations. Nevertheless, the performance of the theory given by the dashed lines is very good. We therefore conclude that the approach described in section 6.2 works well for the whole range $|u_{\text{attr}}| \to 0$ to $u_{\text{attr}} \to -\infty$. The 2-particle distributions depicted in the figures can be used to obtain the pressure via e.g., the compressibility route. This is well possible [7] but we have not yet executed such a program.
Figure 6.5: Simulations (symbols) and calculations (lines) of the 2-particle distribution function at $\eta = 0.5073$ (■, lower curves) and $\eta = 0.3014$ (●, upper curves). The full lines are obtained with the lattice-RISM model and the dashed lines are the result of the associating fluid model at $u_{\text{attr}} \to -\infty$.

Fig. 6.5 also contains the predictions of the cubic lattice version of the RISM-equation for dimeric molecules [32]. The RISM-calculations are performed within the Percus-Yevick approximation with the intramolecular distribution function $\omega(l, m, n)$ taken to be characteristic of a dimeric molecule

$$
\begin{align*}
\omega(0, 0, 0) &= 1 \\
\omega(l, m, n) &= \frac{1}{6} \quad \text{if } r = 1 \\
\omega(l, m, n) &= 0 \quad \text{otherwise}
\end{align*}
$$

(6.37)

The total 2-particle distribution that is plotted in Fig. 6.5 is in RISM-language given by the sum of the inter- and intramolecular 2-particle distributions as in Eq. 6.32. It is seen in the figure that both the RISM- and the associating fluid theory provide accurate descriptions of the correlations present in a dimeric liquid. Some of the data of Fig. 6.5 are stored in Tables 6.1 and 6.2.

It is seen from Tables 6.1 and 6.2 that the RISM-theory is the most accurate at the higher density but that the associating fluid theory is more accurate at the lower density where the correlations are more pronounced. Note that the input parameters used in the associating fluid theory are $\eta$ and $u_{\text{attr}} \to -\infty$ whereas in the RISM-theory they are $\eta$ and $\omega(l, m, n)$ (Eq. 6.37). In the RISM approach one
explicitly feeds the equation with the molecular structure, while in the associating fluid theory the dimers are constructed via an infinitely strong attraction. This offers possibilities to extract the intramolecular 2-particle distribution from the theory as is shown in the next section.

### 6.4.2 Mixtures

In Fig. 6.6 the total AA- and AB-correlations are depicted for an equimolar mixture of A and B particles. In the limit of infinitely strong directional attractions between A and between B particles, and no directional attraction between A and B particles, a mixture of AA and BB dimers results. The AA and BB molecules are distinguishable but further identical. This labelling allows for calculation of the intramolecular contribution $\omega^{AA}(l, m, n)$ to $G^{AA}(l, m, n)$ as was explained in section 6.2. For the situation depicted in Fig. 6.6 we have calculated according to Eq. 6.33 that $\omega^{AA}(l, m, n)$ is given by

$$
\begin{align*}
\omega^{AA}(0, 0, 0) &= 1 \\
\omega^{AA}(l, m, n) &= 0.1 \times (2.368459 - 0.701792) = \frac{1}{6} \text{ if } r = 1 \\
\omega^{AA}(l, m, n) &= 0 \quad \text{if } r > 1
\end{align*}
$$

(6.38)

At all other overall packing fractions that were studied the same result, Eq. 6.38, was found. The labelling method thus allows for calculation of the intramolecular distribution function $\omega(l, m, n)$. The result for $\omega(l, m, n)$ obtained for the model

<table>
<thead>
<tr>
<th>$G(l, m, n)$</th>
<th>MC</th>
<th>RISM</th>
<th>Ass. Fl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0,0)</td>
<td>1.279</td>
<td>1.299123</td>
<td>1.271956</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>0.969</td>
<td>0.971886</td>
<td>0.972468</td>
</tr>
<tr>
<td>(1,1,1)</td>
<td>1.004</td>
<td>1.003938</td>
<td>1.004149</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>0.984</td>
<td>0.985817</td>
<td>0.986091</td>
</tr>
</tbody>
</table>

Table 6.1: $G(l, m, n)$ at $\eta = 0.3014$

<table>
<thead>
<tr>
<th>$G(l, m, n)$</th>
<th>MC</th>
<th>RISM</th>
<th>Ass. Fl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0,0)</td>
<td>1.091</td>
<td>1.097586</td>
<td>1.081557</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>0.982</td>
<td>0.983238</td>
<td>0.985905</td>
</tr>
<tr>
<td>(1,1,1)</td>
<td>1.004</td>
<td>1.004228</td>
<td>1.003576</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>0.990</td>
<td>0.991360</td>
<td>0.992731</td>
</tr>
</tbody>
</table>

Table 6.2: $G(l, m, n)$ at $\eta = 0.5073$
studied in this chapter is the exact intramolecular distribution function of a dimer on a cubic lattice (see Eq. 6.37). Therefore, the method is promising to apply to a fluid of particles with two associative sites. In that case it is possible to simultaneously extract the average inter- and intramolecular distribution function of a lattice fluid consisting of flexible polymer molecules. This is in great contrast to the polymer RISM approach [33] in which the intramolecular distribution of the flexible polymer molecules is required as an input quantity.

6.5 Conclusions

In this chapter we have applied Wertheim's associating fluid theory [1,2] to study dimerization in singly associating 1-component systems and binary mixtures on a cubic lattice. The results for the structural correlations were tested against Monte Carlo simulations for the whole range of association strengths, $u_{attr} \to 0$ to $u_{attr} \to -\infty$. Very good overall agreement was found, indicating that the formalism is nearly quantitative in incorporating the effect of the directional attractions on the fluid structure. Therefore, it is expected that an accurate equation of state and other thermodynamic properties can be obtained for associating fluids from this ap-
We have also investigated a labelling method that allowed for separation of the total 2-particle distribution in an inter- and an intramolecular part. The method works well for the dimeric fluid studied here, and can be applied to polymerizing fluids. The simultaneous calculation of the inter- and intramolecular 2-particle distribution is desirable, especially if flexible (polymer) molecules for which there is an intrinsic coupling of both quantities are considered [34].
References


Chapter 7

Lattice fluid of associating particles with two directional attractive forces: Condensation polymerization

7.1 Introduction

In this chapter, a new cubic lattice model for polymerizing fluids is presented. It is an application of the associating fluid theory of Wertheim [1-4]. The fluid consists of non-overlapping particles that occupy exactly one lattice site and are able to form two directional attractive interactions with other particles. The structural properties of the model are tested by comparison to Monte Carlo simulations that use a new move based on the Configurational bias MC-scheme of Siepmann and Frenkel [5] and the cluster scheme of Wu, Chandler and Smit [6].

For weakly attractive interactions (\(|u_{\text{attr}}| << k_B T\)), the theory provides a description of the structural correlations in associating fluids, but if the attractions are strong enough (\(|u_{\text{attr}}| >> k_B T\)), the contacts can serve as covalent bonds. Polymeric chains can then be formed on the lattice. In that case, the fluid particles serve as the monomeric segments from which the polymer chains are built [7]. The lattice fluid described above, is an example of a condensation polymerization product [8]. In this chapter we are interested in calculating the average 2-particle distribution function \(G(1,2)\), the number and mass average chain lengths \(\bar{L}_N\) and \(\bar{L}_W\), and the width of the chain length distribution of such fluids.

The method that will be outlined below has the advantage that both the intramolecular and intermolecular 2-particle distribution functions \(\omega(1,2)\) and \(g(1,2)\) can be obtained simultaneously from the theory. Such is also possible with the self con-
sistent polymer-RISM theory [9-11]. Other approaches that are used to obtain the structural correlations in polymeric liquids, such as the standard polymer-RISM model [12,13] and Chiew's Percus-Yevick integral equation theory [14,15] only allow for the calculation of \( g(1,2) \). Chiew's theory takes intramolecular correlations only approximately into account, and in the polymer-RISM theory, \( \omega(1,2) \), which is a measure of the molecular conformation, is needed as an input quantity for the calculation of \( g(1,2) \). This is an important disadvantage of the polymer-RISM theory because for non-rigid molecules there is an interdependence of the intermolecular 2-particle distribution function \( g(1,2) \) and the intramolecular 2-particle distribution \( \omega(1,2) \). Due to this interdependence, \( g(1,2) \) and \( \omega(1,2) \) cannot be obtained separately, except in 1-component polymer systems at sufficiently high density for which Flory's ideality hypothesis [16] is confirmed experimentally [17]. It states that flexible chain molecules behave ideally, meaning that intramolecular excluded volume interactions are counter-balanced by the intermolecular forces present in the liquid, which causes the average distance between the ends of a chain \( < R^2 > \) to scale linearly with the number of bonds between the segments of the chain. This property can be used to obtain accurate approximations for \( \omega(1,2) \) which can then be employed to calculate \( g(1,2) \) [13]. Deviations from the average ideal dimensions of a chain conformation in polymer solutions [18] and in mixtures [18,19], make that the ideality hypothesis can not be used in such systems. For these cases, it therefore seems appropriate to use an approach which does not rely on the input of an intramolecular distribution \( \omega(1,2) \).

A reason for adopting a lattice within the OZ-matrix formalism was to allow for comparisons to other lattice models that are commonly used to assess the thermodynamic properties of polymeric systems [20-25]. As a first step towards such a comparison, we have focussed on the structural correlations between the particles, for these form the basis for calculating the thermodynamic properties of the model. A second justification for resorting to discretized space is that there is a complete absence of liquid-like ordering effects in our lattice model. This allows to investigate the abilities of the theory to incorporate the effect of the directional attractions on the structural correlations, without an interference of liquid-like ordering effects caused by the repulsive cores of the particles. These ordering effects are pre-dominant in continuum model systems at higher packing fractions.

The outline of the rest of this chapter is as follows. In section 7.2 we present the basic expressions for a 1-component lattice fluid of particles that can form two directional attractive bonds [3,4]. Investigations of analogous models for continuum fluids have recently been presented [26-29]. The two attractive sites on each particle are considered to be identical. Therefore, we rely on the approach of Kalyuzhnyi and Stell [30] who have rewritten Wertheim's formalism, which considers distinguishable sites, for the case of two identical attractive sites. The
average orientation independent 2-particle distribution \( G(1, 2) \) will be calculated from the theory by solving the complete set of equations presented in the next section. These results are compared to an approximate solution method due to Chang and Sandler [28] in section 7.2.2.

The equations for a 2-component mixture of A and B particles will be presented in section 7.2.3, together with a labelling method that is used to extract both the inter- and intramolecular distribution function [31]. We will also calculate the number- and mass average chain length \( \bar{L}_N \) and \( \bar{L}_W \), and the width of the distribution \( \bar{L}_N/\bar{L}_W \). In section 7.3 a \( NVT \) Monte Carlo simulation for the 1-component lattice fluid is presented. From this simulation the structural correlation data and the length distribution of the chains in the box are obtained. Simulations were performed at varying packing fractions \( \eta \) and attractive particle-particle strength \( u_{\text{attr}} \). Longer chains \( (\bar{L}_N \geq 10) \) are only formed at \( |u_{\text{attr}}| \geq 5k_B T \), where conventional brute force MC moves of a single particle become increasingly difficult. Therefore, we have employed a cocktail of special MC moves [5,6,32-38]. In section 7.4, all results are presented and discussed. We will end the chapter with some concluding remarks in section 7.5.

### 7.2 Lattice formulation of the 3-density formalism

In section 7.2.1 the lattice version [39] of the 3-density formalism for a 1-component system of particles with two associating sites is presented. It is outlined how to calculate the 2-particle distributions of such systems as a function of overall packing fraction \( \eta \) and strength of the associative interparticle interaction \( u_{\text{attr}} \). The number and mass average chain lengths \( \bar{L}_N \) and \( \bar{L}_W \) of the chains that are formed will also be calculated. In section 7.2.2 we present the lattice analog of an approximate solution proposed by Chang and Sandler [28]. In section 7.2.3 we will present the formalism for mixtures of particles A and B and outline how we can divide the total 2-particle distributions in inter- and intramolecular contributions.

#### 7.2.1 1-Component systems

In this section the basic equations of the 3-density formalism for particles with two identical attractive sites on a 3D cubic lattice are outlined. It is a 3-density formalism because for particles with two attractive sites three types of particles can be distinguished. The overall packing fraction \( \eta \) can be split in \( \eta_0 \), \( \eta_1 \) and \( \eta_2 \) that denote respectively the non-bonded (free monomers), the singly bonded (chain end) and doubly bonded packing fractions

\[
\eta = \eta_0 + \eta_1 + \eta_2
\]
Non-overlapping particles on a 3D cubic lattice fill exactly one lattice site and have two sticky sites located at two of the edges of the lattice site. If the sticky sites of two neighboring particles point towards each other, bond formation occurs. The particle-particle interaction potential is given by

\[ u(1, 2) = u_R(1, 2) + \sum_{s_1=1}^{2} \sum_{s_2=1}^{2} u_{s_1,s_2}(1, 2) \]  

(7.2)

where the coordinates 1 and 2 denote the positions \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) of particles 1 and 2 and the orientations of their sticky sites, via orientation parameter \( \Omega_s \) associated to each sticky site \( s \). On the cubic lattice, it is only the relative position \( \mathbf{r}_2 - \mathbf{r}_1 = (l, m, n) \) that is of importance. The \( u_R(1, 2) \) is the orientation independent repulsive part of the particle-particle potential

\[ u_R(0, 0, 0) \rightarrow \infty \]
\[ u_R(l, m, n) = 0 \quad \text{otherwise} \]  

(7.3)

and \( u_{s_1,s_2}(1, 2) \) is an attractive, orientation dependent site-site potential

\[ u_{s_1,s_2}(0, 0, 0, \Omega_{s_1}, \Omega_{s_2}) = 0 \]
\[ u_{s_1,s_2}(l, m, n, \Omega_{s_1}, \Omega_{s_2}) = u_{\text{attr}} \]
\[ \text{if } \Omega_{s_1} = -\Omega_{s_2} \text{ and } l^2 + m^2 + n^2 = 1 \]
\[ \text{and } \text{sgn}(l + m + n) (l^2 + 2m^2 + 3n^2) = \Omega_{s_1} \]
\[ u_{s_1,s_2}(l, m, n, \Omega_{s_1}, \Omega_{s_2}) = 0 \quad \text{otherwise} \]  

(7.4)

On the cubic lattice there are six possible orientations. They are characterized by \( \Omega_s \): \( \Omega_s = +1 \) if site \( s \) points in the +l-direction, \( \Omega_s = -1 \) if \( s \rightarrow -l \), \( \Omega_s = \pm 2 \) if \( s \rightarrow \pm m \) and \( \Omega_s = \pm 3 \) if \( s \rightarrow \pm n \). In Eq. 7.4 \( \text{sgn}(l + m + n) \) denotes the sign of \( l + m + n \). In Eqs. 7.2-7.4 it is assumed that the attractive sites on a fluid particle do not affect each other, there is no restriction on the angle between the two sites. Thus, the chains that are formed are fully flexible, i.e., they do not show excluded volume properties [18,40-42]. The imposed independence of the sticky sites is an approximation that is not present in the graphical analysis [3,4] which underlies the equations that are presented in this section. However, it is adopted here in order to solve the equations that result from the graphical analysis.

The main quantity of interest for the model outlined above, is the orientation averaged 2-particle distribution function \( G(l, m, n) \) at fixed \( \eta \) and \( u_{\text{attr}} \). Physically, \( \eta G(l, m, n) \) is the probability that there is a particle 2 at \( \mathbf{r} = (l, m, n) \) on condition that there is a particle 1 located at the origin \( \mathbf{0} = (0, 0, 0) \). Once \( G(l, m, n) \) is known the equation of state of the lattice fluid can be obtained, e.g., via the compressibility theorem [43]. Apart from \( G(l, m, n) \), we are also interested in the mass- and number average chain lengths \( \overline{L_N} \) and \( \overline{L_W} \) of the model.

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The basic ingredients needed to calculate the quantities mentioned above, are an Ornstein-Zernike-like matrix equation, a set of Percus-Yevick-like closure equations and a self-consistent mass balance equation [3,4]. The diagrammatic derivation of the equations has been presented by Wertheim [3,4] for the case of two distinguishable attractive sites per particle. Kalyuzhnyi and Stell [30] have used this derivation to arrive at analogous expressions for the case of two indistinguishable sites per particle.

The OZ-matrix equation that results from the diagrammatic analysis reads when transplanted to the cubic lattice [30]

\[
\mathbf{H}(1,2) = \mathbf{C}(1,2) + \frac{1}{6} \sum_{r_n,s_3} \mathbf{C}(1,3) \sigma \mathbf{H}(3,2)
\]  

(7.5) in which \((1,2)\) denotes the dependence of the quantities on the coordinates, position and orientation of sites, of particles 1 and 2. The matrix \(\mathbf{H}(1,2)\) is given by

\[
\mathbf{H}(1,2) = \begin{pmatrix}
 h_{00} & h_{01} & h_{02} \\
 h_{10} & h_{11} & h_{12} \\
 h_{20} & h_{21} & h_{22}
\end{pmatrix}
\]  

(7.6)

The \((1,2)\) on the rhs of this equation denotes that all elements of the matrix are dependent on \((1,2)\). The matrix for \(\mathbf{C}(1,2)\) is of identical form, and the density matrix is given by

\[
\sigma = \begin{pmatrix}
 \sigma_2 & \sigma_1 & \sigma_0 \\
 \sigma_1 & \sigma_0 & 0 \\
 \sigma_0 & 0 & 0
\end{pmatrix}
\]  

(7.7)

with

\[
\sigma_i = \sum_{j=0}^{i} \eta_{ij}
\]  

(7.8)

For the elements of \(\mathbf{H}(1,2)\) and \(\mathbf{C}(1,2)\) we have the physically plausible symmetry relations \(h_{ij}(1,2) = h_{ji}(1,2)\) and \(c_{ij}(1,2) = c_{ji}(1,2)\). The element \(h_{ij}(1,2)\) denotes a part of the total 2-particle correlation \(H(1,2)\) in which particle 1 is bonded to \(i\) other particles and particle 2 is bonded to \(j\) other particles, where \(\{i, j\} \in \{0, 1, 2\}\). The elements \(h_{ij}(1,2)\) do not have a physical meaning by themselves, but the calculations have to be performed in terms of these variables to be able to incorporate the effect of directional association into the Ornstein-Zernike theory.

The matrix equation is supplemented with a PY-type closure set given by [30]

\[
c_{ij}(1,2) = g_{ij}(1,2) - y_{ij}(1,2)
\]  

(7.9)

and the exact set

\[
g_{ij}(1,2) = c_R(1,2)(y_{ij}(1,2) + (1 - \delta_{i0})(1 - \delta_{j0})f_A(1,2)y_{i-1,j-1}(1,2))
\]  

(7.10)
where \( f_A(1,2) = e^{-\beta u_{s1,s2}(1,2)} - 1 \) and \( u_{s1,s2}(1,2) \) is given by Eq. 7.4. The \( \delta_{ij} \) is a Kronecker delta. The second term in Eq. 7.10 accounts for the bonding between particles. In Eqs. 7.9 and 7.10 \( \{i, j\} \in \{0, 1, 2\} \).

The relation between the partial correlations \( h_{ij}(1,2) \) and the partial 2-particle distributions \( g_{ij}(1,2) \) is given by [30]

\[
h_{ij}(1,2) = g_{ij}(1,2) - \delta_{ij}\delta_{0}
\]

From the partial 2-particle correlations \( h_{ij}(1,2) \) we can construct the total 2-particle correlation \( H(1,2) \) as shown further on. The set Eqs. 7.5-7.11 can be solved for fixed values of \( \eta \) and \( u_{\text{attr}} \) if it is known how \( \eta \) is distributed among \( \eta_0, \eta_1 \) and \( \eta_2 \). This is provided by the self-consistent mass balance equation that is obtained if Eq. 7.12 and Eq. 7.13 are substituted in Eq. 7.1. It gives the \( \eta_i \)'s in terms of the partial correlations present in the fluid. We have [30]

\[
\eta_1 = \eta_0 C_1 \\
\eta_2 = \eta_0 (C_1^2 + C_2)
\]

where

\[
C_1 = \frac{\sigma_1}{6} \sum_{r_2,\Omega_2} y_{00}(1,2)e_R(1,2)f_A(1,2) + \frac{\eta_0}{6} \sum_{r_2,\Omega_2} y_{10}(1,2)e_R(1,2)f_A(1,2)
\]

\[
C_2 = \frac{\sigma_1}{6} \sum_{r_2,\Omega_2} y_{10}(1,2)e_R(1,2)f_A(1,2) + \frac{\eta_0}{6} \sum_{r_2,\Omega_2} y_{11}(1,2)e_R(1,2)f_A(1,2)
\]

(7.13)

with \( e_R(1,2) = e^{-\beta u_R(1,2)} \).

The set Eqs. 7.1-7.13 has to be solved for the partial correlations \( h_{ij}(1,2) \) in order to obtain the total orientation averaged 2-particle distribution \( G(l, m, n) \).

The independence of the sticky sites assumed in Eqs. 7.2-7.4 is a necessary approximation [28] in orientation averaging of the OZ-matrix Eq. 7.5. A second approximation necessary to be able to write the closure equation, Eq. 7.10, and the mass balance equations, Eq. 7.13, in an orientation independent form, is pre-averaging of \( f_A(1,2) \) over the orientations \( \Omega_{s1} \) and \( \Omega_{s2} \) of the sticky sites [28]

\[
f_A(l, m, n) = \frac{1}{36} \sum_{\Omega_{s1}, \Omega_{s2}} (e^{-\beta u_{s1,s2}(l,m,n,\Omega_{s1},\Omega_{s2})} - 1)
\]

(7.14)

which gives

\[
f_A(l, m, n) = \frac{1}{36}(a - 1) \quad \text{if} \quad l^2 + m^2 + n^2 = 1
\]

\[
f_A(l, m, n) = 0 \quad \text{otherwise}
\]

(7.15)
with \( a = e^{-\beta_{\text{attr}}} \). The pre-averaging of \( f_A(1,2) \) and the assumed independence of the sticky sites eliminate the details of the angular dependence of the partial correlation functions \( h_{ij}(1,2) \) \[28\]. Nevertheless, in the graphical analysis \[3,4\] that underlies the equations presented here, the orientational dependence of \( f_A \) and the independence of the sticky sites on a particle are present explicitly and used to arrive at the equations that we solve here. Thus, the influence of the directionality of the attractive potentials on \( G(l, m, n) \) is still present in Eqs. 7.1-7.15. A procedure to obtain the \( h_{ij}(l, m, n) \) from Eqs. 7.1-7.15 is presented in Appendix C.

The total orientation averaged correlation \( H(l, m, n) \) is obtained from the partial orientation averaged 2-particle correlations \( h_{ij}(l, m, n) \) via \[30\]

\[
\sigma^2 H(l, m, n) = \sigma^2 h_{00}(l, m, n) + 2\sigma_1\sigma_2 h_{10}(l, m, n) + 2\sigma_0\sigma_2 h_{20}(l, m, n) + \\
\sigma^2 h_{11}(l, m, n) + 2\sigma_0\sigma_1 h_{21}(l, m, n) + \sigma^2 h_{22}(l, m, n)
\] (7.16)

and the 2-particle distribution \( G(l, m, n) \) is finally found from

\[
H(l, m, n) = G(l, m, n) - 1
\] (7.17)

Apart from \( G(l, m, n) \), we are also interested in the number and mass average chain lengths, \( \bar{L}_N \) and \( \bar{L}_W \), and in the chain size distribution of the model fluid. A well known measure of the size distribution is the width parameter defined by \( \bar{L}_W/\bar{L}_N \) \[8\]. Flory has expressed \( \bar{L}_N \) and \( \bar{L}_W \) in terms of the extent of reaction \( p \), which is the probability that a particle has formed a bond with another particle, as \[44\]

\[
\frac{\bar{L}_N}{\bar{L}_W} = \frac{1}{1-p}
\] (7.18)

For the model outlined here we can express \( p \) in terms of the packing fractions \( \eta_i \), as

\[
p = \frac{\eta_1 + 2\eta_2}{2\eta}
\] (7.19)

and therefore

\[
\bar{L}_N = \frac{2\eta}{2\eta_0 + \eta_1}
\]
\[
\bar{L}_W = \frac{2\eta_0 + 3\eta_1 + 4\eta_2}{2\eta_0 + \eta_1}
\]
\[
\frac{\bar{L}_W}{\bar{L}_N} = \frac{2\eta_0 + 3\eta_1 + 4\eta_2}{2\eta}
\] (7.20)

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The expression for $\overline{L}_N$ that is obtained in this way is equal to the expression given by Wertheim [4]. In order to obtain the results of Eqs. 7.18-7.20, the possibility of ring formation was neglected. From Eq. 7.18 it is seen that for a complete ($p = 1$) condensation polymerization $\overline{L}_W/\overline{L}_N$ approaches the value of 2. This limit is also observed experimentally [8]. Note that the values for $\overline{L}_N$ and $\overline{L}_W$ are obtained directly from the densities $\eta_0$, $\eta_1$ and $\eta_2$ and that no approximations are involved apart from the neglect of ring formation. This is in contrast to the approach of Ott Weist and Glandt [27] who developed a scheme based on integral equations that were used previously to describe the percolation phenomenon [45-47]. Their approach does not only neglect the formation of rings, but also relies on approximate closure relations for the integral equations.

In a recent paper, Ott Weist and Glandt [27] have presented a continuum model of a fluid of particles with two attractive sites that is closely related to the model presented above. The main difference, apart from the discretization of space, lies in the fact that the attractive parts of the potentials used in the Ott Weist and Glandt approach are symmetric around the particle origin. They do not have a direction. With help of the 3-density formalism, Ott Weist and Glandt restrict the maximum number of bonds per particle in their model to two. It can be shown that the orientation averaged equations of the model presented above (Eqs. 7.1, 7.8, 7.12, C.3-C.8) are equal to the equations obtained from the cubic lattice version of the Ott Weist and Glandt model if

$$\frac{a_W - 1}{a_{OWG} - 1} = 36 \quad (7.21)$$

where $a_W = e^{-\beta_{attr}}$ for the model of particles with directional forces (Eq. 7.4), and $a_{OWG}$ is the same quantity for the model studied by Ott Weist and Glandt. This analogy of both models also exists for the case of particles with one attractive site [48,31].

It is seen from Eq. 7.21 that in order to obtain the same 2-particle distribution $G(l, m, n)$ for both models, a much higher attractive interaction is needed if directional attractions are considered. Obviously, in the case of directional potentials, bond formation is more restricted. In the lattice version of the Ott Weist - Glandt model bond formation occurs between nearest neighbor particles which both have less than two bonds with other particles. In the case of directional attractions, we need to supplement these conditions by the condition that both particles must have attractive sites that point towards each other.

We have chosen to study the model of particles with directional attractions because we believe that one should not use the 3-density formalism to limit the number of bonds that a particle can form to two as Ott Weist and Glandt do but that one should adjust the number of densities used in the matrix formalism to the saturation number of the particle potentials [30]. Although the lattice version of the Ott Weist - Glandt model and the orientation averaged version of
the model presented here can be mapped onto each other with help of Eq. 7.21, we think that the above mentioned objection is not purely formal: it is not clear how to incorporate the saturation of the attractive potentials in a Monte Carlo simulation of the Ott Weist and Glandt model. An unambiguous MC-test of this model can therefore not be performed. One does not have this problem for a MC simulation of a fluid of particles with directional forces (see section 7.3).

Finally, we want to make a practical remark about the chain lengths that can be achieved for our lattice model. The average chain length that is reached depends on $\eta$ and $u_{\text{attr}}$. It is demonstrated in the simulation-section 7.3 that in order to obtain large chain lengths ($L_N \geq 10$) strong interactions are needed ($|u_{\text{attr}}| \geq 5k_B T$). For such large interaction strengths the solution scheme presented in Appendix C is unstable, and a re-combination of variables is needed to control the numerical scheme. Such a re-combination is presented in Appendix D.

7.2.2 Chang-Sandler approximation for the 1-component system

In this subsection we present an approximate method to obtain $G(l, m, n)$ for the model potential given in Eqs. 7.2-7.4. The method was first used by Chang and Sandler for a continuum polymerizing fluid. The results of their comparison of the 2-particle distribution to MC-simulations of monodisperse fluids were good at high and intermediate packing fraction [28]. Recently, they have also reported an investigation of hard sphere chain fluid mixtures with asymmetries in the segment size [29]. Here we investigate their solution method on the cubic lattice. The extra approximation Chang and Sandler make, amounts to neglecting all subgraphs that contain $\sigma_0$-factors in the graphical expansions of $h_{ij}(l, m, n)$ and $c_{ij}(l, m, n)$ in terms of the $f_R$, $F$-bonds and the $\sigma_i$'s [3,4,28]: graphically it means that all $s$-mer subgraphs with $s \geq 3$ are neglected. This results in

$$C_1 = \frac{\sigma_1}{6} \sum_{r_2, \Omega_2} y_{00}(1,2)e_R(1,2)f_A(1,2)$$

$$C_2 = 0$$

$$c_{i2}(l, m, n) = c_{i1}(l, m, n) = 0$$

$$h_{i2}(l, m, n) = h_{i1}(l, m, n) = 0$$

(7.22)

Physically, Eq. 7.22 results in a vanishing of the intramolecular correlations [28]. The absence of $s = 3$-mer graphs and other higher order $s$-mer graphs implies that particles that are part of the same chain cannot feel each others repulsive cores (via the $f_R$-bonds present in the $s \geq 3$-graphs). The chain molecules are thus not subject to excluded volume interactions [18,40-42]. The solution of the OZ-matrix formalism with Eq. 7.22 is briefly outlined in Appendix E. In the full
solution of the equations presented in section 7.2.1 approximation Eq. 7.22 is not used, but the chains that are formed don’t have a fully developed excluded volume either. This is not due to the underlying graphical analysis, as in the case of the Chang-Sandler solution, but to the assumption that the two attractive sites on a particle are fully independent of each other (see Eqs. 7.2-7.4 and Appendix C). Therefore, it can be expected that Eq. 7.22 is of little influence on the solution of the problem. This is confirmed in section 7.4 where we compare the full solution of the lattice model and the Chang-Sandler solution to 3D Monte Carlo simulations. The full solution only gives slightly better results. The fact that the intramolecular excluded volume is not fully incorporated in the model does not mean that the intramolecular structure is independent of the thermodynamic state of the system. This is in contrast to the original formulation of the polymer-RISM model as formulated in Ref. [13].

7.2.3 Binary mixtures

In this section we present a method to divide the total 2-particle correlation \( G(l,m,n) \) in intermolecular, \( g(l,m,n) \), and intramolecular, \( w(l,m,n) \), contributions.

We start by considering a mixture of two particle types A and B, both of which can only form covalent bonds with particles of their own type. Thus, no chain molecules of mixed particle type will be formed. The particle-particle interaction potentials are given by

\[
\begin{align*}
  u^{IJ}(1,2) &= u_R^{IJ}(1,2) + \sum_{s_1=1}^{2} \sum_{s_2=1}^{2} u_{s_1,s_2}^{IJ}(1,2) \\
  \text{with} \\
  u_R^{IJ}(0,0,0) &\to \infty \\
  u_R^{IJ}(l,m,n) &= 0 \quad \text{otherwise}
\end{align*}
\]

(7.23)

and

\[
\begin{align*}
  u_{s_1,s_2}^{IJ}(0,0,0,\Omega_{s_1},\Omega_{s_2}) &= 0 \\
  u_{s_1,s_2}^{IJ}(l,m,n,\Omega_{s_1},\Omega_{s_2}) &= \delta_{IJ} u_{\text{attr}} \\
  \text{if } \Omega_{s_1} = -\Omega_{s_2} \text{ and } l^2 + m^2 + n^2 = 1 \\
  \text{and } sgn(l + m + n) (l^2 + 2m^2 + 3n^2) = \Omega_{s_1} \\
  u_{s_1,s_2}^{IJ}(l,m,n,\Omega_{s_1},\Omega_{s_2}) &= 0 \quad \text{otherwise}
\end{align*}
\]

(7.25)

where \( \{I,J\} \in \{A,B\} \) denote the type of particle, \( \{s_1,s_2\} \in \{1,2\} \) denote the sites on the particles. It is clear from Eq. 7.25 that the A-B interaction is purely repulsive and that the attractive strength of the A-A interaction is equal to the
strength of the B-B interaction.
The OZ-matrix equation is still given by Eq. 7.5, but the $\mathbf{H}(1,2)$ and $\mathbf{C}(1,2)$ matrices that have to be considered, now contain 36 elements

$$
\mathbf{H}(1,2) = \begin{pmatrix}
    h_{00}^{AA} & \cdots & h_{02}^{AA} & \cdots & h_{02}^{AB} & \cdots & h_{02}^{BB} \\
    \vdots & \ddots & \vdots & \ddots & \vdots & \ddots & \vdots \\
    h_{20}^{AA} & \cdots & h_{22}^{AA} & \cdots & h_{22}^{AB} & \cdots & h_{22}^{BB} \\
    h_{00}^{BA} & \cdots & h_{02}^{BA} & \cdots & h_{02}^{BB} & \cdots & h_{02}^{BB} \\
    \vdots & \ddots & \vdots & \ddots & \vdots & \ddots & \vdots \\
    h_{20}^{BA} & \cdots & h_{22}^{BA} & \cdots & h_{22}^{BB} & \cdots & h_{22}^{BB}
\end{pmatrix}_{(1,2)}
$$

which is more compactly denoted as

$$
\mathbf{H}(1,2) = \begin{pmatrix}
    H^{AA} & H^{AB} \\
    H^{BA} & H^{BB}
\end{pmatrix}_{(1,2)}
$$

The (1,2) indicate that the elements of the matrices are a function of the coordinates, position and orientation of sticky sides, of particles 1 and 2. The density matrix reads

$$
\sigma = \begin{pmatrix}
    \sigma^A & 0 \\
    0 & \sigma^B
\end{pmatrix}
$$

where

$$
\sigma^A = \begin{pmatrix}
    \sigma_2^A & \sigma_1^A & \sigma_0^A \\
    \sigma_1^A & \sigma_0^A & 0 \\
    \sigma_0^A & 0 & 0
\end{pmatrix}
$$

Also, $\sigma^B$ is given by Eq. 7.29 if $A$ is replaced by $B$. With this compact notation the OZ-equation for the AB-mixture can be written as

$$
\frac{1}{6} \sum_{r_3, r_3} \begin{pmatrix}
    C^{AA} & C^{AB} \\
    C^{BA} & C^{BB}
\end{pmatrix}_{(1,3)} \begin{pmatrix}
    \sigma^A & 0 \\
    0 & \sigma^B
\end{pmatrix} \begin{pmatrix}
    H^{AA} & H^{AB} \\
    H^{BA} & H^{BB}
\end{pmatrix}_{(3,2)}
$$

in which the elements $H^{IJ}$, $\sigma^I$ and $C^{IJ}$ are $3 \times 3$-matrices.

If we limit ourselves to the case of equal concentrations of A- and B-particles, then

$$
H^{AA}(1,2) = H^{BB}(1,2)
$$

$$
H^{AB}(1,2) = H^{BA}(1,2)
$$

and

$$
\sigma^A = \sigma^B
$$

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Symmetries similar to Eq. 7.31 apply to the C-component of the OZ-matrix equation. With help of Eqs. 7.31 and 7.32, the $6 \times 6$ OZ-matrix equation reduces to two $3 \times 3$ equations

$$
H^{AA}(1, 2) = C^{AA}(1, 2) + \frac{1}{6} \sum_{r_3, \Omega_3} (C^{AA}(1, 3)\sigma^A H^{AA}(3, 2) + C^{AB}(1, 3)\sigma^A H^{AB}(3, 2))
$$

$$
H^{AB}(1, 2) = C^{AB}(1, 2) + \frac{1}{6} \sum_{r_3, \Omega_3} (C^{AA}(1, 3)\sigma^A H^{AB}(3, 2) + C^{AB}(1, 3)\sigma^A H^{BB}(3, 2))
$$

(7.33)

To be able to calculate the numerical values of the elements of the matrices in Eq. 7.33, it is supplemented with standard PY-like closures [3,4]

$$
c^{ij}_{ij}(1, 2) = g^{ij}_{ij}(1, 2) - y^{ij}_{ij}(1, 2)
$$

(7.34)

and the exact relations

$$
g^{ij}_{ij}(1, 2) = \epsilon_R(1, 2) \left( y^{ij}_{ij}(1, 2) + \delta_{ij}(1 - \delta_{j0})(1 - \delta_{i0})f_A(1, 2)y^{ij}_{i-1,j-1}(1, 2) \right)
$$

(7.35)

Apart from the OZ-matrix equation and the closure equations, there also is a self-consistency relation for each particle type

$$
\eta^f = \eta_0^f + \eta_1^f + \eta_2^f
$$

$$
\eta_1^f = \eta_0^f C_1^f
$$

$$
\eta_2^f = \eta_0^f \left( C_1^{II} + C_2^f \right)
$$

(7.36)

with

$$
C_1^f = \frac{\sigma_1^f}{6} \sum_{r_2, \Omega_2} y^{II}_{10}(1, 2)\epsilon_R(1, 2)f_A(1, 2) + \frac{\eta_0^f}{6} \sum_{r_2, \Omega_2} y^{II}_{10}(1, 2)\epsilon_R(1, 2)f_A(1, 2)
$$

$$
C_2^f = \frac{\sigma_1^f}{6} \sum_{r_2, \Omega_2} y^{II}_{10}(1, 2)\epsilon_R(1, 2)f_A(1, 2) + \frac{\eta_0^f}{6} \sum_{r_2, \Omega_2} y^{II}_{11}(1, 2)\epsilon_R(1, 2)f_A(1, 2)
$$

(7.37)

where $\epsilon_R(1, 2) = e^{-\beta_{uR}(1,2)}$ and $f_A(1, 2) = e^{-\beta_{uattr} - 1}$.

An additional step required to solve Eqs. 7.30-7.37 along the same lines as outlined in Appendix C for a 1-component system, is a decomposition of Eq. 7.33. Such is possible with help of the intermediate variables

$$
h^P_{ij}(1, 2) = h^{AA}_{ij}(1, 2) + h^{AB}_{ij}(1, 2)
$$

$$
h^M_{ij}(1, 2) = h^{AA}_{ij}(1, 2) - h^{AB}_{ij}(1, 2)
$$

(7.38)
Note that this decomposition is only possible if we study equimolar mixtures of A and B particles \( \eta_A = \eta_B \).

Once the partial correlations \( h_{ij}^A(l, m, n) \) and \( h_{ij}^B(l, m, n) \) are known (see Appendix C, the total correlations are found from

\[
\sigma_2^I \sigma_2^J H_{IJ} (l, m, n) = \sigma_2^I \sigma_2^J h_{00}^I (l, m, n) + 2 \sigma_0^I \sigma_2^J h_{10}^I (l, m, n) + 2 \sigma_0^I \sigma_0^J h_{00}^J (l, m, n) + 2 \sigma_0^I \sigma_0^J h_{11}^I (l, m, n) + \sigma_0^I \sigma_0^J h_{11}^J (l, m, n) + 2 \sigma_0^I \sigma_1^J h_{21}^I (l, m, n) + \sigma_0^I \sigma_0^J h_{22}^I (l, m, n)
\]

(7.39)

for \( \{I, J\} \in \{A, B\} \). The total orientation averaged 2-particle distributions \( G_{IJ}^I(l, m, n) \) are then obtained from

\[
H_{IJ} (l, m, n) = G_{IJ}^I (l, m, n) - 1
\]

(7.40)

The \( G_{AB}^A(l, m, n) \) and \( G_{BB}^B(l, m, n) \) consist of an inter- and an intramolecular part, due to the possibility of covalent A-A and B-B bonding, whereas \( G_{AB}^A(l, m, n) \) only consists of an intermolecular part, thus

\[
\eta^I G_{IJ}^I (l, m, n) = \delta_{IJ} (\omega_{IJ}^I (l, m, n) - \delta_{00}^I \delta_{m0}^I \delta_{n0}^I) + \eta^I g_{IJ}^I (l, m, n)
\]

(7.41)

where \( \omega_{IJ}^I (l, m, n) \) accounts for the intramolecular part and \( g_{IJ}^I (l, m, n) \) accounts for the intermolecular part of the total correlation. The \( \delta_{00}^I \delta_{m0}^I \delta_{n0}^I \) corrects for the self-correlation that is not present in the \( G_{IJ}^I (l, m, n) \). For the equimolar mixtures of A and B particles [31], we have

\[
\omega_{AA}^A (l, m, n) = \delta_{00}^A \delta_{m0}^A \delta_{n0}^A + \eta^A \left( G_{AA}^A(l, m, n) - G_{AB}^A(l, m, n) \right)
\]

\[
g_{AA}^A(l, m, n) = G_{AB}^A(l, m, n)
\]

(7.42)

This labelling method resembles methods to obtain contrast in neutron scattering experiments [49]. From Eq. 7.42, it is possible to obtain both the intra- and intermolecular 2-particle distribution of a fluid consisting of flexible polymeric molecules. This is in contrast to the RISM-equation, in which the intramolecular 2-particle distribution is an input quantity for the calculation of the intermolecular 2-particle distribution. Chang and Sandler [28] have also devised a method to make a separation of \( G \) in inter- and intramolecular parts. They use the distinguishability of the attractive sites present in their model to accomplish this.

### 7.3 MC simulation

The structural correlations that were obtained from the theory have been tested with a Monte Carlo simulation in the canonical \((NVT)\) ensemble. The simulation concerned the cubic lattice model of particles with two attractive sites. The sites of different particles could interact with each other via orientation dependent nearest neighbor potentials. In the simulations, the two attraction sites of
a fluid particle do never point in the same direction. The sites are therefore not independent of each other, and the chains that are formed have a fully developed excluded volume, contrary to the chains in the model calculations. The total 2-particle distribution \( G(l, m, n) \) was obtained from the simulations, and a procedure was developed to split it in an intermolecular part \( g(l, m, n) \) and an intramolecular part \( \omega(l, m, n) \). Box sizes were chosen large enough to minimize finite box-size effects [31]. Apart from the structural correlation data, we have monitored the average internal energy \( E \) and the packing fractions \( \eta_0, \eta_1 \) and \( \eta_2 \). We have tested systems at two overall packing fractions, \( \eta = 0.5 \) with 864 particles in a \( 12 \times 12 \times 12 \) box and \( \eta = 0.3015 \) with 1235 particles in a \( 16 \times 16 \times 16 \) box. The boxes had periodic boundaries in all three directions. All runs consisted of an equilibration part of at least \( 80 \times 10^6 \) moves. Averages were calculated after equilibration over at least \( 35 \times 10^6 \) moves. We have performed runs with \( u_{\text{attr}} \) varying from \(-0.5k_BT\) up to \(-7.0k_BT\). For \( u_{\text{attr}} = -7.0k_BT \), the box contained chains of an average length \( \bar{L} \) of roughly 15 segments at \( \eta = 0.5 \) and of 12 segments at \( \eta = 0.3015 \). Statistical errors were estimated from runs for the same system in a different initial configuration, by dividing some of the runs in 20 parts to check for drift in the averages that were calculated, and by blocking of data. The blocking method of Flyvbjerg and Petersen [50] was used to calculate the standard deviation of the averages belonging to the uncorrelated data and to check for the abilities of the simulation recipe to produce uncorrelated data sets.

Simulation of the system is increasingly difficult for large site-site attractive interactions (\(|u_{\text{attr}}| > 5.0k_BT\)). For such \( u_{\text{attr}} \), most particles will be part of a polymer chain and thus have one (head or tail of the chain), or more likely, two (mid-segments) bonds with other fluid particles. A brute force move will then consist of breaking of a chain by flipping a monomer out of the chain, and putting it back on the lattice without forming new bonds, because the new neighbors will almost certainly already have formed two bonds. Therefore, the acceptance probability for such a move will be very low and we thus need to resort to other options. The simulation recipe that was used consisted of 5 different types of moves: brute force moves, bond-flips, double bond-flips, generalized reptation moves and biased cluster moves.

The brute force move simply consists of randomly choosing a new position and two orientations for the sticky sides of a randomly chosen particle. Acceptance of the move is determined by the conventional Metropolis acceptance criterion [32]. The number of broken and newly formed bonds determines the energy difference between the old and new configuration and thus governs the acceptance. The second move, the bond-flip, simply attempts to change the orientation of one of the sticky sides of a particle without moving the particle. The bond-flip move is meant to sample the creation/destruction of chain ends in the polymerized
fluid. Acceptance of the move is again determined via the Metropolis criterion. The third move, the double bond-flip samples the chain length distribution by imitating a metathesis reaction (see Fig. 7.1). It was used by Olaj and Lantschbauer [33] and by Mansfield [34] for the simulation of a polydisperse polymeric lattice fluid at full packing.

The fourth move is a "generalized reptation" move. It consists of randomly choosing two chain ends and flipping the end-segment of one chain to the other chain. This move helps to sample the particle distribution on the lattice. Note that, for both the double bond-flip move and the generalized reptation move, there will be no energy difference between the old and the new configurations. Thus, these moves are always accepted, which greatly enhances the efficiency of the simulation. For the generalized reptation move there is one exception: the move should be rejected in case the free bond of the particle that is moved from one chain-end to the other, is reoriented in such a way that the particle forms a bridge between two chains, or in other words, if the particle that is moved forms two bonds. If one would allow these moves, chain ends will occasionally end up in the middle of a chain. A middle segment, on the other hand, will never become a chain end. Hence, detailed balance is not obeyed and the move should be rejected.

The last move that we have employed is the biased cluster move. It consists of two parts. The first part, the cluster part, is concerned with the selection of a part of a chain. This selected part of the chain, the cluster, is attempted to be moved through the box. The cluster move was used for Ising systems by Swendsen and Wang [35], Niedemayer [36] and by Wu, Chandler and Smit [6]. Due to the fact that the linear cluster can be large (it can contain as many segments as the chain from which it originates), the acceptance probability for a cluster move will be very low, except if the form of the cluster can be altered in such a way that the cluster fits in the voids present between the other particles in the box. This is what the second part of the move is concerned with: the Configurational bias MC scheme [5,37,38,51,52] is introduced in the cluster scheme which allows the form of the cluster to be changed in the way described above. The bias is corrected
Figure 7.2: Standard deviations for 1: pure brute force simulation (●) and 2: 90% biased cluster moves (■) with \( p = 0.95 \). The \( \eta = 0.5 \) and \( u_{attr} = -5.0k_B T \); box size is 12 \( \times \) 12 \( \times \) 12.

for in the acceptance criterion. The final scheme has the additional feature that it samples chain lengths. This last property is most welcome in the simulation of our model (Eqs. 7.2-7.4) in which the chains do not have fixed lengths. The biased cluster move is outlined in detail in Appendix F.

To assess the efficiency of the biased cluster move, we have depicted in Fig. 7.2 the standard deviation of the average internal energy, calculated with the blocking method of Ref. [50], for two simulation recipes at \( \eta = 0.5 \) and \( u_{attr} = -5.0k_B T \). Simulation 1 only uses brute force moves and simulation 2 attempts 10% brute force moves and 90% biased cluster moves. It is seen from the figure that the standard deviations are smaller for equal amounts of CPU time in the case of biased cluster moves. Fig. 7.2 thus indicates that the biased cluster scheme is more efficient than conventional brute force moves. The difference between the efficiency of both recipes grows for stronger attractions, when longer chains are created. For stronger interactions the CPU time increases exponentially and, for \( |u_{attr}| > 5.0k_B T \), a recipe that only uses brute force moves is not suitable anymore (\( e^{2\eta u_{attr}} < 5 \times 10^{-5} \)). We have not explicitly tested the influence of the other moves on the efficiency of the simulation, but an enhancement is expected for the metathesis move and the generalized reptation move, especially at higher \( \eta \) and \( u_{attr} \), because there is no energy difference associated with these moves leading
to automatic acception.
In the figures of the next section we have not drawn error bars because the stan­
dard deviations that were calculated are smaller than the symbols used in the
figures.
The simulation recipe used to study strongly interacting fluids ($|u_{\text{attr}}| > 5.0k_B T$)
typically consisted of 10% brute force, 10% single bond flip, 15% double bond
flip, 15% generalized reptation, and 50% biased cluster move attempts. In con­
structing the clusters, the bond acceptance probability $p$ (see Appendix F) is
chosen to be 0.95, which on average corresponds to 1 in 20 bonds that is broken.
For weakly interacting systems, the biased cluster moves and the double bond
flips were replaced by brute force and generalized reptation moves. The obtained
averages were checked to be independent of the exact constitution of the recipe.

All simulations presented in the next section are performed in non-parallel
runs on a fourteen MIPS R8000 processor Silicon Graphics Power Challenge XL
with an IRIX 6.0 operating system. A typical run for $u_{\text{attr}} = -3.0k_B T$ took
approximately five CPU hours which increased to approximately ten hours for
the strongly interacting systems with $u_{\text{attr}} = -7.0k_B T$. The simulation results
are available on request via e-mail tgpken@urc.tue.nl.

7.4 Results and discussion

7.4.1 1-Component systems

The mass distributions that are typically found from the simulations are depicted
in Fig. 7.3 for a weakly interacting fluid and in Fig. 7.4 for a strongly interacting
fluid. In Figs. 7.3 and 7.4, $P(l) = L_l/L_0$ is the mass fraction of chains of length
l. $L_0$ is the total number of particles in the fluid and $L_l$ is the number of $l$-mers.
The mass fraction is normalized as $\sum_l P(l) = 1$. In the simulation of Fig. 7.3,
chain lengths up to 10 segments occurred and in the simulation of Fig. 7.4, chains
of up to 150 were occasionally encountered. In the case of the weakly interacting
fluid (Fig. 7.3), a sharp rapidly decaying distribution in which most particles
are not bonded to other particles is found. For the strongly interacting fluid
(Fig. 7.4), a very broad and oscillating distribution with a maximum at the 4­
mer is obtained. The overall mass distribution is built from a smooth distribution
of linear chains and an oscillatory distribution of rings that is depicted in Fig. 7.5.

Note that the mass distribution of rings is sharp. Approximately 50% of the
particles in ring-shaped molecules are present in a 4-mer which is the smallest ring
possible on the cubic lattice. Odd numbered rings are not possible on the cubic
lattice, which explains the oscillatory behavior of the distribution. From Fig. 7.6
it is seen that, for the simulation depicted in Figs. 7.4 and 7.5 ($u_{\text{attr}} = -7.0k_B T$),
there is roughly 10% of the monomers present in ring-shaped molecules. It is then
Figure 7.3: Mass distribution at $\eta = 0.3015$ and $u_{\text{attr}} = -1.0k_B T$.

Figure 7.4: Mass distribution at $\eta = 0.3015$ and $u_{\text{attr}} = -7.0k_B T$. 
Figure 7.5: Mass distribution of rings at $\eta = 0.3015$ and $u_{\text{attr}} = -7.0k_BT$.

Figure 7.6: Percentage of particles present in rings at $\eta = 0.5$ (■) and $\eta = 0.3015$ (○).
easy to verify that the peaks in Fig. 7.4 can be fully attributed to the formation of ring-shaped molecules.

The number average chain lengths have been obtained from the distributions of Fig. 7.3 and Fig. 7.4 as

\[
\overline{L}_N = \frac{1}{\sum_i P(i)}
\]  

(7.43)

This analysis does not neglect the formation of rings. On the other hand, Eq. 7.20 does not incorporate the possibility of ring formation and therefore results in higher average chain lengths. Results of both methods to determine \( \overline{L}_N \) are depicted in Fig. 7.7. It is seen that the differences between the two methods increase with \( \overline{L}_N \), as ring formation becomes more important. For higher \( \overline{L}_N \) it is therefore best to make the analysis on the basis of the full distribution, and not based on \( \eta_0 \), \( \eta_1 \) and \( \eta_2 \) alone. Unfortunately, the distributions that include ring formation cannot be obtained from the theory, and we are therefore forced to use Eq. 7.20 for the determination of \( \overline{L}_N \) and \( \overline{L}_W \) from the theory. Hence, to make the comparisons between the theory and the simulations as fair as possible we also resort to Eq. 7.20 for the analysis of the simulations. In Fig. 7.8, the packing fractions \( \eta_0 \), \( \eta_1 \) and \( \eta_2 \) of non-bonded, singly bonded and
doubly bonded particles obtained from theory and simulations are plotted as a function of the attractive interaction strength. Results for the model obtained in the Chang-Sandler (CS) approximation [28] are also shown. The full- and CS-solution give results that are very close. This was to be expected, since the absence of excluded volume interactions, explicitly assumed in the CS-solution via Eq. 7.22, is also implicitly embodied in the full solution presented in section 7.2. In the full solution, the absence of excluded volume is due to the independence of the attractive sites. The comparison between simulated and calculated packing fractions is less satisfactory. For $|u_{attr}| > 5k_B T$, the agreement is reasonable but for lower attractive strength the difference grows rapidly. This can be attributed to different definitions of $\eta_0$, $\eta_1$ and $\eta_2$ that have to be used in the theory and simulations [53,31], and does not mean that the 2-particle distribution $G(l, m, n)$ that is obtained for $|u_{attr}| \to 0$ is incorrect: in both theory and simulations we observe the physically correct limit $G(l, m, n) \to 1$ for $|u_{attr}| \to 0$. In both cases, the simple monatomic cubic lattice fluid is thus correctly recovered. The reason for the observed differences is that in the simulations, $\eta_0$, $\eta_1$ and $\eta_2$ are determined by analyzing the nearest neighbor contacts of marked particle-edges, i.e., the attractive sites of the particles, and in the theory they are defined differently by the graphical definitions Eqs. 7.1, 7.12 and 7.13. Note that the definitions used in the theory are in terms of the physically meaningless $g_{ij}$. Therefore, they
can not be used in the simulations. The graphical definitions reduce in the limit \(|u_{\text{attr}}| \to 0\) to \(\eta_0 = \eta\) and \(\eta_1 = \eta_2 = 0\). This corresponds to a cubic lattice fluid without attractive sites on the particles, and therefore no bonds are formed. The limits that are observed in the simulations for \(|u_{\text{attr}}| \to 0\) can also be assessed because we are dealing with a fully uncorrelated lattice fluid \((|u_{\text{attr}}| \to 0)\): for \(|u_{\text{attr}}| \to 0\), the probability that the marked edge of a particle forms a bond (of strength \(|u_{\text{attr}}| \to 0\)) with another particle is given by

\[
q = \frac{\eta}{3}
\]  

(7.44)

The \(\eta_0\), \(\eta_1\) and \(\eta_2\) are then given by

\[
\eta_0 = \eta(1 - q)^2 \\
\eta_1 = 2\eta q (1 - q) \\
\eta_2 = \eta q^2
\]  

(7.45)

Eq. 7.45 is thus based on the contacts between marked edges that occur in a cubic lattice fluid of particles that each have two marked (but non-interacting) edges that are distinguishable from the other four edges of the particles.

The packing fractions \(\eta_0\), \(\eta_1\) and \(\eta_2\), presented in Fig. 7.8, can directly be used to determine \(\bar{L}_N\) via Eq. 7.20. The results are plotted in Fig. 7.9. The results of the approximate CS-solution (dashed line) is not as good as the full solution, but still acceptable for the region of \(u_{\text{attr}}\) that we have tested. In the region \(|u_{\text{attr}}| < 5k_B T\), where the disagreement between the definitions of the \(\eta_i\) in the theory and the simulations is large, a very low average chain length is obtained, as seen in Fig. 7.9. The number average chain length \(\bar{L}_N\) only starts to built up in the region \(|u_{\text{attr}}| > 5k_B T\) where the comparisons between the theoretical and the simulated definitions of the \(\eta_i\) is reasonable. Therefore, we argue that it is valid to assign physical relevance to the average chain lengths \(\bar{L}_N\) of polymerized systems obtained from the theory, even though the \(\eta_i\)’s from which the \(\bar{L}_N\) are obtained show a physically incorrect limit for \(|u_{\text{attr}}| \to 0\). Note from Eqs. 7.20 and 7.45 that \(\bar{L}_N = 1/(1 - q)\), instead of the physically correct value 1, for \(|u_{\text{attr}}| \to 0\).

In Fig. 7.10 the width of the chain length distribution is displayed. It is seen that \(\bar{L}_N/\bar{L}_W \to 2\) for higher \(u_{\text{attr}}\) indicating that we are dealing with a condensation polymerization product [7,8]. The full and the CS-solution produce comparable results. In the region \(|u_{\text{attr}}| < 5k_B T\), we again see a disagreement resulting from the different definitions of the \(\eta_i\)’s in the theory and simulations.

The structural correlations that are obtained for the model are depicted in Fig. 7.11 and Fig. 7.12. We have depicted the 2-particle distribution as \(G = G(r)\) with \(r = \sqrt{l^2 + m^2 + n^2}\). The total 2-particle distribution \(G\) is a discrete quantity that only exists for integer values of \(l,m,n\). Lines are drawn through the
Figure 7.9: Number average chain length for varying attractive interaction strength at $\eta = 0.5$ (■) and $\eta = 0.3015$ (○). The symbols are obtained from simulation, and the full and dashed lines are respectively the full- and CS-solution of the model.

calculated points to clearly distinguish them from the simulation values that are denoted by the symbols. The comparisons between the theory and the simulations are made at fixed values of $\eta$ and $u_{\text{attr}}$. From Fig. 7.11 it is seen that the agreement between the theory and the simulations is far from quantitative for the values of $u_{\text{attr}}$ that we have considered, and worsens for stronger attractions. We find a severe underestimation of the contact value of $G$. The accuracy of the CS-solution (dashed lines) is comparable to the full solution (full lines) of the OZ-matrix equation. Results for higher $\eta$ are depicted in Fig. 7.12 and indicate that the theory is slightly more accurate at these packing fractions. This is obviously due to fact that the overall correlations, i.e., deviations of $G(l, m, n)$ from 1, become smaller at higher packing fractions.

The disagreement that we have found, seems to be in contrast to results obtained previously by Chang and Sandler [28] for a continuum model closely related to the lattice model presented here. They reported good agreement between the overall 2-particle distribution function obtained from theory and MC-simulations at high and intermediate packing fractions for chain lengths of 4, 8 and 16 monomers. At low packing fractions they also observed a deteriorating agreement. We think that the agreement might be better in continuum than on the cubic lattice for intermediate and high packing fractions because, in a continuum model, the total 2-particle distribution function $G$ is largely determined by liquid-like ordering.
effects and not so much by the directional attractions present between the particles. This is in contrast with the lattice model for which liquid-like ordering effects are absent and the directional attractions alone determine $G$.

Our argument is supported by the results for the lowest packing fractions that Chang and Sandler have tested. At these densities, for which liquid-like ordering effects are suppressed, they also find severe underestimations of $G$ that are larger for the higher chain lengths (stronger attractive energies).

Therefore, we think that the lattice model provides a more stringent test of the approximations made to solve the OZ-matrix than a continuum analog. Due to the absence of liquid-like packing effects on the lattice, the directional attractions alone are responsible for the observed correlations [54].

Reasons for the disagreement that we have observed, most likely lie in the independence of the attraction sites on a particle, and in the pre-averaging of the $f_A$. These approximations remove the details of the orientational dependence of the particle-particle interactions. Another reason could be the inadequacy of the closures but, based on the excellent results of previous work on associating lattice fluids [31], we do not expect this to be true. A third reason could be that the graphical analysis which underlies the equations presented in this work does not fully incorporate the steric incompatibilities present in flexible polymer fluids.

Figure 7.10: Simulated (symbols) and calculated (lines) width of chain length distribution as a function of the attractive particle-particle strength for $\eta = 0.5$ (■) and $\eta = 0.3015$ (●). The dashed line is the CS-solution and the full line corresponds to the full solution.
Figure 7.11: Simulated (symbols) and calculated (lines) 2-particle distributions at $\eta = 0.3015$ and $u_{\text{attr}} = -1.0k_BT$ (●), $u_{\text{attr}} = -4.0k_BT$ (■) and $u_{\text{attr}} = -7.0k_BT$ (▲). For $u_{\text{attr}} = -1.0k_BT$ and $-4.0k_BT$ the CS- (dash) and full (full line) solution are virtually on top of each other.

Figure 7.12: Caption as in Fig.7.11, $\eta = 0.5$. 

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7.4.2 Mixtures

Figure 7.13: \( G^{AA} (\square) \) and \( G^{AB} (\bullet) \) for an equimolar mixture of \( \eta_A + \eta_B = 0.5 \), \( u^{AA}_{\text{attr}} = u^{BB}_{\text{attr}} = -7.2477 k_B T \) and \( u^{AB}_{\text{attr}} = 0 k_B T \). The symbols are calculated values, the lines are to guide the eye.

In Fig. 7.13 the total AA- and AB-distribution functions for an equimolar A/B mixture are depicted. Due to the absence of AB-bonds only A- and B-mers are formed. The \( G^{AB}(l, m, n) \) shows a correlation hole [13,55] because it is of purely intermolecular origin, whereas \( G^{AA}(l, m, n) \) consists of an inter- and an intramolecular component. The intramolecular 2-particle distribution \( \omega^{AA}(l, m, n) \) for flexible chains of \( \bar{L}_N = 12.53 \) is drawn in Fig. 7.14. The \( \omega^{AA}(l, m, n) \) is obtained from the mixture of Fig. 7.13 with the labelling method, Eq. 7.42. In Fig. 7.14 the \( \omega(l,m,n) \) of a \( L = 12 \) Random Walk (RW) is also drawn. It is seen that \( \omega^{AA}(l,m,n) \) obeys exclusion of particle overlap, i.e., \( \omega^{AA}(0,0,0) = 1 \). This originates from the closures, Eqs. 7.9 and 7.10, which enclose the condition \( G^{AA}(0,0,0) = G^{AB}(0,0,0) = 0 \). The RW-chain of Fig. 7.14 does not show this property. It is shown elsewhere [56-58,40] that exclusion of particle overlap is very important for the equation of state and other thermodynamic properties. Note that \( \omega^{AA}(0,0,0) = 1 \) does not mean that the model fully incorporates the chain excluded volume, as is already discussed in section 7.2.2.

It is easily understood that the numerical values of \( \omega^{AA}(l,m,n \neq 0,0,0) \) largely
Figure 7.14: The $\omega^{AA}(r)$ for the same system as in Fig. 7.13 (□). The upper curve (●) denotes the intramolecular 2-particle distribution of a Random Walk chain consisting of 12 segments.

underestimate the correct values for the model. For a stiff linear 12-mer on a cubic lattice, one has for instance $\omega(1, 0, 0) = \frac{10 \times \frac{3}{4} + 2 \times \frac{1}{3}}{12} = 0.3055$, for a RW 12-mer this value is given by $\omega(1, 0, 0) = 0.49060948$ (see Fig. 7.14). The $\omega(1, 0, 0)$ for a flexible chain of $\bar{L}_N \approx 12$ with full excluded volume should be in between these limits. The incorrectness of $\omega^{AA}(l, m, n)$ (□) could be anticipated from the observation that the $G(l, m, n)$ for a 1-component system is largely underestimated when compared to MC-simulation results. For the 2-component system presented here, it means that $G^{AA}(l, m, n)$ and $G^{AB}(l, m, n)$ do not fully capture the correlations present on the lattice: $G^{AA}(l, m, n)$ should have a higher correlation peak and $G^{AB}(l, m, n)$ a deeper correlation hole. The difference between the curves, which is proportional to $\omega^{AA}(l, m, n)$ (see Eq. 7.42), is therefore not large enough. Possible reasons for the observed underestimations are the mutual independence of the sites of the particles and the pre-averaging of $f_A$ as was already discussed in section 7.4.1. A consequence of the underestimation of the intermolecular correlations of the model is that $\sum_{l,m,n} \omega^{AA}(l, m, n)$ is not properly normalized to $\bar{L}_N$. 
7.5 Conclusions

In this chapter we have applied Wertheim's associating fluid theory [3,4] to study polymerization on a cubic lattice. We also developed a biased cluster MC-move, based on the Configurational biased MC-scheme [5], to efficiently test the average chain lengths and the 2-particle distribution functions that the theory predicts. The chain lengths found from theory and simulations are in good agreement, contrary to the 2-particle distribution functions that are severely underestimated by the theory.

A labelling method that allowed for separation of the total 2-particle distribution in an inter- and intramolecular part was studied. Separation of the total 2-particle distribution in inter- and intramolecular terms has proven possible, but due to incorrect values of the total 2-particle distribution we do not find accurate results for the inter- and intramolecular 2-particle distributions. We believe that the lattice version of the associating fluid model studied here provides an accurate test of the approximations involved in the associating fluid theory. Due to the absence of a liquid-like ordering, that is predominant at liquid-like densities in continuum models, the effects of the directional attractive forces on the structural correlations can be singled out and tested accurately. From the comparison to the MC-simulations, we conclude that it is necessary to improve on the approximations that are made in the solution procedure used to obtain \(G(l, m, n)\), before we can extract thermodynamic data from the model, as these data rely on an accurate input of the structural correlations in the fluid.
References


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[58] S. Wang and E. Nies, *to be published*
Chapter 8

Associating lattice fluids near hard and interacting walls

8.1 Introduction

An associating fluid is a fluid that is characterized by short range directional attractions between the particles. Studies of the bulk properties of such fluids include the classical chemical theory of solutions [1] in which the associative interactions are modelled as chemical reactions, lattice theories in which the free energy is minimalized within the quasi-chemical approximation [2,3], computer simulation and integral equation approaches (see Ref. [4] and references cited therein). The integral equation approaches attempt to accurately calculate the structural correlations between the fluid particles. The macroscopic thermodynamic properties can then be calculated from these correlations [5].

In this chapter the associating fluid theory of Wertheim for fluids with one [6,7] and two [8,9] directional attractive sites per particle is adapted to study the adsorption of associating cubic lattice fluids at an impenetrable wall. The wall is allowed to have a non-associative attractive interaction with the fluid particles. The method relies on the accurate calculation of the correlations between the lattice fluid particles and the wall via discretized integral equations. Recently similar approaches based on somewhat different principles have also been developed for continuum associating fluids [4,10].

In this work we are especially interested in the adsorption of strongly associating fluids for which the attractive interaction between the particles obeys $u_{\text{attr}} \gg k_B T$. In that case, the directional attractions form more or less permanent bonds that are not easily broken by the thermal motion of the particles: the attractions are used to model covalent bonding. Our model of a fluid with two directional attractive sites per particle near an impenetrable wall then serves to model the adsorption of a polydisperse polymeric chain fluid.

The adsorption profiles calculated with the approach that will be outlined here,
have been compared to Monte Carlo simulations. For the fluid with one directional attractive force per particle, we could simulate the profiles by standard brute force [11] Monte Carlo. In the doubly associating fluid the particles can click into chains. This fluid was simulated with a biased cluster move [12] which combines the Configurational bias scheme [13] and a cluster move of Wu, Chandler and Smit [14].

In section 8.2 we delineate the equations for the calculation of the adsorption/depletion profiles of particles with one directional attractive force. Some attention is paid to the limit of infinitely strong attractions between the fluid particles. In this limit full association of the fluid particles into dimers occurs. Comparisons are made to results obtained previously with the adsorption-RISM equation [15,16] for dimeric lattice systems [17]. In section 8.3 an extension of the formalism to fluids consisting of particles with two directional attractive forces is presented. For the case of strong associations between the particles, a polydisperse lattice fluid of polymeric chains near an impenetrable wall is formed. The calculation of the adsorption profiles of such polydisperse polymeric lattice fluids might lead to insight that is of interest in designing better polymeric coatings and composite materials [18].

The method that is used in sections 8.2 and 8.3 to introduce a wall into the fluid was developed by Henderson, Abraham and Barker [19] to study the adsorption of a continuum fluid at a structureless surface. It was used by Yethiraj and Hall [16] to obtain the static adsorption characteristics of a polymeric fluid at a hard wall within the RISM-approach [15]. The method consists of mixing a simple fluid particle [5], that does not have a directional attractive potential, into the associating fluid after which the particle is blown up in two directions to form a flat wall. It is shown in sections 8.2 and 8.3 that it is particularly easy to employ this method on the cubic lattice.

In section 8.4 we briefly outline the Monte Carlo simulation method used for the singly associating lattice fluid. The method that was employed in the simulation of the polymerizing fluid is considered in somewhat greater detail. In section 8.5, the calculated adsorption profiles for the dimerizing and polymerizing fluids near hard and interacting walls are compared to simulation data and the results are discussed. Conclusions are collected in section 8.6.

8.2 Adsorption of particles with one directional attractive force

In this section the 2-density formalism [6,7] is adopted for the calculation of the adsorption profiles of a 3D cubic lattice fluid of singly associating particles at an impenetrable wall. The particles occupy exactly one lattice site and can bind into dimers due to an off-center associative particle-particle interaction. The walls are
allowed to have a non-associative interaction with the particles in the layer closest to the wall. The method that is used to introduce the wall into the fluid, is due to Henderson, Abraham and Barker [19] who used it to study the static adsorption behavior of hard sphere fluids near an impenetrable structureless wall. Its basic steps are as follows.

In the Ornstein-Zernike matrix equation for a mixture of associating and simple (non-associating) particles [5], the packing fraction of the simple fluid particles is reduced to zero: \( \eta_M \rightarrow 0 \). This assures that encounters of non-associating simple particles are absent. After this limit is taken, the simple particles are "blown up" along the \( m- \) and \( n- \)axis of the \((l, m, n)\)-coordinate system by removing the \( m- \) and \( n- \)dependence of the correlations between the simple and associating particles. The average correlation between the wall and an associating particle can then directly be related to the concentration of the associating particles near the wall.

The potential model used to describe the interactions between the associating particles is [20]

\[
\begin{align*}
  u(1, 2) &= u_R(1, 2) + u_{s_1, s_2}(1, 2) \\
\end{align*}
\]

where the repulsive part is only dependent on the distance between the particles 1 and 2

\[
\begin{align*}
  u_R(0, 0, 0) &\rightarrow \infty \\
  u_R(l, m, n) &= 0 \quad \text{otherwise} \quad (8.2)
\end{align*}
\]

Note that \( u_R(l, m, n) \) regulates that the particles occupy exactly one lattice site. The attractive part of the potential is a function of the interparticle distance \((l, m, n)\) and of the orientations \( \Omega_1 \) and \( \Omega_2 \) of the attractive sites \( s_1 \) and \( s_2 \) of the particles

\[
\begin{align*}
  u_{s_1, s_2}(0, 0, 0, \Omega_1, \Omega_2) &= 0 \\
  u_{s_1, s_2}(l, m, n, \Omega_1, \Omega_2) &= u_{\text{attr}} \quad \text{if } \Omega_1 = -\Omega_2 \text{ and } l^2 + m^2 + n^2 = 1 \text{ and } \\
  &\quad \text{sgn}(l + m + n)(l^2 + 2m^2 + 3n^2) = \Omega_1 \\
  u_{s_1, s_2}(l, m, n, \Omega_1, \Omega_2) &= 0 \quad \text{otherwise} \quad (8.3)
\end{align*}
\]

where an attractive site can point in the directions \(+l \ (\Omega_i = 1)\), \(-l \ (\Omega_i = -1)\), \(+m \ (\Omega_i = +2)\), \(-m \ (\Omega_i = -2)\), \(+n \ (\Omega_i = +3)\) and \(-n \ (\Omega_i = -3)\). The conditions \( \Omega_1 = -\Omega_2 \), \( l^2 + m^2 + n^2 = 1 \), and \( \text{sgn}(l + m + n)(l^2 + 2m^2 + 3n^2) = \Omega_1 \) assure that bond formation only occurs between nearest neighbor particles that have their attractive sites oriented towards each other. The interactions that involve the non-associating simple particles are considered further on.

In the 2-density formalism, the packing fraction \( \eta \) of the associating particles, which is the fraction of the lattice-volume filled with associating particles, will
be split in a fraction of particles that have \( \eta_1 \) and have not \( \eta_0 \) formed a bond with another associating particle \[6\]

\[ \eta = \eta_0 + \eta_1 \] (8.4)

The simple fluid particles do not have a directional attractive potential. Therefore, they are not involved in associative bonding and their packing fraction is not divided in parts as in Eq. 8.4. The Ornstein-Zernike matrix equation for a mixture of associating particles at packing fraction \( \eta \) and simple fluid particles at \( \eta_M \) is then given by \[6\]

\[ \mathbf{H}(1, 2) = \mathbf{C}(1, 2) + \frac{1}{6} \sum_{r_3, \Omega_3} \mathbf{C}(1, 3) \sigma \mathbf{H}(3, 2) \] (8.5)

where the argument \( (1, 2) \) denotes the dependence of \( \mathbf{H} \) and \( \mathbf{C} \) on the coordinates, position and orientation of the associating site, of particles 1 and 2. The matrix \( \mathbf{H}(1, 2) \) is given by

\[
\mathbf{H}(1, 2) = \begin{pmatrix}
    h_{00} & h_{01} & h_0 \\
    h_{10} & h_{11} & h_1 \\
    h_0 & h_1 & h
\end{pmatrix} \quad (1, 2)
\] (8.6)

The density matrix is given by

\[
\sigma = \begin{pmatrix}
    \eta & \eta_0 & 0 \\
    \eta_0 & 0 & 0 \\
    0 & 0 & \eta_M
\end{pmatrix}
\] (8.7)

The \( (1, 2) \) on the rhs of Eq. 8.6 denotes that all elements of \( \mathbf{H} \) depend on \( (1, 2) \). The matrix \( \mathbf{C}(1, 2) \) is of the same form as \( \mathbf{H}(1, 2) \). The \( h_{ij}(1, 2) \) in Eq. 8.6 denote a part of the total correlation between two associating particles, the \( h_i(1, 2) \) denote a part of the total correlation between an associating and a simple particle, and \( h(1, 2) \) denotes the total correlation between two simple particles. The \( c_{ij}(1, 2) \), \( c_i(1, 2) \) and \( c(1, 2) \) denote respectively the partial direct correlations between two associating particles, an associating and a simple particle, and two simple particles \[6\]. The elements of \( \mathbf{H}(1, 2) \) and \( \mathbf{C}(1, 2) \) depend on the orientation \( \Omega_s \) of the attractive site \( s \) of each associating particle that is considered

\[
\begin{align*}
    h_{ij}(1, 2) &= h_{ij}(l, m, n, \Omega_1, \Omega_2) \\
    h_{i}(1, 2) &= h_{i}(l, m, n, \Omega_1) = h_i(l, m, n, \Omega_2) = h_i(l, m, n) \\
    h(1, 2) &= h(l, m, n)
\end{align*}
\] (8.8)

We write \( h_i(l, m, n, \Omega_i) = h_i(l, m, n) \), because explicit orientational dependence only arises in case of an interaction between two associating particles. If the third particle in Eq. 8.5 is a simple non-associating particle, there is only a formal dependence on the orientation of this particle, and \( \sum_{\Omega_3} \) can simply be replaced
by a factor 6.

Before the closure equations necessary to calculate the adsorption profiles are introduced, we perform the matrix multiplications in Eq. 8.5, and take the limit $\eta_M \to 0$ to exclude interactions between simple fluid particles. The result is nine equations divided over four sets. The four sets are given by

$$h_{ij}(1,2) = c_{ij}(1,2) + \frac{1}{6} \sum_{r_3,\Omega_3} (c_{0}(1,3)\eta h_{0j}(3,2) + c_{0}(1,3)\eta_0 h_{1j}(3,2) +$$

$$c_{i}(1,3)\eta_0 h_{0j}(3,2))$$

$$h_i(1,2) = c_i(1,2) + \frac{1}{6} \sum_{r_3,\Omega_3} (c_{0}(1,3)\eta h_{0i}(3,2) + c_{0}(1,3)\eta_0 h_{1i}(3,2) +$$

$$c_{i}(1,3)\eta_0 h_{0i}(3,2))$$

$$h_{i}(1,2) = c_{i}(1,2) + \frac{1}{6} \sum_{r_3,\Omega_3} (c_{0}(1,3)\eta h_{0i}(3,2) + c_{0}(1,3)\eta_0 h_{1i}(3,2) +$$

$$c_{i}(1,3)\eta_0 h_{0i}(3,2))$$

$$h(1,2) = c(1,2) + \frac{1}{6} \sum_{r_3,\Omega_3} (c_{0}(1,3)\eta h_{0i}(3,2) + c_{0}(1,3)\eta_0 h_{1i}(3,2) +$$

$$c_{i}(1,3)\eta_0 h_{0i}(3,2)) (8.9)$$

with $\{i,j\} \in \{0, 1\}$. The set for $h_{ij}(1,2)$ in Eq. 8.9 is identical to the equations that were solved previously in Ref. [20] to obtain the bulk correlations in the dimerizing fluid. The first set in Eq. 8.9 can thus be solved independently from the other sets in Eq. 8.9. The method to obtain the $h_{ij}(1,2)$ for fixed values of $\eta$ and $\eta_0$ is outlined in detail in Ref. [20]. Note that with $\eta_0$, the degree of association $\eta_i/\eta$ is set via Eq. 8.4. Fixation of $(\eta, \eta_0)$ is therefore analogous to setting of $\eta$ and the strength of the associative interaction, $u_{attr}$. The last set in Eq. 8.9 consists of a single equation for the total correlation $h(1,2)$ between two simple particles. It is of no concern to us, due to the limit $\eta_M \to 0$ that we have taken. Furthermore, we only need to consider one of the two sets, the second or third in Eq. 8.9, for the wall-associating particle correlations $h_{i}(1,2)$. Both these sets can be employed but we choose to use the third. This set which consists of two equations, can be written in an orientation independent form without approximation, because we are considering parts of the orientation independent (see Eq. 8.8) distribution of an associating and a simple particle. Therefore, we can write

$$h_i(l,m,n) = c_i(l,m,n) +$$

$$\sum_{l',m',n'} ((\eta h_{0i}(l',m',n') + \eta_0 h_{1i}(l',m',n')) c_0(l-l',n-n',m-m') +$$

$$\eta_0 h_{0i}(l',m',n') c_{i}(l-l',m-m',n-n')) (8.10)$$

with $i \in \{0, 1\}$. 180
The next step is the creation of a wall from the simple fluid particles. Removing \( m \)- and \( n \)-coordinates of the \( h_i(l, m, n) \) and the \( c_i(l, m, n) \), effectively extends the simple particle in \( m \)- and \( n \)-direction. Only the \( l \)-distance of the associating particle to the simple particle is retained and thus, the simple fluid particle behaves as a wall

\[
h_i(l) = c_i(l) + \sum_{l', m', n'} \left( (\eta h_{0i}(l', m', n') + \eta_0 h_{1i}(l', m', n')) c_0(l - l') + \eta_0 h_{0i}(l', m', n') c_1(l - l') \right)
\]

(Eq. 8.11)

Eq. 8.11 is the central result of this section. Note that the \( h_{ij}(l, m, n) \), which are the parts of the correlation between two associating particles, are still dependent on three coordinates.

The \( h_i(l) \), that are found from Eq. 8.11 upon combination with an appropriate closure equation, are the partial wall-associating particle correlations that can be used to construct the concentration profile of the associating fluid at the wall. We have complemented Eq. 8.11 with a Percus-Yevick type closure relation, given by

\[
y_i(l) = g_i(l) - c_i(l) \tag{8.12}
\]

and the exact relations

\[
g_i(l) = e^{-\beta u_W(l)} y_i(l) \tag{8.13}
\]

in which \( u_W(l) \) is the symmetric \((u_W(+l) = u_W(-l))\) wall-associative particle potential. It is given by

\[
\begin{align*}
u_W(0) &= +\infty \\
u_W(\pm 1) &= u_W \\
u_W(\pm l) &= 0 \quad \text{otherwise}
\end{align*}
\]

(Eq. 8.14)

Note that \( u_W(l) \) is orientation independent, the orientation of the associating fluid particles are of no influence on the wall-particle interaction \( u_W(l) \). The relations between the partial wall-fluid distribution, \( g_i(l) \), and the partial wall-fluid correlation, \( h_i(l) \), are

\[
h_i(l) = g_i(l) - \delta_{i0} \tag{8.15}
\]

in analogy with \( h_{ij}(l, m, n) = g_{ij}(l, m, n) - \delta_{im}\delta_{jn} \) (Eq. 6.15 of Ref. [20]) which is used in finding the bulk 2-particle distribution \( G(l, m, n) \) of an associating fluid. In Eq. 6.15, two sub-indices \( i \) and \( j \) appear because there we are considering with the correlations between two associating particles. In Eq. 8.15 (and Eqs. 8.12 and 8.13) is dealt with only one associating particle, which explains the single index. Eqs. 8.11-8.15 form a complete set of equations that can be solved for the \( h_i(l) \), if we obtain the \( h_{ij}(l, m, n) \) and \( c_{ij}(l, m, n) \) from the first set in Eq. 8.9 with the methods outlined in Ref. [20]. The solution method for obtaining the
$h_i(l)$ is outlined in Appendix G. Once the $h_i(l)$ are known, the partial wall-fluid distributions $g_i(l)$ are found from Eq. 8.15. The concentration profile can then be constructed from

$$\eta g(l) = \eta g_0(l) + \eta_0 g_1(l) \quad (8.16)$$

In Eq. 8.16 there is again only one index $i$ because only one associating fluid particle is considered in the partial wall-particle distributions $g_i(l)$. From the concentration profile $\eta g(l)$, an excess adsorbed amount $\Gamma$ is defined by

$$\Gamma(\eta) = \sum_{i=1}^{l_{bulk}} \eta (g(l) - 1) \quad (8.17)$$

where $g(l) - 1$ denotes the deviation of the associating fluid distribution at the wall from the bulk value 1. The $l_{bulk}$ should be chosen large enough, for the summation to reach into the bulk of the adsorbing fluid. An adsorption isotherm can be constructed by plotting $\Gamma(\eta)$ versus $\eta$.

Note that the theory outlined in this section does not provide the correlations between the associating particles in the interfacial layers. It only considers wall-fluid correlations. The method outlined in this section can also be used to study the adsorption of associating particles on an attracting "rod", if only one coordinate is removed in going from Eq. 8.10 to Eq. 8.11. Results for the behavior of the singly associating fluid near an attracting wall are presented in section 8.5. The results will be compared to MC-simulation results.

### 8.3 Adsorption of a polymerizing cubic lattice fluid

In this section the 3-density formalism [8,9] is adapted to calculate the concentration profiles of a cubic lattice fluid consisting of particles with two directional attractive forces at an impenetrable wall. The wall is again allowed to have a non-specific nearest neighbor interaction with the particles that occupy one lattice site each. The method is completely analogous to the method described in the previous section for particles with only one directional attraction, and consists of mixing a non-associating simple fluid particle in a system of associating particles, after which the simple particle is turned into a wall. The partial wall-fluid distributions are then calculated and used to construct the density profile of the associating fluid at the wall. If the attractions between the associating particles are relatively strong ($|u_{attr}| > 5k_BT$), permanent bonding between the associating particles will occur and chain molecules will be formed [12]. The density profiles thus are the result of the adsorption of a polydisperse polymeric fluid at an impenetrable wall. The method by which the wall is created, is already described in the previous section. The potential model that is used involves a
summation over the two attractive sites of each particle.

\[ u(1, 2) = u_R(1, 2) + \sum_{s_1=1}^{2} \sum_{s_2=1}^{2} u_{s_1,s_2}(1, 2) \]  

(8.18)

The potentials \( u_R \) and \( u_{s_1,s_2} \) are defined by Eqs. 8.2 and 8.3 respectively. We have chosen the sites on a particle to be indistinguishable. Kalyuzhnyi and Stell [21] have generalized Wertheim's approach [8,9] to such systems, and here we rely on their graphical analysis.

The OZ-matrix equation for a system of simple particles at packing fraction \( \eta_M \) and doubly associating particles at packing fraction \( \eta \) is still given by Eq. 8.5 with the modified matrices [21]

\[
\mathbf{H}(1, 2) = \begin{pmatrix}
    h_{00} & h_{01} & h_{02} & h_0 \\
    h_{10} & h_{11} & h_{12} & h_1 \\
    h_{20} & h_{21} & h_{22} & h_2 \\
    h_0 & h_1 & h_2 & h
\end{pmatrix}
\]

(1, 2)  

(8.19)

and

\[
\sigma = \begin{pmatrix}
    \sigma_2 & \sigma_1 & \sigma_0 & 0 \\
    \sigma_1 & \sigma_0 & 0 & 0 \\
    \sigma_0 & 0 & 0 & 0 \\
    0 & 0 & 0 & \eta_M
\end{pmatrix}
\]

(8.20)

in which

\[
\sigma_i = \sum_{j=0}^{i} \eta_j
\]

(8.21)

with \( \{i, j\} \in \{0, 1, 2\} \) and \( \eta = \sigma_2 \). The \( \eta_j \) in Eq. 8.21 denote the packing fractions of the associating particles that have formed \( j \) specific bonds. The matrix for \( \mathbf{C}(1, 2) \) is of the same form as the \( \mathbf{H}(1, 2) \)-matrix. The \( h_{ij}(1, 2) \) in Eq. 8.19 denote parts of the total 2-particle correlation between two associating particles, the \( h_i(1, 2) \) concern an associating- and a simple particle, and \( h(1, 2) \) is the total correlation between two simple particles.

Matrix multiplication of Eq. 8.5 and taking the limit \( \eta_M \to 0 \) results in sixteen equations that are divided over four sets (see section 8.2):
\begin{align*}
  h_{ij}(1, 2) &= c_{ij}(1, 2) + \frac{1}{6} \sum_{r_3, \Omega_3} (c_{io}(1, 3)\sigma_2 h_{0j}(3, 2) + c_{i1}(1, 3)\sigma_1 h_{0j}(3, 2) + \\
  &\quad c_{i2}(1, 3)\sigma_0 h_{0j}(3, 2) + c_{i0}(1, 3)\sigma_1 h_{ij}(3, 2) + \\
  &\quad c_{i1}(1, 3)\sigma_0 h_{ij}(3, 2) + c_{i0}(1, 3)\sigma_0 h_{2j}(3, 2)) \\
  h_{i}(1, 2) &= c_i(1, 2) + \frac{1}{6} \sum_{r_3, \Omega_3} (c_{io}(1, 3)\sigma_2 h_{0i}(3, 2) + c_{i1}(1, 3)\sigma_1 h_{0i}(3, 2) + \\
  &\quad c_{i2}(1, 3)\sigma_0 h_{0i}(3, 2) + c_{i0}(1, 3)\sigma_1 h_{1i}(3, 2) + \\
  &\quad c_{i1}(1, 3)\sigma_0 h_{1i}(3, 2) + c_{i0}(1, 3)\sigma_0 h_{2i}(3, 2)) \\
  h(1, 2) &= c(1, 2) + \frac{1}{6} \sum_{r_3, \Omega_3} (c_{0}(1, 3)\sigma_2 h_{0i}(3, 2) + c_{1}(1, 3)\sigma_1 h_{0i}(3, 2) + \\
  &\quad c_{2}(1, 3)\sigma_0 h_{0i}(3, 2) + c_{0}(1, 3)\sigma_1 h_{1i}(3, 2) + \\
  &\quad c_{1}(1, 3)\sigma_0 h_{1i}(3, 2) + c_{0}(1, 3)\sigma_0 h_{2i}(3, 2)) \quad (8.22)
\end{align*}

The first set in Eq. 8.22 comprises nine equations and the second and third set each contain three equations. The fourth set contains only one equation. The set for the $h_{ij}(1, 2)$ in Eq. 8.22 contains the equations that determine the parts of the total 2-particle correlations in the bulk associating fluid. It was solved in Ref. [12] by combining it with PY-type closures and mass balance equations. In obtaining the $h_{ij}(l, m, n)$, it was crucial [22,12] to assume independence of the two interaction sites on the associating fluid particles, and to pre-average the site-site potential $u_{s1, s2}$ over the orientations of the sites. The pre-averaging is given by

\begin{equation}
  f_A(l, m, n) = \frac{1}{36} \sum_{\Omega_1, \Omega_2} (e^{-\beta u_{s1, s2}(l,m,n,\Omega_1, \Omega_2)} - 1) \quad (8.23)
\end{equation}

which results in

\begin{align*}
  f_A(l, m, n) &= \frac{1}{36} (a - 1) \quad \text{if } l^2 + m^2 + n^2 = 1 \\
  f_A(l, m, n) &= 0 \quad \text{otherwise} \quad (8.24)
\end{align*}

with $a = e^{-\beta_{\text{water}}}$. The $f_A$ appears in the closure and mass balance equations of the bulk fluid. The $h_{ij}(l, m, n)$ for the bulk fluid are needed in this section as an input for the calculation of the adsorption profiles. In this section, we therefore also assume independence of interaction sites on an associating particle, and employ the pre-averaging of Eq. 8.24.
The last set of Eq. 8.22 is a single equation for the total distribution of two simple particles. It is not considered here, because \( \eta_M \rightarrow 0 \) guarantees that encounters of simple fluid particles do not occur.

The concentration profiles of the associating fluid near the impenetrable wall can be calculated from the second or third set in Eq. 8.22. We will only consider the third set. The simple particle can be extended in \( m \)– and \( n \)–direction in the same way as outlined in the previous section. The result is

\[
\begin{align*}
\bar{h}_i(l) = & \ c_i(l) + \\
& \sum_{l', m', n'} ((\sigma_2 h_{0k}(l', m', n') + \sigma_1 h_{1k}(l', m', n') + \sigma_0 h_{2k}(l', m', n'))c_0(l - l') + \\
& (\sigma_1 h_{0k}(l', m', n') + \sigma_0 h_{1k}(l', m', n'))c_1(l - l') + \sigma_0 h_{0k}(l', m', n')c_2(l - l')) \\
\end{align*}
\]

Eq. 8.25 is the central equation of this section. The \( h_{ij}(l, m, n) \)'s and the \( \sigma_i \)'s that appear in Eq. 8.25 are determined from the solution of the bulk properties of the associating lattice fluid [12]. The partial wall-associating fluid distributions \( h_i(l) \) can now be found from Eq. 8.25 by combining it with a closure equation. We again employed the Percus-Yevick-like closure Eqs. 8.12 and 8.13. The wall-associating particle interaction potential is non-specific and given by Eq. 8.14. The relation of \( h_i(l) \) to the partial wall-particle distributions \( g_i(l) \) is given by Eq. 8.15. The index \( i \) that appears in Eqs. 8.12-8.15 and 8.25 now runs over \( \{0, 1, 2\} \).

Eqs. 8.12-8.15 and 8.25 constitute a set of six equations in the six unknowns \( c_0(0), c_0(1), c_1(0), c_1(1), c_2(0) \) and \( c_2(1) \) that is solved along the lines outlined in Appendix G. Once the unknowns are found, the \( h_i(l) \) can directly be constructed (see Appendix G).

The concentration profile of the fluid at the impenetrable wall is finally obtained from

\[
\eta g(l) = \sum_{i=0}^{2} \sigma_i g_{2-i}(l)
\]

in which \( g(l) \) is the total wall-associating particle distribution function. An adsorption isotherm can be constructed from Eq. 8.26 via Eq. 8.17.

### 8.4 Adsorption of associating fluids: Monte Carlo simulations

The concentration profiles of the dimerizing fluid (section 8.2) and the polymerizing fluid (section 8.3) were also determined by NVT-MC simulation, to rightly judge the quality of the outlined theoretical approaches. The simulations used a box that was bounded by hard impenetrable walls on both sides along the \( l \)-axis.
The box had periodic boundaries in the $m$- and $n$-directions. Layers were defined as $mn$-planes parallel to the impenetrable walls. Systems with zero or attractive wall-particle energy $u_W$ were considered. The concentration profiles were determined by counting the numbers of particles in each layer. Equilibration was assured by monitoring the internal energy $E$ of the fluid in the box, and by checking that the obtained concentration profiles were symmetric along the $l$-axis. A blocking method [23] was used to calculate the standard deviations of the averages that were monitored and to assure that the simulation recipe is able to produce uncorrelated data. Thus far, we have only determined the concentration profiles from the simulations, but in the case of the polydisperse chain fluid it might be interesting to study ordering-, reorientation- [24,25], and chain length segregation effects that are induced by the impenetrable wall. We expect these effects to be relatively small for the simulations of the polymerizing fluid that were performed in this work: we have not considered average chain lengths exceeding 15 segments. It is in principle also possible to obtain an equation of state from the simulated adsorption profiles by varying the wall-fluid interaction potentials from $u_W \rightarrow 0$ to $u_W \rightarrow +\infty$ [26,27].

Both types of fluids that we have considered were tested at two box filling fractions: $\eta' = 0.5$ with 1000 particles in a $20 \times 10 \times 10$ $lmn$-box and $\eta' = 0.3$ with 1536 particles in a $20 \times 16 \times 16$ $lmn$-box (the overall box filling fractions are denoted as $\eta'$ to distinguish them from the packing fraction $\eta$ of the bulk region). The walls were non-interacting or had a favorable attractive energy of $u_W = -0.25k_BT$ or $u_W = -0.5k_BT$ with the particles in the layers closest to the wall. Runs were performed for attractive associating particle interactions varying from $u_{attr} = -1.0k_BT$ to $u_{attr} = -7.0k_BT$ in steps of $-0.5k_BT$ or $-1.0k_BT$.

The simulation recipe that was used is different for both fluid types. For the simulation of the fluid consisting of particles with one attractive force, we have used a combination of brute force moves, and moves in which a particle was taken from a dimer and bonded to a free non-bonded monomer. The latter move is included in the recipe because there is generally no energy difference associated with this move. This leads to automatic acceptance which enhances equilibration. Only if a particle is moved from or to a layer next to the wall, we have to take the wall-associating particle interaction energy into account in the acceptance criterion of this bond-swap move. The bond-swap move samples the distribution of the particles over the lattice, but does not sample the number of particles bonded into a dimer. Therefore, we need to include a sufficient amount of brute force moves in the recipe. A recipe was employed in which 70% brute force and 30% bond swap moves were attempted. The average energy in the box and the concentration profiles were tested to be independent of the exact constitution of the recipe.
The simulation recipe of the polymerizing fluid was used previously to obtain the structural properties of the bulk region of the fluid [12]. It includes brute force moves (10%), bond-flips (10%), double bond-flips (15%), generalized reptation moves (15%), and biased cluster moves (50%). Indicated between the brackets are the percentages of attempts for the type of move. The polymerizing fluid particles interact via the model potential of Eqs. 8.2, 8.3 and 8.18 but in the simulations it was forbidden for the two sites on a particle to overlap. The chains that are formed thus show the full excluded volume. All moves used in the recipe were discussed in Ref. [12]. The biased cluster move was outlined in detail in Appendix F. It samples the particle distribution over the lattice and the average chain length. The difference with the simulations of Ref. [12] is the incorporation of the wall-particle interaction $U_w$ into the acceptance criterion, and the inclusion of impenetrable walls on $+l$ and $-l$-side of the simulation box. The acceptance criterion is given by [12-14]

$$acc(1 \rightarrow 2) = \min \left( 1, \frac{W(2)}{W(1)} \right)$$

where the Rosenbluth factor $W(1)$ of conformation 1 is now given by

$$W(1) = e^{-\beta u_1} \left( \prod_{i=2}^{l} Z_i \right) \left( (1 - p)e^{-\beta u_{attr}} \right)^{b_1}$$

with $l$ being the number of segments within the cluster, and $b_1 = \{0, 1, 2\}$ is the number of bonds that is broken in creating the cluster (see Appendix F). The $p$ is the probability for including a segment into a cluster (see Appendix F). We have chosen $p$ to be 0.95 in all the simulations performed in this work. This means that on average 1 in 20 bonds is broken in creating a cluster from a chain. In Eq. 8.28, the attractive potential $u_{attr}$ defines the bond strength of the interaction between two associating particles (see Eq. 8.3), and $u_1$ is a potential that belongs to the first particle of the linear cluster. If the position of particle 1 is already taken by another particle, then $u_1 \rightarrow \infty$. If the position of particle 1 is not taken then $u_1 = 0$, except if particle 1 is located in the layer closest to the wall, for which $u_1 = u_W$. Note that $u_1$ does not account for the possibility of bond formation between particle 1 and another particle that is not part of the cluster. This is accounted for separately by the factor $((1 - p)e^{-\beta u_{attr}})^{b_1}$. The $Z_i$ in Eq. 8.28 is the sum of Boltzmann factors of segment $i$, if placed on the nearest neighbor sites of segment $i - 1$. Only 5 out of 6 nearest neighbor positions are checked, because one of them is already taken by segment $i - 2$ (or by an attractive cluster edge if $i = 2$ [12]). $Z_i$ is given by

$$Z_i = \sum_{j=1}^{5} e^{-\beta u_{i,j}}$$

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where \( u_{i,j} \) denotes the value of the potential of segment \( i \) if placed in position \( j \)
\[
    u_{i,j} = u_{Ri,j} + u_{Wi,j} 
\]
(8.30)

with
\[
    u_{Ri,j} \to \infty \quad \text{if position } j \text{ is taken} \\
    u_{Ri,j} = 0 \quad \text{otherwise} 
\]
(8.31)
and
\[
    u_{Wi,j} = u_W \quad \text{if position } j \text{ is in layer next to wall} \\
    u_{Wi,j} = 0 \quad \text{otherwise} 
\]
(8.32)

We can thus apply the biased cluster move to simulate the adsorption profiles of the associating fluids, if Eqs. 8.27-8.32 are obeyed.

The Rosenbluth factor \( W \) incorporates the restrictions that the wall imposes on a chain conformation: if we consider a chain near a wall, then \( W \) is the quotient of the number of ways a particular conformation can be obtained in the neighborhood of a wall and the number of conformations \( (= 5^{l-1}) \) that an isolated Non Reversal Random Walk (NRRW) of the same length can attain [28,29].

In the next section the results of the simulations of both fluids will be presented. The simulations were performed on a fourteen MIPS R8000 processor Silicon Graphics Power challenge XL with an IRIX 6.0 operating system in non-parallel runs. Simulations for the dimerizing fluid took up to two CPU hours for the strongly interacting fluids \( (u_{attr} = -7.0k_BT) \). The polymerizing fluid simulations took up to ten CPU hours for \( u_{attr} = -7.0k_BT \) and five hours for \( u_{attr} = -3.0k_BT \). The results are available on request via e-mail at tgpken@urc.tue.nl.

8.5 Results and discussion

In section 8.5.1, the concentration profiles of the singly associating fluid at an impenetrable wall are presented and compared to results of the simulations. The adsorption profiles of a fully associated \( (u_{attr} \to -\infty) \) dimeric lattice fluid are also compared to the profiles of dimeric molecules obtained from a lattice version of the RISM-theory [16]. In section 8.5.2 the concentration profiles of the polymerizing lattice fluid near an impenetrable wall are presented and compared to simulation results.

8.5.1 Dimerizing fluid

In Fig. 8.1 some concentration profiles of the singly associating lattice fluid are presented. Walls are located at layer \( l = 0 \) and layer \( l = 21 \). Symmetric profiles along the \( l \)-axis are obtained, but here only layers 1 to 8 are shown. Three

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Figure 8.1: Concentration profiles of a singly associating fluid near a wall with $u_W = -0.5k_B T$ (▲), $u_W = -0.25k_B T$ (■) and $u_W = 0.0k_B T$ (●). The symbols are the results of simulations. The simulations were performed for box filling fraction $\eta' = 0.3$ and $u_{\text{attr}} = -7.0k_B T$. From the simulations we have found $\eta$ and $\eta_0$ to be 0.2852 and 0.03127 (▲), 0.2939 and 0.0320 (■) and 0.3019 and 0.0320 (●). With these values of $\eta$ and $\eta_0$ we have calculated the lines in the figure according to section 8.2.

wall-fluid nearest neighbor energies were considered in Fig. 8.1: $u_W = 0.0k_B T$ (●), $u_W = -0.25k_B T$ (■) and $u_W = -0.5k_B T$ (▲). In the simulations (symbols), we have set the strength of the particle-particle associative interaction at $u_{\text{attr}} = -7.0k_B T$. This corresponds to roughly 90% of the particles being bonded into dimers [20]. It is seen from the simulations that the influence of the wall only reaches two layers deep into the fluid, even for a relatively strong wall-fluid interaction $u_W = -0.5k_B T$ that causes a large accumulation of fluid particles in the layer closest to the wall. The depth of the profile is obviously related to the length of the main axis of the dimers: a dimer with its main axis oriented perpendicular to the wall, only reaches into the second layer. In Fig. 8.1 it is seen that the fluid tends to accumulate near the walls, if the wall-fluid interaction is favorable (■ and ▲). If the wall is non-interacting, a depletion is observed. Such a depletion is absent for non-associating particles ($u_{\text{attr}} \rightarrow 0$), and can be fully attributed to the entropic restrictions that the impenetrable wall imposes on the dimeric molecules that are formed if $|u_{\text{attr}}| > 0$. The results of the theory of section 8.2 are depicted by the lines in Fig. 8.1. We have drawn connecting lines through the theoretical packing fractions $\eta g(l)$, to make the distinction between
the calculated and simulated points as clear as possible. It does not mean that the theory predicts a continuous profile. Comparisons with the theory are made at fixed bulk packing fraction $\eta$ and fixed packing fraction of non-bonded particles $\eta_0$. The values of $\eta$ and $\eta_0$ in the bulk region of the fluid (layers 4 to 16) are in general slightly different from the overall box values $\eta'$ and $\eta'_0$. The $\eta$ and $\eta_0$ that are used for comparison with the theory, are obtained from the simulations and are indicated in the caption of Fig. 8.1. We have not monitored the concentration profile of $\eta_0$, but its bulk value was estimated from the whole box value as $\eta_0 = \eta'_0 \eta/\eta'$. This procedure is not fully correct because it can be expected that the degree of association $1 - \eta_0/\eta$ is a function of the layer number $l$. The agreement between theory and simulation is nevertheless excellent, which indicates that the wall only has a minor influence on the overall degree of association in the box.

Note that the most appropriate comparison between the theory and the simulations would have been at fixed $\eta$ and $u_{\text{attr}}$ because it are these two quantities that determine $\eta_0$. It was outlined previously that it is fully justified to make the comparison at fixed $\eta$ and $\eta_0$ if $|u_{\text{attr}}| > 3k_BT$ (see Fig. 6.2 of Ref. [20]).

![Figure 8.2: Simulated (symbols) and calculated (lines) adsorption in layer closest to the wall for $\eta' = 0.5$ and $u_W = -0.5k_BT$ (▲), $u_W = -0.25k_BT$ (■) and $u_W = 0.0k_BT$ (●) as a function of the associative interaction strength.](image)

Comparisons between the theory and simulations for other bulk packing fractions and degrees of association have been performed and show the same excellent
agreement. Therefore, we have not depicted the full concentration profiles for such situations. An overview of the adsorption behavior at box filling fraction $\eta' = 0.5$ and $u_W = 0.0k_B T$ (●), $u_W = -0.25k_B T$ (■) and $u_W = -0.5$ (▲) is given in Fig. 8.2, where the amount of adsorbed material in the layer closest to the wall is plotted versus the associative interaction strength $u_{\text{attr}}$ (g(1) in Fig. 8.2 is the packing fraction in the first layer divided by the bulk packing fraction). The comparison of the simulations with the theory are for the $\eta$ and $\eta_0$ observed from the simulations. Therefore, the (very small $\approx \pm 0.001$) numerical inaccuracies in the $\eta$ and $\eta_0$ obtained from the simulations also show up in the calculated curves, which explains why the curves in Fig. 8.2 are not completely smooth.

Several interesting aspects can be observed from Fig. 8.2. First of all it is seen that the agreement between theory and simulation is excellent for the $u_W$ that have been considered. Secondly, comparing the $g(1)$ of Figs. 8.1 ($g(1) = 1.460$) and 8.2 ($g(1) = 1.2715$) for $u_W = -0.5k_B T$ and $u_{\text{attr}} = -7.0k_B T$ shows that in the case of the higher bulk packing fraction ($\eta = 0.2852$ in Fig. 8.1, and $\eta = 0.4854$ for $u_{\text{attr}} = -7.0k_B T$ in Fig. 8.2) the tendency of the fluid to accumulate at the wall is less strong. This effect is identical to the diminishing of the particle-particle correlations that is observed in bulk lattice fluids if the packing fraction is increased [20].

It is also seen in Fig. 8.2 that $g(1)$, i.e., the amount of adsorbed material, is almost fully determined by $u_W$ and that $u_{\text{attr}}$ is only of minor influence. This means that the favorable energetic wall-particle interaction is more important than the entropic depletion, which occurs due to ordering of the dimeric molecules at the wall. It is shown in the next subsection that the effect of $u_{\text{attr}}$ on the concentration of the fluid near the wall is more influential for polymerizing fluids, because in that case $u_{\text{attr}}$ has a large effect on the size of the molecules that are formed.

A last aspect of Fig. 8.2 is observed by looking at the dependency of $g(1)$ on $u_{\text{attr}}$ for the three lines in the figure. The lower curve for which $u_W = 0.0k_B T$ shows a decrease of $g(1)$ for higher $|u_{\text{attr}}|$: a somewhat deeper depletion hole is observed for a more highly dimerized fluid. Thus, the entropic depletion, which is the only determining factor near a non-interacting wall, is more important for more highly dimerized systems. For the upper curve, for which $u_W = -0.5k_B T$, the situation is reversed. Not only do the fluid particles tend to accumulate ($g(1) > 1$) at the wall, the accumulation also increases for a stronger associative interaction $u_{\text{attr}}$: the dimers have a stronger tendency to accumulate at the wall than the non-bonded particles, in spite of the entropic restrictions that the wall imposes on the dimers. This is because the gain in energy that accompanies the adsorption of a dimer, is larger than the entropy loss. For $u_W = -0.25k_B T$ this is not the case. Although an accumulation of particles at the wall is observed from Fig. 8.2 for $u_W = -0.25k_B T$, we see a slight decrease of $g(1)$ for a stronger associating fluid: the wall-particle interaction is not strong enough to counterbalance the entropic restriction the wall imposes on the adsorbing dimers. A decrease of $g(1)$ is therefore observed for increasing $|u_{\text{attr}}|$.
In Fig. 8.3, the adsorption profile in the limit of infinitely strong association, \( u_{\text{attr}} \rightarrow -\infty \), for which a fully dimerized lattice fluid is obtained [20], is drawn (full line). The dashed line is the adsorption profile obtained previously with a discretized RISM-equation [15] that was modified along the lines described in Refs. [16,17,19]. The adsorption-RISM equation was complemented with a standard Percus-Yevick closure equation. The symbols in Fig. 8.3 denote points obtained with a previously outlined \( NpT \)-simulation method [30,17]. The simulation method does not attempt to break bonds between particles. This would lead to immediate rejection of the move for the fully associated fluid (\( u_{\text{attr}} \rightarrow -\infty \)). Therefore, we have only sampled the distribution of the dimers over the lattice by moving them in a reptation like fashion [31] through the simulation box.

Fig. 8.3 clearly demonstrates the accurateness of the associating fluid theory for \( u_{\text{attr}} \rightarrow -\infty \). This is in contrast to the discretized RISM theory, that significantly underestimates the depletion of the dimeric fluid. Comparisons of both theories at other packing fractions (up to 0.7) have been made, and identical results have been found.

We conclude from the results presented in this section that the general performance of Wertheim's formalism [6,7] is excellent when applied to study the
adsorption profiles of singly associating cubic lattice fluids at hard and interacting impenetrable walls. Therefore, it is expected that it is possible to extract an accurate equation of state for the bulk associating fluid from the calculated profiles with the method of Dickman [26].

8.5.2 Polymerizing fluid

In Fig. 8.4, some adsorption profiles of a polymerizing fluid with $u_{\text{attr}} = -7.0k_B T$ at overall box filling fraction $\eta' = 0.3$ near an impenetrable wall are depicted. The symbols indicate the simulation results and the lines depict the results obtained from the theory. The lines are only drawn to distinguish between theoretical and simulation results. The bulk packing fractions that were monitored are summarized in Table 8.1, together with the number average chain length $\bar{L}_N$ and width of the chain length distribution $\bar{L}_W/\bar{L}_N$. These were obtained from the simulations with Flory's formulae [32,12]

$$\bar{L}_N = \frac{2\eta'}{2\eta'_0 + \eta'_1}$$

$$\frac{\bar{L}_W}{\bar{L}_N} = \frac{2\eta'_0 + 3\eta'_1 + 4\eta'_2}{2\eta'}$$

(8.33)

where the $\eta'$, $\eta'_0$, $\eta'_1$ and $\eta'_2$ in Eq. 8.33 denote whole box averages. In Eq. 8.33, the formation of rings is neglected [32]. This results in an overestimation of the actual chain length of up to 10% for the systems considered here [12]. Although it is well possible to obtain the actual $\bar{L}_N$ and $\bar{L}_W/\bar{L}_N$ from the simulations by monitoring the full chain length distribution [12], it is not possible to obtain the

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<td>Fig. 8.4</td>
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<td>Fig. 8.5</td>
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<td>0.5113</td>
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Table 8.1: Overview of number average chain lengths and widths of distribution. $u_{\text{attr}} = -7.0k_B T$ in all cases.
Figure 8.4: Adsorption profiles of a polymerizing fluid. Symbols are simulation results, lines correspond to the solution of the equations of section 8.3 with $u_W = 0.0k_BT$ (dashed line, •) and $u_W = -0.25k_BT$ (full line, ■). In both cases, $u_{attr} = -7.0k_BT$ and $\eta' = 0.3$.

Figure 8.5: Caption as in Fig. 8.4 but for $\eta' = 0.5$. 
full chain length distribution from the theory of section 8.3. To compare identical quantities we therefore also use Eq. 8.33 to analyze the simulation results. The \( \overline{L_N} \) and \( \overline{L_W/L_N} \) monitored from the simulations, are a function of the layer number, but thus far we have not monitored the \( \eta_i \) for each layer separately. Therefore, we have only calculated whole box averages, although it is expected that there is a preference for shorter chains close to the wall: the entropic restrictions that the wall imposes on the molecules (restrictions on molecule conformation and surface induced ordering of the molecules) are smaller for shorter chains. Monitoring of the fractions of free, singly bonded and doubly bonded particles for each layer separately would allow to study this surface induced segregation effect. In Fig. 8.4, we are dealing with relatively short chains, \( \overline{L_N} \approx 12 \), for which we expect the effect to be small. Although we have no direct proof of this, we can nevertheless see from Table 8.1, by comparing the whole box averages obtained in this work with the averages obtained previously for the bulk region [12], that the surface segregation is not strong enough to cause strong deviations of the overall \( 20 \times 10 \times 10 \) box values of \( \overline{L_N} \) and \( \overline{L_W/L_N} \) from the values for the bulk region. This does not imply however, that the influence of the walls is unimportant in the layers close to the wall.

Fig. 8.5 is identical to Fig. 8.4 but for \( \eta' = 0.5 \). Bulk packing fractions, number average chain lengths, and widths of the distribution are again given in Table 8.1. The bulk values taken from Ref. [12] are also reported in Table 8.1. Comparison with the bulk values again shows that the walls do not have a large influence on the overall averages obtained from the box.

The agreement between the calculated and simulated adsorption profiles in Figs. 8.4 and 8.5 is not overall good. In the case of non-interacting walls (dashed lines) the theory seems to be qualitatively correct. It does predict a depletion hole, although the hole is not deep enough when compared to the simulation results. The origin of the depletion hole is the entropic penalty that the wall imposes on the fluid. It is not compensated by an attractive wall-fluid interaction, and therefore, a depletion of the fluid near the wall is observed.

For the interacting walls, \( u_W = -0.25k_BT \) (full lines), both the theory and the simulations show an accumulation of particles at the wall. This accumulation is due to a energetically favorable wall-fluid interaction \( u_W \) that compensates the entropic depletion. For \( u_W = -0.25k_BT \) (full curve) in Fig. 8.4, the theory and the simulations both show an accumulation of particles near the wall, but we find that the theory underestimates the total amount of adsorbed material, especially in the second layer from the wall. For \( u_W = -0.25k_BT \) (full curve) in Fig. 8.5, the theory predicts an almost flat profile: the entropic depletion and energetic accumulation are nearly balanced in the theory. The simulations, on the other hand, show a net accumulation of particles near the wall.

In both figures, the simulations for \( u_W = -0.25k_BT \) show the formation of a block profile near the wall. Especially in Fig. 8.4, the two layers closest to the wall are
To obtain a clearer view on the adsorption behavior of the polymerizing lattice fluid, we have depicted an overview for box filling fraction $\eta' = 0.5$ in Figs. 8.6 and 8.7, where respectively the normalized packing fractions in the first and second layer are plotted versus the strength of the interaction between the associating particles. From Fig. 8.6 it is seen that the theory and the simulations roughly have the same dependence of $g(1)$ on $u_{attr}$. Note that although there is an accumulation ($g(1) > 1$) of associating particles at the wall for $u_W = -0.25k_B T$ (■), there is a decrease of the adsorption for increasing $|u_{attr}|$. This was also observed in Fig. 8.2 for the adsorption of the dimerizing fluid at a wall with $u_W = -0.25k_B T$. The decrease of $g(1)$ with increasing $u_{attr}$ can be attributed to a higher entropic penalty that the wall imposes on a fluid of longer chains. It is seen from Fig. 8.2 and Fig. 8.6 that the decrease of $g(1)$ with $u_{attr}$ is more pronounced for the doubly associating fluid, which is to be expected because association is much more important in polymerizing fluids.

From Fig. 8.7 it is seen that the theory is also qualitatively correct for $g(2)$ if the wall is non-interacting (●). For the interacting wall (■) the theory and the simulations appear to behave differently. The simulations show an increase of the adsorbed amount in the second layer, whereas the theory shows a maximum. Note that the decrease of $g(1)$ (■ in Fig. 8.6) and the increase of $g(2)$ (■ in Fig. 8.7) for $u_W = -0.25k_B T$ lead to the block profiles observed in Figs. 8.4 and 8.5. It is seen in Figs. 8.6 and 8.7 that, in the simulations for $u_W = -0.25k_B T$ (■), the decrease in $g(1)$ and the increase in $g(2)$ flatten for higher $u_{attr}$. It is most likely that for a certain $u_{attr}$ they will reach respectively a maximum and a minimum value, simply because it is improbable that the packing fraction in the second layer will surpass the packing fraction in the first layer. For higher $|u_{attr}|$ we certainly expect to monitor an increase of $g(3)$ with increasing $|u_{attr}|$, although this increase will be shifted towards higher $|u_{attr}|$ when compared to $g(2)$. This corresponds to the formation of an adsorbed layer that extends deeper into the fluid if the average length of the molecules is increased.

The theory for the adsorption of a polymerizing fluid, for which some results have been presented in this subsection, is based on an exact diagrammatical analysis of the wall-fluid and fluid-fluid correlations [8,9]. Despite this fact, the results are at most qualitatively correct. Reasons must lie in the approximations that were made to obtain a solvable set of equations for the bulk correlations of the polymerizing fluid. These approximations are the assumed independence.
Figure 8.6: Normalized packing fraction, $g(1)$, in the layer closest to the wall, versus associative interaction strength. Symbols are simulation- and lines are calculated results. (■): $u_w = -0.25k_BT$, (○): $u_w = 0.0k_BT$.

Figure 8.7: Caption as in Fig. 8.6, but for the next nearest neighbor layer to the wall.
of the interaction sites on each particle, and the pre-averaging of the site-site potential \( u_{s_1,s_2}(1,2) \) over the orientations of \( s_1 \) and \( s_2 \) in the closure and mass balance equations that are used to obtain the bulk correlations [12,22]. Another reason could in principle be the approximate nature of the closure equations, but this is less likely because the closures have proven to function extremely well in the calculation of the adsorption profiles of dimerizing fluids, as was shown in the previous subsection.

### 8.6 Conclusions

New cubic lattice models of singly and doubly associating fluids, based on Wertheim's Ornstein-Zernike matrix formalism [6-9], have been studied to assess the adsorption behavior of dimerizing and polymerizing fluids at impenetrable interacting walls.

The concentration profiles have been tested with Monte Carlo simulations. The simulation of the doubly associating lattice fluid near an impenetrable wall employed a biased cluster move [12].

The overall agreement between the theory and the simulations is quantitative for the singly associating fluid. These results therefore suggest that Wertheim's graphical analysis is also suitable to accurately study polymerizing fluids. Unfortunately, the results obtained for polymerizing fluids suggest that better approximations have to be adopted in solving the equations that result from Wertheim's formalism: we do not find quantitative, but only qualitative agreement for the adsorption profiles at a non-interacting wall. The adsorption of the polymerizing fluid at an interacting wall seems to be incorrectly described by the theory. The simulations show the formation of a block-profile, whereas the theory shows a smoothly decreasing adsorption profile.

Finally, the method presented here forms an alternative to the polymer RISM-[16,17] and other approaches [18] to study polymer adsorption. The method does, contrary to the polymer RISM-approach, not use the concept of an intramolecular distribution function to capture the conformations of the molecules near the interface, and incorporates polydispersity in an elegant way. Thus far, we have not made numerical comparisons to the polymer RISM-theory of Ref. [17].
References


Appendix A

NRRW-chain intramolecular distribution

To be able to calculate the real space jump probabilities $W_i(l, m, n)$ of a Non Reversal Random Walk (NRRW), we need to separate the $W_i(l, m, n)$'s in six parts

$$W_i(l, m, n) = W_i((l, m, n); (l + 1, m, n)) + W_i((l, m, n); (l - 1, m, n)) + W_i((l, m, n); (l, m + 1, n)) + W_i((l, m, n); (l, m - 1, n)) + W_i((l, m, n); (l, m, n + 1)) + W_i((l, m, n); (l, m, n - 1))$$

(A.1)

The two arguments of the jump probabilities on the rhs of this equation denote the positions of the last two segments, $i+1$ and $i$, after $i$ jumps. For each of the jump probabilities on the rhs we can now write the equivalent of Chandrasekhar's expression, Eq. 3.22, e.g., for $W_i((l, m, n); (l - 1, m, n))$ we have

$$W_i((l, m, n); (l - 1, m, n)) = \tau W_{i-1}((l - 1, m, n); (l - 2, m, n)) + \tau W_{i-1}((l - 1, m, n); (l - 1, m + 1, n)) + \tau W_{i-1}((l - 1, m, n); (l - 1, m - 1, n)) + \tau W_{i-1}((l - 1, m, n); (l - 1, m, n + 1)) + \tau W_{i-1}((l - 1, m, n); (l - 1, m, n - 1))$$

(A.2)

with $\tau = \tau(1, 0, 0)$ being the probability for a single jump. The arguments of $W_{i-1}$ denote the coordinates of the last two segments $i$ and $i-1$ after $i - 1$ jumps. In Eq. A.2 we have left out the prohibited jump $\tau(1, 0, 0)W_{i-1}((l - 1, m, n); (l, m, n))$ which corresponds to direct back folding. The single jump probability $\tau(1, 0, 0)$ equals 1/5 if direct back folding is forbidden.

From $W_1((1, 0, 0); (0, 0, 0)) = 1/6$ one can immediately evaluate the $W_2(l, m, n)$ with help of Eq. A.1 and Eq. A.2. Further recursive use of these relations leads to the desired $W_{s-1}$.
The method becomes increasingly time consuming for long chains but the chains of this chapter (up to $s = 30$) could easily be studied in this way.
Appendix B

Solution method for the singly associating fluid

The set Eqs. 6.12-6.16 is solved most conveniently in Fourier space. For that purpose the equations first have to be written in a symmetrical, orientation independent form by averaging over $\Omega_1$ and $\Omega_2$. For the orientation averaged fluid, the 3D-lattice Fourier transformation is defined by the series (Ref. [17] of chapter 6)

$$\hat{f}(u,v,w) = \sum_{l,m,n} f(l,m,n) \cos lu \cos mv \cos nw$$

and the inverse transformation

$$f(l,m,n) = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{f}(u,v,w) \cos lu \cos mv \cos nw \, du \, dv \, dw$$

Summing the OZ-equation, Eq. 6.12, over $\Omega_1$ and $\Omega_2$ and dividing by 36 (see Eq. 6.9), Fourier transformation (Eq. B.1), and performing the matrix multiplication results in the orientation independent equations

$$h_{ij}(u,v,w) = C_{ij}(u,v,w) + \eta_0 h_{ij}(u,v,w) + \eta_0 h_{ij}(u,v,w) + \eta_0 h_{ij}(u,v,w)$$

Note that orientation averaging in Eq. B.3 does not involve an approximation. We then substitute $u_{attr}(1,2)$ (Eq. 6.8) in $f_A(1,2)$ (see below Eq. 6.14)

$$f_A(l,m,n,\Omega_1,\Omega_2) = a - 1$$

if $\Omega_1 = -\Omega_2$ and $l^2 + m^2 + n^2 = 1$ and

$$\text{sgn}(l + m + n) \left( l^2 + 2m^2 + 3n^2 \right) = \Omega_1$$

$$f_A(l,m,n,\Omega_1,\Omega_2) = 0 \quad \text{otherwise}$$

where $a = e^{-\beta u_{attr}}$.

Substitution of Eq. B.4 and the self-consistency equation Eq. 6.16 in Eq. 6.14
allows to write the \( \hat{c}_{ij}(u, v, w) \) in an orientation independent way. After Fourier transformation we obtain

\[
\hat{c}_{ij}(u, v, w) = -y_{ij}(0, 0, 0) + \frac{1}{3} \delta_{i1} \delta_{j1} \frac{\eta - \eta_0}{\eta^2} (\cos u + \cos v + \cos w) \quad (B.5)
\]

with help of the closures Eq. 6.13 and Eq. 6.14. Note that \( y_{10}(0, 0, 0) = y_{01}(0, 0, 0) \).

We also have the physically exact non-overlap conditions \( h_{ij}(l, m, n) = -\delta_{ij} \delta_{l0} \) that are implicit in Eq. 6.13 and Eq. 6.14. If Eq. B.3 is written explicitly for the \( \hat{h}_{ij}(u, v, w) \) in terms of the \( \hat{c}_{ij}(u, v, w) \) and if Eq. B.5 is substituted in these expressions, an explicit set of equations for the \( \hat{h}_{ij}(u, v, w) \) in terms of the unknowns \( y_{00}(0, 0, 0), y_{10}(0, 0, 0), \) and \( y_{11}(0, 0, 0) \) is obtained. We set \( \eta \) and \( \eta_0 \) in advance.

This is equivalent to the physically more natural procedure of setting the parameters \( u_{attr}(1, 2), \eta \), as is seen from the self consistency equation Eq. 6.16. We choose to set \( \eta \) and \( \eta_0 \) for computational convenience. Inverse transformation of the \( \hat{h}_{ij}(u, v, w) \) according to Eq. B.2 and using the non-overlap conditions \( h_{ij}(0, 0, 0) = -\delta_{ij} \delta_{l0} \) which serve as the closure relations, gives a set of only 3 equations in the unknowns \( y_{00}(0, 0, 0), y_{10}(0, 0, 0), \) and \( y_{11}(0, 0, 0) \). This set can be solved with a Newton-Raphson procedure combined with a 3D numerical integration routine. Once the \( y_{ij}(0, 0, 0) \) are known the \( h_{ij}(l, m, n) \) are found from (see Eq. B.2)

\[
h_{ij}(l, m, n) = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{h}(u, v, w) \cos lu \cos mv \cos nw \, du \, dv \, dw \quad (B.6)
\]

The total distribution function \( G(l, m, n) \) is then found from Eq. 6.10 and the orientation averaged version of Eq. 6.11 with \( \eta_1 = \eta - \eta_0 \).

The \( G^{AA}(l, m, n), G^{AB}(l, m, n) \) and \( G^{BB}(l, m, n) \) of the binary fluid mixture of section 6.2.3 are obtained from Eqs. 6.19-6.31 in the same way as the \( G(l, m, n) \) for the 1-component associating fluid. Therefore, we consider the procedure only very briefly.

First, the OZ-equation, Eq. 6.21, is written in an orientation independent form, after which it is Fourier transformed with Eq. B.1. Restating the matrix equation explicitly in terms of the elements \( \hat{h}_{ij}(u, v, w) \) then gives 16 equations. Due to the symmetry in the problem, only 10 of the equations are needed to find \( H^{AA}(1, 2), H^{AB}(1, 2) \) and \( H^{BB}(1, 2) \). These 10 equations are constructed by inverse transformation of \( \hat{h}_{ij}(u, v, w) \) to \( h_{ij}(l, m, n) \) (see Eq. B.2) and applying the non-overlap conditions

\[
h_{ij}^{IJ}(0, 0, 0) = -\delta_{ij} \delta_{l0} \quad (B.7)
\]

that are implicit in Eqs. 6.26-6.29.

The resulting equations are in the variables \( y_{00}^{AA}(0, 0, 0), y_{00}^{AB}(0, 0, 0), y_{00}^{BB}(0, 0, 0), y_{10}^{AA}(0, 0, 0), y_{10}^{AB}(0, 0, 0), y_{10}^{BB}(0, 0, 0), y_{11}^{AA}(0, 0, 0), y_{11}^{AB}(0, 0, 0) \) and

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$y_{i1}^{BB}(0,0,0)$ for given $\eta^A, \eta^B, \eta_0^A$ and $\eta_0^B$. The equations are solved with a Newton-Raphson scheme combined with a 3D numerical integration procedure. Once the constants are known, the partial correlations $h_{ij}^{IJ}(l,m,n)$ follow via the analogs of Eq. B.6. From the orientation independent versions of Eqs. 6.24 and 6.25 we obtain the total correlations $H^{AA}(l,m,n)$, $H^{AB}(l,m,n)$ and $H^{BB}(l,m,n)$. The overall 2-particle distributions $G^{IJ}(l,m,n)$ with $\{I,J\} \in \{A,B\}$ are then obtained from

$$H^{IJ}(l,m,n) = G^{IJ}(l,m,n) - 1$$

(B.8)
Appendix C

Solution method for the doubly associating fluid

The OZ-matrix, closure relations and mass balance equations, Eqs. 7.5-7.15, form a complete set that can be solved in Fourier space after the independence of the sticky sites and the pre-averaging of $f_A$ are used to write the equations in an orientation averaged form.

The 3D Fourier transformation is defined by

$$f(u, v, w) = \sum_{l,m,n} f(l, m, n) \cos lu \cos mv \cos nw \quad (C.1)$$

and the inverse transformation

$$f(l, m, n) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{f}(u, v, w) \cos lu \cos mv \cos nw \, du \, dv \, dw \quad (C.2)$$

where $f$ can be $h_{ij}$ or $c_{ij}$. Fourier-sine contributions do not have to be considered in applying the Fourier transforms to the symmetrical orientation averaged model-equations. From Eq. 7.5, we obtain after orientation averaging and Fourier transformation the nine equations

$$\hat{h}_{ij}(u, v, w) = \hat{c}_{ij}(u, v, w) + \hat{c}_{i0}(u, v, w)\sigma_2\hat{h}_{0j}(u, v, w) + \hat{c}_{i1}(u, v, w)\sigma_1\hat{h}_{0j}(u, v, w) + \hat{c}_{i2}(u, v, w)\sigma_0\hat{h}_{0j}(u, v, w) + \hat{c}_{i0}(u, v, w)\sigma_1\hat{h}_{1j}(u, v, w) + \hat{c}_{i1}(u, v, w)\sigma_0\hat{h}_{1j}(u, v, w) + \hat{c}_{i0}(u, v, w)\sigma_0\hat{h}_{2j}(u, v, w) \quad (C.3)$$

where $\{i, j\} \in \{0, 1, 2\}$. The mass balance equations, Eq. 7.13, can be rewritten as

$$C_1 = \frac{\sigma_1}{6} (a - 1) y_{00}(1, 0, 0) + \frac{\eta_0}{6} (a - 1) y_{01}(1, 0, 0)$$

$$C_2 = \frac{\sigma_1}{6} (a - 1) y_{10}(1, 0, 0) + \frac{\eta_0}{6} (a - 1) y_{11}(1, 0, 0) \quad (C.4)$$
with help of the pre-averaging in Eq. 7.15. The Eqs. C.4, 7.12 and 7.1 together constitute a self-consistency relation that regulates how \( \eta \) is divided over \( \eta_0 \), \( \eta_1 \) and \( \eta_2 \).

From the closures Eqs. 7.9-7.10, we see that the \( \hat{c}_{ij}(u, v, w) \) can be written as

\[
\begin{align*}
\hat{c}_{00}(u, v, w) &= -y_{00}(0, 0, 0) \\
\hat{c}_{01}(u, v, w) &= -y_{01}(0, 0, 0) \\
\hat{c}_{02}(u, v, w) &= -y_{02}(0, 0, 0) \\
\hat{c}_{10}(u, v, w) &= -y_{10}(0, 0, 0) \\
\hat{c}_{11}(u, v, w) &= -y_{11}(0, 0, 0) + \frac{2}{36} (a - 1) g_{00}(1, 0, 0) (\cos u + \cos v + \cos w) \\
\hat{c}_{12}(u, v, w) &= -y_{12}(0, 0, 0) + \frac{2}{36} (a - 1) g_{01}(1, 0, 0) (\cos u + \cos v + \cos w) \\
\hat{c}_{20}(u, v, w) &= -y_{20}(0, 0, 0) \\
\hat{c}_{21}(u, v, w) &= -y_{21}(0, 0, 0) + \frac{2}{36} (a - 1) g_{10}(1, 0, 0) (\cos u + \cos v + \cos w) \\
\hat{c}_{22}(u, v, w) &= -y_{22}(0, 0, 0) + \frac{2}{36} (a - 1) (g_{11}(1, 0, 0) - c_{11}(1, 0, 0)) (\cos u + \cos v + \cos w)
\end{align*}
\]

(C.5)

by Fourier transformation of the \( \hat{c}_{ij}(l, m, n) \) after writing the closures in an orientation independent form with Eq. 7.15.

Eq. 7.11 can be orientation averaged as

\[ h_{ij}(l, m, n) = g_{ij}(l, m, n) - \delta_{ij} \delta_{10} \]  

(C.6)

which gives, combined with Eq. 7.10, the non-overlap conditions

\[ h_{ij}(0, 0, 0) = -\delta_{ij} \delta_{10} \]  

(C.7)

Apart from the non-overlap conditions, we can also obtain the contact relations from Eqs. 7.9 and 7.10

\[
\begin{align*}
g_{00}(1, 0, 0) &= 36c_{11}(1, 0, 0)/(a - 1) \\
g_{10}(1, 0, 0) &= 36c_{21}(1, 0, 0)/(a - 1) \\
g_{11}(1, 0, 0) &= 36c_{22}(1, 0, 0)/(a - 1) + c_{11}(1, 0, 0)
\end{align*}
\]

(C.8)

The non-overlap conditions and the contact relations are simply a restated version of the closure relations. The contact relations are a result of the possibility of bond formation between neighboring particles. Eq. 7.8, Eqs. C.3, C.5-C.8 and the self-consistency relations Eq. 7.1, Eq. 7.12 and Eq. C.4 constitute a complete orientation averaged set of equations that can be solved for the partial correlations \( h_{ij}(l, m, n) \) for fixed overall packing fraction \( \eta \) and strength of the
interaction \( a = e^{-\beta u_{\text{attr}}} \) in the nine unknowns \( c_1 = -y_{00}(0,0,0), c_2 = -y_{10}(0,0,0), c_3 = -y_{20}(0,0,0), c_4 = -y_{11}(0,0,0), c_5 = -y_{21}(0,0,0), c_6 = -y_{22}(0,0,0), c_7 = c_{11}(1,0,0), c_8 = c_{21}(1,0,0) \) and \( c_9 = c_{22}(1,0,0) \). The symmetry relations \( y_{ij} = y_{ji} \) have been used to reduce the number of variables. The unknowns are then found from equations that are constructed by substitution of Eq. C.5 in Eq. C.3, after which the \( \hat{h}_{ij} \)'s are written explicitly in terms of the unknowns \( c_1 \) to \( c_9 \). The first six equations are constructed by inverse transformation (Eq. C.2) of the \( \hat{h}_{ij}(u,v,w) \) and applying the non-overlap conditions, Eq. C.7, to \( h_{00}(l,m,n), h_{10}(l,m,n), h_{11}(l,m,n), h_{20}(l,m,n), h_{21}(l,m,n) \) and \( h_{22}(l,m,n) \).

\[
-d_{ij} \delta_{40} = \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{h}_{ij}(u,v,w) du dv dw \quad (C.9)
\]

The last three equations are constructed by invoking the contact equations, Eq. C.8

\[
\frac{36c_7}{a-1} - 1 = \frac{1}{3} \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{h}_{00}(u,v,w) (\cos u + \cos v + \cos w) du dv dw
\]

\[
\frac{36c_8}{a-1} = \frac{1}{3} \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{h}_{10}(u,v,w) (\cos u + \cos v + \cos w) du dv dw
\]

\[
\frac{36c_9}{a-1} + c_7 = \frac{1}{3} \left( \frac{1}{2\pi} \right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{h}_{11}(u,v,w) (\cos u + \cos v + \cos w) du dv dw \quad (C.10)
\]

Once \( c_1 \) to \( c_9 \) are found from Eq. C.9 and Eq. C.10 with help of a Newton-Raphson scheme combined with a 3D integration routine, the \( h_{ij}(l,m,n) \) are obtained from Eq. C.2 for \( f = h_{ij} \). Note that only nine equations in nine unknowns must be solved with a Newton-Raphson procedure to obtain the structural correlations present in the 3D polymerizing lattice fluid.
Appendix D

Solution scheme for strongly interacting systems

For strongly interacting systems, $\sigma_0 \to 0$ and $\sigma_1 \to 0$ and the average chain length, $s \to \infty$. The numerical scheme of Appendix C does not work well in such situations, and a recombination of the $h_{ij}$ and $c_{ij}$ with the $\sigma_i$ is desired. The new variables that we have used are

$$H_0 = \begin{pmatrix} H_{00} & H_{01} & H_{02} \\ H_{10} & H_{11} & H_{12} \\ H_{20} & H_{21} & H_{22} \end{pmatrix} (1, 2) = \begin{pmatrix} h_{00} & \sigma_1 h_{01} & \sigma_1^2 h_{02} \\ \sigma_1 h_{10} & \sigma_1^2 h_{11} & \sigma_1^2 h_{12} \\ \sigma_1^2 h_{20} & \sigma_1^3 h_{21} & \sigma_1^4 h_{22} \end{pmatrix}$$ (D.1)

An identical definition is used for the elements of the direct correlation matrix $C_{ij}(1, 2)$. If definition Eq. D.1 is used, the density matrix Eq 7.7 has to be replaced in Eq. 7.5 by

$$\sigma = \begin{pmatrix} \sigma_2 & 1 & c \\ 1 & c & 0 \\ c & 0 & 0 \end{pmatrix}$$ (D.2)

with $c = \sigma_0 / \sigma_1^2$. The nine unknowns were chosen to be $c_1 = -y_{00}(0, 0, 0)$, $c_2 = -\sigma_1 y_{10}(0, 0, 0)$, $c_3 = -\sigma_1^2 y_{20}(0, 0, 0)$, $c_4 = -\sigma_1^2 y_{11}(0, 0, 0)$, $c_5 = -\sigma_1^2 y_{21}(0, 0, 0)$, $c_6 = -\sigma_1^4 y_{22}(0, 0, 0)$, $c_7 = a\sigma_1^2 g_{00}(1, 0, 0)$, $c_8 = a\sigma_1^2 g_{10}(1, 0, 0)$ and $c_9 = a\sigma_1^4 g_{11}(1, 0, 0)$. The equations that have to be solved are still given by Eqs. C.9 and C.10 if the $c_1$ to $c_9$ are correctly substituted by $c_1'$ to $c_9'$, and if the $\hat{h}_{ij}(u, v, w)$ are replaced by the $\hat{H}_{ij}(u, v, w)$. The OZ-matrix then reads

$$\hat{H}_{ij}(u, v, w) = \hat{C}_{ij}(u, v, w) + \hat{C}_{i0}(u, v, w)\sigma_2 \hat{H}_{0j}(u, v, w) + \hat{C}_{i1}(u, v, w)\hat{H}_{0j}(u, v, w) + \hat{C}_{i2}(u, v, w)\hat{H}_{0j}(u, v, w) + \hat{C}_{i0}(u, v, w)\hat{H}_{ij}(u, v, w) + \hat{C}_{i1}(u, v, w)\hat{H}_{ij}(u, v, w) + \hat{C}_{i2}(u, v, w)\hat{H}_{ij}(u, v, w) + \hat{C}_{i0}(u, v, w)\hat{H}_{2j}(u, v, w)$$ (D.3)
where \( \{i,j\} \in \{0,1,2\} \).

The \( c \) that appears in Eq. D.3 is given by

\[
\sigma_1 = \frac{1}{c} - \frac{1}{6}(1 - \frac{1}{a})c'\gamma - \frac{c}{6}(1 - \frac{1}{a})c'\delta
\]  

(D.4)

in which \( \sigma_1 \) is determined from

\[
\eta = \eta_0 + \frac{1}{6}(1 - \frac{1}{a})c'\gamma + \frac{2c}{6}(1 - \frac{1}{a})c'\delta + \\
\frac{1}{6}c^2(1 - \frac{1}{a})c'9 - \frac{1}{6}c^2\sigma^2_1(a - 1)(1 - \frac{1}{a})c'\gamma
\]

(D.5)

with \( \sigma_0 = ca^2 \). Eq. D.4 is based on \( \eta_1 = \eta_0 C_1 \) (see Eq. 7.12) with \( C_1 \) given in terms of \( (c'1 \ldots c'9) \). Eq. D.5 is based on the mass balance \( \eta = \eta_0 + \eta_1 + \eta_2 \) with \( \eta_1 \) and \( \eta_2 \) expressed in terms of \( (c'1 \ldots c'9) \) (see Eqs. 7.12 and C.4).

The numerical procedure based on Eqs. D.3-D.5 is stable for all interaction strengths that we have tested. Chains of an average length of 200 monomers could easily be formed at \( \eta = 0.5 \). We have employed this procedure for all cases that involved strong interactions ( \( |u_{\text{attr}}| \geq 5k_B T \) ) even if this is not mentioned explicitly.
Appendix E

Solution of OZ-matrix within CS-approximation

Substitution of the approximations, Eq. 7.22, for \( h_{ij} \) and \( c_{ij} \) in Eq. 7.5 gives four equations

\[
\begin{align*}
    h_{ij}(1,2) &= c_{ij}(1,2) + \frac{1}{6} \sum_{r_3,\Omega_3} (c_{i0}(1,3)\sigma_2 h_{0j}(3,2) + c_{i1}(1,3)\sigma_1 h_{0j}(3,2) + \\
    &c_{i0}(1,3)\sigma_1 h_{1j}(3,2) + c_{i1}(1,3)\sigma_0 h_{1j}(3,2))
\end{align*}
\]  

(E.1)

where \( \{i,j\} \in \{0,1\} \). The closure equation Eq. 7.9 and the exact set Eq. 7.10 are still valid, but now for \( \{i,j\} \in \{0,1\} \). The self-consistency relations are given by Eq. 7.1 and Eq. 7.12 and the approximation of Eq. 7.22 for \( C_1 \) and \( C_2 \). From the self-consistency relations it follows that

\[
\begin{align*}
    \sigma_1 &= \frac{\eta_0}{2} + \frac{1}{2} \sqrt{\eta_0^2 + 4\eta_0 (\eta - \eta_0)} \\
    a &= \frac{6\eta_1}{\eta_0\sigma_1 \eta_{00}(1,0,0)} + 1
\end{align*}
\]  

(E.2)

and

\[
\begin{align*}
    a &= \frac{6\eta_1}{\eta_0\sigma_1 \eta_{00}(1,0,0)} + 1
\end{align*}
\]  

(E.3)

with \( \eta_1 = \sigma_1 - \eta_0, \eta_2 = \eta - \eta_1 - \eta_0 \) and \( a = e^{-\beta u_{\text{attr}}} \).

Solution of the problem amounts to solving 3 equations in the unknowns \( y_{00}(0,0), y_{10}(0,0,0) = y_{01}(0,0,0) \) and \( y_{11}(0,0,0) \). The fourth variable \( y_{00}(1,0,0) \) that appears in the OZ-matrix and the closures is obtained in advance from Eq. E.3. The solution procedure of the polymer model within the Chang-Sandler approximation resembles the procedure used for particles with one directional attractive site (Ref. [31] of chapter 7), and only involves three equations in three unknowns. Once the \( y_{ij}(0,0,0) \) are known the \( h_{ij}(l,m,n) \) are found from Eq. C.2 with \( f = h_{ij} \). \( H(l,m,n) \) is obtained from

\[
\eta^2 H(l,m,n) = \eta^2 h_{00}(l,m,n) + 2\eta\sigma_1 h_{10}(l,m,n) + \sigma_1^2 h_{11}(l,m,n) 
\]  

(E.4)

\( G(l,m,n) \) follows via Eq. 7.17.
Appendix F

Biased cluster move

The biased cluster move consists of two parts. The first part is concerned with selecting a part of a chain, the cluster. In a second part of the move, the cluster is re-grown at a different position in the box via the Configurational bias scheme (Ref. [5] of chapter 7).

First we will consider the selection of a cluster. A fluid particle, which is called the central particle of the cluster, is selected at random. If the particle is not bonded to other particles it forms the cluster by itself. If the particle is part of a chain we walk along the chain (in both directions if the segment is not an end segment) to the next segment of the chain and add the segment to the cluster with probability \( p \), where \( p \) can be freely chosen (Ref. [36] of chapter 7). The procedure is repeated until the end of the chain is reached, or until a segment is rejected. This bounds the cluster in the direction under consideration. In this way we generate a cluster which is simply a part of an existing chain. In the limit of \( p \to 1 \) the cluster size and the chain size will be equal. If \( p \to 0 \) on the other hand, we will always have a cluster that contains only the central segment. After creating the cluster, we attempt to move the cluster by randomly choosing a new position on the lattice for one of the cluster ends. At the ends of the cluster, new bonds with neighboring particles can be formed, depending on the orientations of the free attractive sites of the cluster ends and the neighboring particles. A cluster can in principle form two new bonds, one at each cluster end.

The acceptance criterion for a pure cluster move, i.e., move without alteration of the cluster form, can be derived from the detailed balance condition (Refs. [6,36] of chapter 7). Imposing detailed balance gives

\[
\Pi(S_1) P(S_1, C_1) \text{ acc}(C_1 \to C_2) = \Pi(S_2) P(S_2, C_2) \text{ acc}(C_2 \to C_1)
\]  

\( \text{ (F.1) } \)

in which \( \Pi(S_1) \) is the probability of the contents of the box being in state \( S_1 \), \( P(S_1, C_1) \) is the probability of making a cluster \( C_1 \) from a chain that is part of \( S_1 \), and \( \text{acc}(C_1 \to C_2) \) is the acceptance probability for moving the cluster \( C_1 \) to a new position after which it is called cluster \( C_2 \). The probability \( P(S_i, C_i) \) is
given by (Ref. [6] of chapter 7)

\[ P(S_i, C_i) = \sum p^{l-1}(1 - p)^{b_i} \]  

where \( l \) is the number of particles in the cluster, and \( b_i \) is the number of links that were broken in state \( S_i \) in creating the cluster from the chain, \( b_i \) can thus be 0, 1 or 2. The sum is taken over all different ways of making cluster \( C_i \) from the chain. Substituting Eq. F.2 in F.1 and assuming a Boltzmann distribution gives

\[ \frac{\text{acc}(C_1 \rightarrow C_2)}{\text{acc}(C_2 \rightarrow C_1)} = \frac{((1 - p)e^{-\beta \text{u}_{\text{attr}}}b_2}{((1 - p)e^{-\beta \text{u}_{\text{attr}}}b_1} \frac{(e^{-\beta \text{u}_R})_2}{(e^{-\beta \text{u}_R})_1} \]  

The factor \( \frac{(e^{-\beta \text{u}_R})_2}{(e^{-\beta \text{u}_R})_1} \) in Eq. F.3 ensures that the \( l \) cluster particles show no overlaps with other particles. The \( \text{u}_R \) is given by Eq. 7.3. It is seen from Eq. F.3 that, in order to employ a cluster move, one simply has to multiply the Boltzmann factors \( e^{-\beta \text{u}_{\text{attr}}} \) of the bonds formed at the cluster ends by a factor \((1 - p)\). For \( p \rightarrow 0 \) we have \( l = 1 \) and the move becomes a simple brute force move.

In a pure cluster move, the conformation of the cluster is not changed during the move. In order to change the form of the clusters in such a way that they fit in the voids that are left open on the lattice we need to combine the cluster scheme with the Configurational bias MC scheme (Ref. [5] of chapter 7). The scheme consists of placing the cluster, segment by segment, on the lattice and works as follows.

First, a new position for the first segment of the cluster and an orientation for one of the two attractive sites of this segment are chosen at random. Then, the five nearest neighbor positions of this cluster-end that are still unused are scanned to check if they are empty. One of the empty lattice positions is then randomly chosen to place the next segment of the cluster on the lattice. We then grow the cluster segment by segment, by repeating the whole procedure until the last segment of the cluster is placed on the lattice. If it happens that all positions for the next segment that has to be placed on the lattice are taken, the move is rejected and the old configuration is restored. The final step of the re-growing procedure is the random choice, out of 5 positions, of the orientation of the free attractive site of the last segment of the cluster. The free attractive sites at the beginning and the end of the cluster can be oriented in such a way that bonding between the cluster and other particles occurs.

A Conformational bias move is accepted with probability (see Ref. [5] of chapter 7)

\[ \text{acc}(1 \rightarrow 2) = \min \left( 1, \frac{W(2)}{W(1)} \right) \]  

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where \( W(1) \) is the Rosenbluth weight factor. For our model \( W(1) \) is given by

\[
W(1) = e^{-\beta u_{R1}} \left( \prod_{i=2}^{l} \frac{Z_i}{5} \right) \left( e^{-\beta u_{attr}} \right)^{b_i}
\]  

(F.5)

where

\[
Z_i = \sum_{j=1}^{5} e^{-\beta u_{Ri,j}}
\]  

(F.6)

\( Z_i \) is the sum of the Boltzmann factors of segment \( i \) if placed on the five available nearest neighbor sites of segment \( i-1 \). Note that only 5 out of 6 nearest neighbor positions have to be checked because one is already taken by segment \( i-2 \) (or a free attractive cluster edge if \( i = 2 \)). The \( u_{Ri,j} \) is the repulsive potential of segment \( i \) if placed on position \( j \),

\[
\begin{align*}
    u_{Ri,j} & = \infty & \text{if position } j \text{ is taken} \\
    u_{Ri,j} & = 0 & \text{otherwise}
\end{align*}
\]  

(F.7)

For our problem \( Z_i \) simply takes one of the values \( \{0 \ldots 5\} \). Note that the move will be rejected if \( Z_i = 0 \), because in that case all neighboring sites of segment \( i-1 \) are taken. The first factor \( e^{-\beta u_{R1}} \) in \( W(1) \) assures that the first segment of the cluster is placed on an empty lattice position. The \( \prod_{i=2}^{l} Z_i/5 \) does the same for the other \( l-1 \) segments. The last term accounts for the fact that at the edges of the cluster bond formation might occur. The Rosenbluth weight factor is simply a measure for the number of ways a conformation can be constructed.

A Configurational bias move thus consists of calculating the Rosenbluth factor for the old chain conformation, determining a new conformation with the void filling procedure, calculating \( W \) for the new conformation, and accepting/rejecting the move according to Eq. F.4. In Ref. [5] of chapter 7 it is shown that this scheme generates a Boltzmann distribution of configurations.

The acceptance criterion for a biased cluster move, which combines the cluster and Conformational bias steps, can now easily be derived. From the acceptance criterion for the cluster move, Eq. F.3, we have learned that in order to apply the cluster scheme, the Boltzmann factors for the attractive interactions at the cluster ends need to be multiplied with a factor \( 1-p \), \( p \) being the probability that a bond is accepted in making the cluster. Incorporating this factor in the bias scheme leads to replacement of Eq. F.5 respectively

\[
W(1) = e^{-\beta u_{R1}} \left( \prod_{i=2}^{l} \frac{Z_i}{5} \right) \left( (1-p) e^{-\beta u_{attr}} \right)^{b_i}
\]  

(F.8)

The acceptance criterion Eq. F.4 thus remains unchanged, if Eq. F.8 is used. Hence, Eq. F.4 is the acceptance probability for a cluster move which uses the
void filling procedure.
The biased cluster move obviously consumes more CPU-time than a brute force move but the move concerns more than one monomer at the time. An advantage, when compared to the brute force move, is that the bond acceptance probability $p$ lowers the weight of the attractive strength in the acceptance criterion by multiplying $e^{-\beta u_{\text{attractive}}}$ with $(1 - p)$. This increases the acceptance probability. By adjusting $p$, it is also possible to create clusters in such a way that on average only one bond of the chain from which the cluster is created is broken. This is an extra advantage over the brute force move because most of the latter moves that are attempted in a highly polymerized fluid imply breaking of two bonds in the old configuration without forming new bonds in the new configuration. A biased cluster move then obviously has a higher acceptance probability for a move.
The biased cluster move only works for linear clusters. Nevertheless, it can sample ring-shaped molecules, because bond breakage can occur when creating a cluster. If bond breakage does not occur a ring-shaped cluster results. If such a cluster appears, it was tried to move the cluster without altering its form. Such a move was accepted if no overlap with other particles occurred.
Appendix G

Associating particles near an impenetrable wall

Here, we outline the method for obtaining the $h_i(l)$ from Eqs. 8.11-8.15 for known $h_{ij}(l, m, n)$ and $c_{ij}(l, m, n)$. Solution of Eq. 8.11 is conveniently performed in Fourier space. Therefore, we apply the 1D-Fourier transform

$$\tilde{f}(u) = \sum_l f(l) \cos lu \quad \text{(G.1)}$$

with inverse

$$f(l) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \tilde{f}(u) \cos lu \, du \quad \text{(G.2)}$$

If it is assumed that the concentration profile is the same on both sides of the wall, i.e., $h_i(+l) = h_i(-l)$, we can write Eq. 8.11 as

$$\hat{h}_i(u) = \hat{c}_i(u) + (\eta_0 \hat{h}_{i0}(u, 0, 0) + \eta_0 \hat{h}_{i1}(u, 0, 0)) \hat{c}_0(u) + \eta_0 \hat{h}_{i0}(u, 0, 0) \hat{c}_1(u) \quad \text{(G.3)}$$

where the $\hat{h}_{ij}(u, 0, 0)$ are given by 3D Fourier transform

$$\hat{f}(u, v, w) = \sum_{l, m, n} f(l, m, n) \cos lu \cos mv \cos nw \quad \text{(G.4)}$$

and

$$f(l, m, n) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \tilde{f}(u, v, w) \cos lu \cos mv \cos nw \, du \, dv \, dw \quad \text{(G.5)}$$

for $v = 0$ and $w = 0$.

The $\hat{h}_{ij}(u, 0, 0)$ in Eq. G.3 can be obtained separately from the solution of the bulk equations (see chapter 6). Once the $\hat{h}_{ij}(u, 0, 0)$ are known, a numerically simple problem in four unknowns ($c_0(0)$, $c_0(1)$, $c_1(0)$ and $c_1(1)$) results. The
unknowns are found as follows. From Eq. 8.15 and the closures, Eqs. 8.12 and 8.13, we obtain the non-overlap conditions

\[ h_i(0) = -\delta_{i0} \]  

(G.6)

and the contact relations

\[ c_i(1) = (h_i(1) + \delta_{i0})(1 - e^{\beta \omega_w}) \]  

(G.7)

Note that the partial direct correlation functions \( c_i(l) \) are only non-zero for \( l \leq 1 \). This is a direct consequence of the use of the Percus-Yevick-like closure, Eq. 8.12, and limits the number of unknowns to four. The unknowns are now directly found from equations that result from combining Eqs. G.2, G.3, G.6 and G.7

\[
\begin{align*}
-\delta_{i0} &= \frac{1}{2\pi} \int_{-\pi}^{\pi} \tilde{h}_i(u) \, du \\
\frac{c_i(1)}{1 - e^{\beta \omega_w}} - \delta_{i0} &= \frac{1}{2\pi} \int_{-\pi}^{\pi} \tilde{h}_i(u) \cos u \, du
\end{align*}
\]  

(G.8)

with \( \tilde{c}_i(u) = c_i(0) + 2c_i(1) \cos u \), according to Eq. G.1. The \( c_i(0) \) and \( c_i(1) \) are obtained from Eq. G.8 with a Newton-Raphson procedure combined with a 1D-quadrature routine. Once the unknowns are found, we obtain the \( h_i(l) \) from Eqs. G.2 and G.3 for \( f = h_i \).
Summary

In this thesis we have been concerned with the calculation of the structural properties (i.e., molecular organization) of polymeric materials, and the quantitative inference of the thermal properties, e.g., the equation of state and phase behavior, of the materials from their molecular organization. The theoretical routes chosen to establish this link between the molecular level and macroscopic material properties were based on integral equation formalisms, which have been introduced less than ten years ago in polymer science. The general objective of the work described in this thesis was therefore to explore the merits of these relatively new approaches in the statistical mechanics of polymer systems.

If a polymeric material is seen as a collection of molecules consisting of a linear sequence of spherical segments, we can attribute the molecular organization of the material to three ordering effects among the segments: covalent bonding, and (non-covalent) attractive and repulsive interactions. The repulsive segmental interactions are the most influential factor in determining the fluid structure. The packing that is caused by the repulsive interactions is comparable to the ordering that appears in a fish-tank filled with marbles. The effects of the attractive interactions and the chain-connectivity appear as perturbations on the basic "marbles in a fish-tank" structure. Despite their relative unimportance in determining the fluid structure, attractive segmental interactions and chain-connectivity are very important factors in determining the macroscopic thermal properties of a polymeric material. Therefore, it is very important to accurately include the attractive interactions and chain-connectivity in a molecular model of e.g., the phase behavior of polymeric materials.

Thus far, all integral equation studies of polymer systems have been concerned with continuum space fluids. In this thesis we investigate lattice fluids in which each polymer segment occupies exactly one lattice site. In such lattice models, which are very common in polymer science, the "marbles in a fish-tank" structure disappears. This allows to single out the subtle effects of attractive interactions and chain-connectivity. Comparisons to Monte Carlo simulations then provide us with direct answers regarding the effects of chain-connectivity and attractive interactions on the structure and the thermal properties of polymer fluids.
Another point that is addressed in this thesis is the self-consistency problem inherent in the best known polymer-integral equation theory, the polymer-RISM approach. This theory is formulated in terms of an intermolecular and an intramolecular (conformational) segmental distribution. In the approach, the intermolecular distribution is expressed in terms of the intramolecular distribution. However a relation that, in turn, expresses the intramolecular distribution in terms of the intermolecular distribution does not exist, although for flexible molecules, the intramolecular distribution certainly is a function of the intermolecular distribution. Therefore, the intramolecular distribution is not determined by the theory, but is needed as an input quantity in the theory. This absence of self-consistency is a central problem in the polymer-RISM theory. Although a consistent version of the polymer-RISM theory has been developed, we have chosen to employ a different integral equation route, which is not formulated in terms of an inter- and intramolecular distribution. This route, which was originally formulated to study associating fluids, uses directional forces between the fluid particles to click the particles into (polymer) molecules.

outline and results

In chapter 2 we have singled out the effect of (non-covalent) attractive interactions on the fluid structure by considering the monatomic 3D nearest neighbor fluid within the Ornstein-Zernike integral equation approach. Main result of the comparison to \( NpT \)-Monte Carlo (MC) simulations is that the Ornstein-Zernike formalism is able to accurately capture the effects of the attractive interactions on the fluid structure, equation of state and liquid-gas spinodal upon using the Mean Spherical Approximation. The Percus-Yevick (PY) approximation also accurately reproduces the fluid structure, but shows fundamental deficiencies in describing the thermal properties. Such deficiencies have also been reported by Baxter for the sticky sphere model, when considered within the PY-approximation. This model can be considered as the continuum space analog of the 3D nearest neighbor fluid, and the deficiencies found within the PY-approximation are therefore not lattice artifacts.

In chapters 3-5 we study a polymeric lattice model by introducing chain-connectivity on the lattice via the polymer-RISM equation. In chapter 3 we have singled out the effect of chain-connectivity on the structure and equation of state of athermal, i.e., purely repulsive, polymer molecules. By comparison to MC-simulations it is shown that the polymer-RISM theory accurately reproduces the fluid structure of such systems, but that the equation of state obtained from the approach cannot meet the comparison with conventional work on lattices. Nevertheless, the approach is interesting and it is shown that systematic improvements can be made.

In chapter 4 an extension to interacting polymer molecules is made and the equation of state and liquid-gas spinodal are studied. In this chapter we consider the
combined effects of non-covalent and covalent attractions. Comparison to MC-simulations indicates that the polymer-RISM formalism is not yet able to account for non-covalent attractive interactions. Both the structural and thermal properties show large deviations from the simulation results, and an extreme sensitivity of the outcome of the calculations on the exact form of the intramolecular distribution is found.

In chapter 5 the polymer-RISM approach is extended to calculate the adsorption of an interacting polymeric fluid at an impenetrable wall. The adsorption profiles are compared to the Scheutjens-Fleer (SF) theory and to MC-simulations. Thus far, the profiles calculated from the integral equation approach cannot meet the comparison with the SF-theory, but since the SF-theory is relatively complex and certainly not perfect, and since it is shown that there is room for large improvements in the polymer-RISM based approach, it seems useful to further investigate the approach of chapter 5.

The line of work considered in chapter 6-8 is based on the associating fluid integral equation theory of Wertheim. The basic formalism does not use an inter- and intramolecular distribution, and therefore, it is internally consistent. In chapter 6 we calculate the structural correlations in an associating lattice fluid of particles that can covalently bind into dimers. Comparison to MC-simulations shows a nearly quantitative agreement. It is also shown that by considering mixtures of two types of particles, the overall particle distribution (the overall structure) can be divided in an inter- and intramolecular part.

In chapter 7 the approach is extended to a lattice fluid of polymerizing particles. Comparison of the structural properties of the model to MC-simulations reveals that the approximations involved in solving the integral equations governing the model have to be improved. In chapter 8 we have studied the dimerizing and polymerizing lattice fluids near an impenetrable wall. Comparison to adsorption profiles obtained from MC-simulations again illustrates that the theory is nearly perfect for the dimerizing fluid, but that the polymerizing fluid theory needs improvement. The MC-simulations for the polymerizing fluid of chapters 7 and 8 use a new biased cluster move that is based on the Conformational bias scheme of Siepmann and Frenkel. The move has the additional advantage that it samples the average chain length in the polymerizing fluid.

Generally, we conclude that integral equation modelling of polymeric systems has not yet been developed far enough to provide quantitative results that are of general use to polymer scientists. This does not mean however that the approaches are without value for people working in the molecular modelling-field: when compared to cell and lattice theories, that are commonly used in molecular based modelling of polymeric systems, integral equations do provide us with a lot of insight on the relation between the molecular and macroscopic level of polymer systems. Also, for low molecular weight compounds, i.e., \( Cl_2, N_2 \) and \( CO_2 \), favor-
able comparisons of calculated to experimentally obtained structures have been made, and in the future, despite the complex nature of polymeric systems, such might also be the case for polymers, if the integral equations and accompanying closures can be improved far enough to take chain-connectivity and non-covalent attractive interactions into account more accurately than to date.
Samenvatting

Een gesmolten plastic (polymere smelt) is een viskeuze vloeistof, die bestaat uit extreem lange, draadvormige en flexibele moleculen.

In het onderzoek beschreven in dit proefschrift zijn met behulp van klassieke statistische mechanica relaties gelegd tussen enerzijds de moleculaire organisatie van zo'n polymere smelt (de manier waarop de moleculen gerangschikt zijn in de vloeistof), en anderzijds de thermodynamische, macroscopische eigenschappen die door zo'n moleculaire organisatie bepaald worden. De interesse ging vooral uit naar de manier waarop de toestandsvergelijking (dat is de relatie tussen druk, temperatuur en volume van een hoeveelheid stof) en het fasengedrag (denk aan het koken van water of aan de ontmenging die optreedt in olie/water systemen) bepaald worden door de moleculaire organisatie van de polymere smelt.

Ter bestudering van het hierboven beschreven probleem zijn twee roostermodellen ontwikkeld, die gebruik maken van integraalvergelijkingen die een sterke verwantschap tonen met de Ornstein-Zernike vergelijking. Zulke theorieën worden sinds eind jaren '50 gebruikt in de vloeistof-natuurkunde voor de berekening van de structuur van vloeistoffen van kleine, niet of nauwelijks flexibele moleculen als $N_2$, $Cl_2$ en $CO_2$. In de polymerchemie, waar we te maken hebben met veel complexere zeer lange en flexibele moleculen, zijn zulke theorieën minder dan tien jaar geleden geïntroduceerd, en zijn er nog nauwelijks kwantitatieve voor-spellingen met betrekking tot de structuur en macroscopische eigenschappen van polymere materialen gedaan. Om meer inzicht te krijgen in de mogelijkheden van integraal vergelijkingen binnen de polymerchemie hebben wij ze toegepast op polymere rooster vloeistoffen. Zulke vloeistoffen zijn zeer veel bestudeerd in de polymerchemie, en bieden de mogelijkheid om behaalde resultaten met andere aanpakken te vergelijken.

Het eerste model van de polymere vloeistof dat is gebruikt bestaat uit een collectie van kralenkettingen (polymeer moleculen), allen van dezelfde lengte, op een rooster. Elke kraal (de chemische eenheid waaruit elk polymeermolecuul is opgebouwd) neemt een roosterhokje in beslag (Fig. I). Het tweede model bestaat uit afzonderlijke kralen die met kralen op naburige roosterhokjes kunnen binden, zodat er een mengsel van kettingen van verschillende lengte ontstaat (Fig. II). Naburige kralen binden indien de orientatie-afhankelijke bindingskrachten (de
Figure I: Roostermodel I: Weergegeven is een polymere smelt van moleculen die elk uit vijf segmenten bestaan.

Figure II: Roostermodel II: Een condensatie polymerisatie product.
zwarte spots in Fig. II) die aanwezig zijn op de kralen in elkaars richting wijzen. Dit model lijkt zeer sterk op het product van een, in de polymeerchemie bekende, condensatie polymerisatie. Van beide modellen konden aan de hand van de spatiële correlaties (structuur) tussen de kralen, de toestandsvergelijking en het fasengedrag uitgerekend worden. Tevens zijn de beide modellen intensief getest met Monte Carlo simulaties en vergeleken met andere roostertheorieën.

Het beschreven onderzoek was er op gericht meer inzicht te krijgen in de relaties tussen het moleculaire en macroscopisch thermodynamische gedrag van een polymere smelt, en heeft willen bijdragen aan de verdere ontwikkeling van moleculaire modellen van polymere systemen. Het belangrijkste resultaat dat geboekt is, is dat de veel bestudeerde roostermodellen voor het eerst met behulp van integraalvergelijkingen beschreven zijn.
Curriculum Vitae

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