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Deutschsprachiger Abstract

Wir haben ein effektives Modell für die Beschreibung von semiflexiblen Ring Polymeren entwickelt. In dieser Theorie werden die Ringe als weiche Scheiben modelliert, wobei die Wechselwirkung durch ein Potential gegeben ist, welches das gegenseitige Überlappen der effektiven Teilchen erlaubt. Wir zeigen, dass dieses Modell in der Lage ist interessante Strukturbildungen von semiflexiblen Ringen zu beschreiben, welche in einem effektiven Modell mit isotropen Wechselwirkungen verlorengehen würden. Um die Formierung von Säulen aus Ring Polymeren zu charakterisieren, haben wir einen Algorithmus eingeführt, der zylinderförmige Anordnungen von Ringen erkennt. Wir haben weiters bidisperse Mischungen von Ringpolymeren untersucht und Dichtefunktionaltheorie angewandt, um vorherzusagen wie sich Ringe in der Nähe von harten Wänden anordnen. Außerdem haben wir Simulationen von geknoteten Polymerketten durchgeführt, um zu analysieren, warum sich ein Knoten auf einem Polymer mit inhomogener Steifigkeit mit der größten Wahrscheinlichkeit in einem Bereich der Kette aufhält, der eine nicht verschwindende Biegesteifigkeit aufweist. Durch Einführung einer zweidimensionalen räumlichen Einschränkung oder durch Simulation komplexerer Knotentypen, kann die Wahrscheinlichkeit dafür erhöht werden, dass der Knoten den optimalen Steifigkeitsbereich aufsucht. Räumliche Einschränkung kann die optimale Rigidität auch zu niedrigeren Werten verschieben.

Abstract

An anisotropic effective pair potential for the effective description of semiflexible ring polymers is derived. In this new coarse-graining strategy the rings are pictured as soft, penetrable disks. We demonstrate that the new model correctly describes interesting structure formation of short and intermediate-length rings, which cannot be captured by an effective pair potential between the rings' centers of mass. To characterize the stack formation observed in the monomer-resolved and the effective model we employ an algorithm which identifies tube-like structures of ring polymers. We investigate bidisperse mixtures of ring polymers and apply density functional theory to predict the ordering of rings close to hard walls. In addition we carried out computer simulations of knotted polymers to analyze the knot localization probability on a polymer chain with varying flexibility. The knot prefers a regime on the polymer chain with non-zero rigidity. By increasing the knot complexity and introducing a 2D confinement the reduction in $\Delta F_{\text{knotting}}$ for a chain with optimal stiffness relative to the flexible chain can be enhanced. The confinement can also shift the optimal stiffness towards lower values.

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Contents

1	Introduction	6
2	An Anisotropic Effective Model for the Simulation of Semiflexible Ring Polymers	13
2.1	Introduction	14
2.2	Anisotropic Effective Model	17
2.3	Simulation Details	21
2.4	The Anisotropic Effective Potential	24
2.5	Monte Carlo Simulations of the Anisotropic Effective Model	30
2.6	Truncation of the Expansion of the Anisotropic Potential	39
2.7	Conclusions	39
3	Anisotropic Effective Interactions and Stack Formation in Mixtures of Semiflexible Ring Polymers	41
3.1	Introduction	42
3.2	Model and Simulation Details	45
3.3	Algorithm for the Identification of Stacks	46
3.4	Derivation of the Effective Potentials	48
3.5	Formation of Stacks in Monodisperse Systems	49
3.6	Effective Model for Binary Mixtures	55
3.7	Correlation functions in binary mixtures	57
3.8	Formation of Stacks in Binary Mixtures	63
3.9	Conclusions	68
4	Density Functional Theory for Isotropic and Anisotropic effective models of Semiflexible Ring Polymers in the bulk and under confinement	71
4.1	Introduction	71
4.2	Density Functional Theory for the Isotropic Effective System in the Bulk	72
4.3	Density Functional Theory for the Anisotropic Effective System in the Bulk	73
4.4	System of Effective Particles in Confined Geometries	79
4.5	Conclusions	94
5	Influence of Rigidity and Knot Complexity on the Knotting of Confined Polymers	98
5.1	Introduction	99
5.2	Model and simulation details	100

5.3	Definition and interpretation of Observables	101
5.4	Analysis of the local bending in the knotted domain	102
5.5	Results	103
5.6	Conclusions	111
6	Conclusions and Outlook	112
A	Calculation of the Anisotropic Effective Potential	114
B	Expansion of the anisotropic pair-correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$	116
C	Density Functional Theory Framework For Isotropic and Anisotropic Models	120
C.1	Self consistent equations for the pair correlation function in a system of identical particles	120
C.1.1	Prerequisites from Density Functional Theory	121
C.1.2	The Ornstein-Zernike Equation	123
C.1.3	The Percus Idea	125
C.1.4	The Hypernetted-Chain and the Percus-Yevick closures	126
C.1.5	Self Consistent Equation from Mean Field Theory	127
C.1.6	Thermodynamic Inconsistency	128
C.1.7	Numerical solution of the self consistent equations	129
C.2	Self consistent equations for the pair correlation function in the anisotropic system	132
C.2.1	A system with multiple types of particles	133
C.2.2	A system with an anisotropic interaction potential	135
C.2.3	Numerical solution of the self consistent equations for the system with anisotropic interactions	136
C.3	Self consistent equations for the density distribution function in the presence of one or between two walls	138

1 Introduction

Soft matter Physics is the science of systems which contain constituents that are at a length scale of nanometers (nm) to micrometers (μm). These supramolecular aggregates can be dissolved in a solvent consisting of much smaller, usually atomic, entities. As suggested by the word *soft*, an important feature of these systems is that the energies required to break apart structures in soft-matter systems are typically much smaller than in atomic ones, which is a consequence of the mesoscopic length-scale of the macromolecules that form these structures [1]. For instance, typical atomic crystals, like a diamond built from carbon atoms, have a lattice constant of several tenths of nm . In soft matter science one investigates crystals built from colloids [2], which correspond to spherical macro-particles with a diameter of several hundred nm , like silicon spheres which can crystallize into the well-known gem opal. Thus the lattice constant in colloidal crystals is around 3 orders of magnitude larger than the one of diamond. If the average number of bindings per lattice site in the two crystals is similar, the average number of bindings per volume is around 9 orders of magnitude smaller in colloidal than in atomic crystals. The strengths of the bindings in colloidal and atomic crystals, on the other hand, is typically of the same order of magnitude and therefore crystals in the field of soft matter science are usually much easier to break, i.e. *softer*, than their atomic counterparts. Also for other states of matter the typical binding energy per volume in systems built from macromolecules is much smaller than in atomic ones, rendering the former systems indeed *softer*. Soft matter materials are therefore easily deformed by external forces, as well as thermal fluctuations at room temperature, which is thus the temperature scale where many interesting phase transitions take place.

One of the founding fathers of Soft Matter science is the French physicist Pierre-Gilles de Gennes, who received the Nobel Price in Physics in 1991 "*for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers*" [3]. In his Nobel lecture (http://www.nobelprize.org/nobel_prizes/physics/laureates/1991/gennes-lecture.pdf) he presents many beautiful examples from the rich world of soft matter, which comprises the aforementioned colloids, but also polymers, granular materials, liquid crystals, foams and gels. One of the examples he talks about is the *vulcanisation* of natural rubber: By drying milky latex extracted from a rubber tree in the open air the oxygen builds bridges between the initially independent polymer chains and the liquid latex becomes a network structure, which is able to resist tension. The big change in the structure of latex is a consequence of very mild chemical reactions, which is again a

typical feature of soft matter systems.

Colloidal suspensions are particularly ubiquitous in our daily life and include milk, mayonnaise, ice cream, gelatin, ink, smoke, fog, as well as countless other examples. The most famous of all macromolecules, the DNA chain, is a polymer and therefore also the scope of soft matter research; Enzymes, which catalyze almost all metabolic processes in the cell, are polymers of amino acids; Blood is yet another example for a colloidal suspension. In fact, Soft Matter systems are also omnipresent in biology, which is almost entirely made up of *living* soft matter.

A problem one faces in the physical description of soft matter systems is that they typically involve vastly different time and length scales. For instance the size difference between the atomic solvent and the dissolved macromolecules is usually huge. It would be unpractical to describe the solvent at the atomic level, since one then had to simulate millions of solvent particles for every macromolecule. On the other hand, it is also completely wrong to ignore the influence of the solvent particles. One can easily understand this by considering two suction cups, which would never attract without the influence of the air, which in this example corresponds to the *solvent* of the suction cups. A modern and efficient approach to deal with this problem is the method of coarse-graining, where one describes the macromolecules in an effective model that does not include the solvent-, but only the macro-particles as explicit degrees of freedom. In such a model the solvent is not neglected, but implicitly taken into account by suitably chosen effective interactions between the large molecules. Simulations in the effective model are computationally much more efficient because, first, one needs to simulate less particles and in addition one can typically increase the time step by many orders of magnitude since the remaining degrees of freedom change much slower in time than the small solvent particles. Naturally, it is also easier to do analytical work for the effective description than for the underlying microscopic model and the important physical features are usually more transparent in the effective model, which allows for a better intuitive understanding of the most important Physics in the system.

The coarse-graining approach has the additional advantage that very different models can map to the same effective description. This means one can sometimes discover *universality* between microscopically different models, which only becomes transparent if one looks at the coarse-grained description of the systems and thus cuts away the obfuscating details. This is for instance of great importance in the theory of long polymer chains, where one can obtain a coarse-grained description by representing several successive molecules on the chain by single monomeric units. If one considers very long polymer chains (in the absence of long range interactions) and chooses monomeric units that en-

compass many molecules, one eventually ends up with a simple model of monomeric units that interact exclusively via excluded volume interactions [4]. In modern textbooks on polymer physics [5] the authors discuss this simple model (which is nevertheless highly non-trivial to solve) in great detail and obtain universal laws applicable to many different microscopic polymer chain models. One can take this approach even further by coarse-graining the coarse-grained model, which again results in a model with excluded volume interactions but with a different volume parameter. In the case of an infinitely long polymer chain this additional coarse-graining step corresponds to a scaling transformation. The fact that the parameters of the theory change means that the model is not scale-invariant. The renormalization-group equations are differential equations, which describe how the parameters of a model change under such a scaling transformation. The property that the coarse-graining only changes the parameters of the model, but not the model itself, is known as *self-similarity* of the model. The scaling laws for long polymer chains are a direct consequence of the self-similarity of their effective-description and they are only explainable in the effective description, where the obfuscating details are cut away.

Another example applicable in soft-matter science, where universality and self-similarity are crucial, is the theory of phase transitions. The reason that toy models, like the Ising model, are capable to make quantitative predictions about the critical exponents of certain classes of *real* Ferro magnets, is that their effective description turns out to be the same as the coarse-grained model for these Ferro magnets close to the critical point[6, 7]. In the theory of critical phenomena the critical exponents correspond to the exponents in the scaling laws of polymer chains.

The question of creating an appropriate effective description for a given microscopic model can also be reversed. There are many interesting (toy) models, with rich and novel phase behavior, which are not realized as systems of atomic particles in nature. However, in soft-matter systems one has ample options to tune the effective interaction between macro-particles, for instance by changing the properties of the solvent, or the constituents of the macromolecules. Therefore soft-matter science offers a versatile toolbox to realize interesting models. For instance spherical particles with ultra-soft interactions, that allow for two particles to overlap, are distinctively different to atomic particles, where an overlap is always excluded. In Ref. [8] it has been shown that a large class of ultra-soft, isotropic interaction potentials allows for the formation of cluster-crystals, which differ in many interesting ways from ordinary solids [9]. Unlike in ordinary crystals several particles can sit at the same lattice site on top of each other and by compressing a cluster crystal one can change its volume as well as its occupation number per lattice site, while the lattice constant remains invariant. In addition the particles in the cluster crystal can hop

between the lattice sites. While atomic particles themselves will not form cluster crystals, since their interaction potentials are hard, one can search for soft-matter systems with macromolecules that have an effective description which falls in the class of models that allows for the formation of this fascinating state of matter. In Ref. [10] Lenz *et al.* have studied dendrimers, which are a special type of branched polymers. They have shown that a coarse-grained description of the dendrimers falls into the class of models which forms cluster-crystals. Moreover, they have shown in monomer-resolved simulations of the dendrimers that they indeed form cluster-crystals [11].

In this work we will look at systems of semiflexible ring polymers. An effective model where these macromolecules are described as point particles also predicts the formation of cluster-crystals. However, at higher densities this isotropic effective description deviates significantly from the monomer-resolved results. We show that the effective description can be improved by taking into account the anisotropic shape of the semiflexible ring polymers. In this novel effective model the ring polymers are described as disk-like particles, which interact via a potential that depends on the relative orientation of the disks. We demonstrate that for the short- and intermediate-length rings the new model captures the Physics of the ring polymers in a quantitative fashion. Therefore, our effective model provides an efficient scheme for the coarse-graining of semiflexible ring polymers, which thus constitute a realistic class of systems for which anisotropic, ultrasoft and penetrable interactions are physically meaningful.

While the semiflexible ring polymers do not form cluster crystals they nevertheless show very interesting behavior at high densities, where they form a so-called cluster glass [12, 13]. This is an arrested-state that also contains some of the features found in the cluster crystal. In this phase the rings form long stacks, which we have detected in both the monomer-resolved as well as the anisotropic effective model by employing an algorithm which is able to identify tube-like structures. As in the cluster crystal phase the overall structure of the system is frozen, while individual particles can still hop between the stacks found in the cluster glass[12]. In figure 1.1 we show a snapshot of a bidisperse mixture of semiflexible ring-polymers at high densities, where stacks are colored.

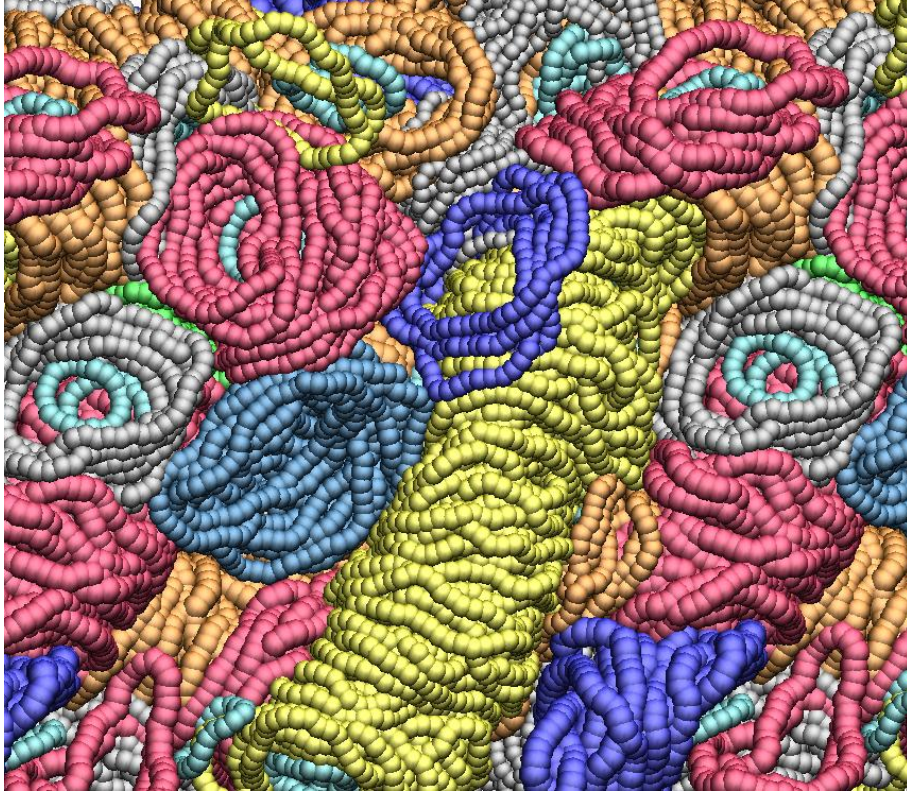


Figure 1.1: Binary mixtures of semiflexible ring polymers form stacks at high densities.

The effective model also predicts interesting behavior for the rings in the vicinity of a wall and between two walls. To investigate this we apply density functional theory for the anisotropic effective model of the semiflexible ring polymers, which predicts that disks close to the wall orient with their surfaces parallel to the wall at intermediate densities, before they re-orient themselves orthogonal to the wall at higher densities. We also observe this behavior in Monte Carlo simulations of the effective system. Moreover, mean field theory of the effective model predicts that rings assemble into layers at high densities, where the orientation of their surfaces in different layers alternates between standing orthogonal and parallel to the wall. While the predictions of mean field theory are quantitatively incorrect the layering is at least to some extent reproduced in Monte Carlo simulations, as can be seen in figure 1.2 which shows a snapshot of a Monte Carlo simulation between two walls.

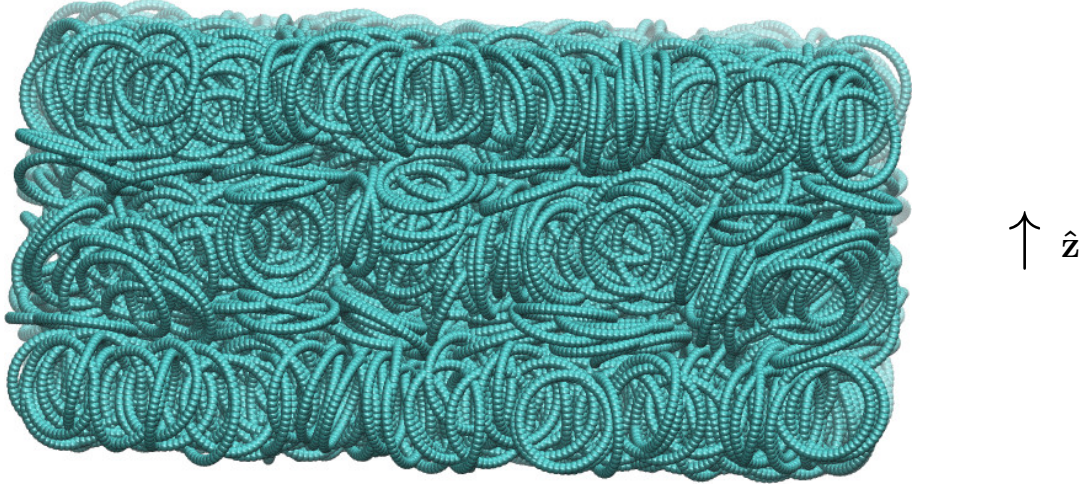


Figure 1.2: Snapshot of a Monte Carlo simulation of the effective system between two walls, which are orthogonal to the vector $\hat{z}$.

Another unique aspect of long, linear macromolecules is their ability to assume different topologies, which has interesting implications in biology, where knots can have significant effects on key processes [14, 15, 16]. The existence of the type II topoisomerase enzymes, which regulate the knotting on DNA chains, is well established [17]. Furthermore, there is evidence that rigidity may depend sensitively on the base sequence [18, 19, 20], which leads to varying flexibility along the DNA chain. We investigate the localization probability of a knot on a long polymer with varying flexibility on different stiffness domains along the chain. In figure 1.3 we show a snapshot of a simulation of a polymer under tension, where the detected knot is colored in red.

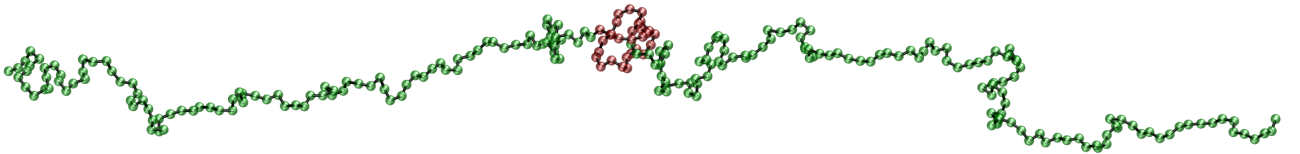


Figure 1.3: Snapshot of a simulation of a polymer chain under tension, where the detected knot is colored in red.

The thesis is organized as follows:

- In chapter 2 we introduce our effective model for the description of semiflexible ring polymers and test its predictions against large scale simulations of the monomer resolved model.

- Chapter 3 presents an analysis of cluster formation in effective, as well as monomer resolved simulations of ring polymers. To simulate bidisperse systems of ring polymers we extend our effective model for the description of ring-polymer mixtures.
- In chapter 4 we deduce an effective ring-wall interaction from the simulation of a monomer resolved ring polymer in the vicinity of a wall. We then proceed to employ density functional theory to make predictions for the anisotropic effective model in the bulk and in the presence of walls. In addition we carry out Monte Carlo simulations between walls to validate the theoretical computations.
- In Chapter 5 we present results from simulations of a knotted polymer under tension and confinement to investigate how the localization probability of a knot depends on the varying stiffness along the chain.

2 An Anisotropic Effective Model for the Simulation of Semiflexible Ring Polymers

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*We derive and introduce anisotropic effective pair potentials to coarse-grain solutions of semiflexible rings polymers of various lengths. The system has been recently investigated by means of full monomer-resolved computer simulations, revealing a host of unusual features and structure formation, which, however, cannot be captured by a rotationally-averaged effective pair potential between the rings' centers of mass [M. Bernabei et al., Soft Matter **9**, 1287 (2013)]. Our new coarse-graining strategy is to picture each ring as a soft, penetrable disc. We demonstrate that for the short- and intermediate-length rings the new model is quite capable of capturing the Physics in a quantitative fashion, whereas for the largest rings, which resemble flexible ones, it fails at high densities. Our work opens the way for the physical justification of general, anisotropic penetrable interaction potentials.*

2.1 Introduction

By the simple process of joining the ends of a linear polymer chain, one obtains a ring polymer (RP)[21]. While the architecture of ring polymers is very simple, they differ in many interesting ways from their linear counterparts and are the subject of active research in Physics, Biology, Chemistry and even pure Mathematics. One interesting consequence is that for a dynamics that disallows strand crossing, there are different classes of configurations of a RP, which can never transform into each other. These are referred to as the *topology classes* or *knot types* of a RP. Knot theory is a fascinating and active branch of mathematics with many open problems concerning the enumeration and classification of knots[22]. A RP that has the topology of a circle is called an *unknotted* RP.

Unlike RPs, linear polymer chains can strictly speaking never be knotted, as every configuration of a linear polymer chain can be continuously transformed to a straight line, without the need for strand crossings. While this is a fundamental difference between linear polymer chains and RPs, it is nevertheless possible to extend the concept of knots to *physical* knots on linear polymer chains[23]. There are many works dealing with the properties of these *physical* knots on linear polymer chains[24, 25, 26, 27, 28, 29, 30, 31], in particular due to their relevance in Biophysics, where they are for instance found in DNA[32, 33] and can have significant effects on key processes[34, 15, 16].

The topological constraint of a ring polymer has important consequences for its physical behavior. It took the work of many authors[35, 36, 37, 38, 39, 40, 41, 42] to establish that the diameter of gyration D_g of an isolated ideal RP with fixed topology scales as $\langle D_g^2 \rangle \sim N^{2\nu}$, where $\nu \approx 0.588$ is the Flory exponent, which also describes the scaling behavior of the radius of gyration of self-avoiding linear chains[43]. This is true for all knot types, even for an ideal unknotted RP (i.e., without monomer excluded volume interactions, just keeping the topological constraints). An ideal linear polymer chain, on the other hand, remains more compact and exhibits the scaling law of a non-self-avoiding random walk $\langle D_g^2 \rangle \sim N$. Another important difference lies in the effective potential between the centers of mass of RPs. While the effective potential vanishes between infinitely thin linear polymer chains and also between an infinitely thin linear polymer chain and a RP, there remains a nonzero repulsive contribution between cyclic polymers with fixed topology[44, 45]. Here one usually speaks of a topological potential. Furthermore, it was shown that the effective potential between two moderately sized RPs increases with the knot complexity of the rings[45].

Also for concentrated systems, the topology of polymer chains plays an important role. The scaling of linear polymer chains in the melt is the one of a non-self-avoiding random

walk $\langle D_g^2 \rangle \sim N$. Simulations of dense systems of RPs[46, 47] on the other hand showed that while short chains also exhibit a Gaussian scaling behavior $\langle D_g^2 \rangle \sim N$, long chains are compact and thus scale as $\langle D_g^2 \rangle \sim N^{2/3}$. In between there is a broad crossover region, where a $\langle D_g^2 \rangle \sim N^{4/5}$ scaling provides a good description of the data. For the dynamics, it is expected that concatenations of ring polymers can have a significant effect, as they are permanent, in contrast to the entanglement of linear polymer chains. However, this implies that those concatenations are there in the first place, i.e., from the very synthesis of the sample on. Even in the absence of concatenations, there are important differences in the dynamics of RPs in the melt with respect to their linear counterparts. For instance recent experiments[48] and simulations[49] revealed a power-law stress relaxation instead of the rubbery plateau found for linear chains.

For the large intermediate density domain between dilute solutions and melts, there are relatively few theoretical results despite the practical relevance of this regime for instance in the field of biophysics, where the topological interactions between chromatin loops plays a crucial role in the creation of chromosome territories[44, 50, 51, 52]. A fruitful and modern approach for the economic description and simulation of macromolecules in this regime is the method of coarse-graining. The idea behind this method is to bridge the time and length scales in the system by describing the macromolecules via an effective model with a reduced set of suitably-chosen effective degrees of freedom (d.o.f.). The microscopic information of the monomer-resolved model is underlying the effective model, as it determines the form of the effective potential, which describes the interaction between the macromolecules. The advantage of this method is not only that every timestep in a simulation requires less computational effort due to the simplified representation, but also that one can often choose a much larger timestep in a simulation of the coarse grained model, as the d.o.f. that remain in the coarse-grained model change much slower in time than their counterparts in the monomer-resolved model[1, 53].

The method of coarse-graining is well-established and has for instance found successful application for polymer chains[54, 55, 56], star polymers[57, 58, 59, 60], star-shaped polyelectrolytes[61, 62], dendrimers[63, 64, 65], and block copolymers[66, 67, 68]. The identification of the relevant degrees of freedom is an essential part in the design of an effective model. One often uses isotropic effective models, where the macromolecules consisting of many individual monomers are reduced to their center of mass. For the semiflexible ring polymers such a model has already been investigated in ref.[69]. Clustering was observed in monomer-resolved simulations of semiflexible ring polymers, as well as in the corresponding isotropic effective model. However, it was also shown that the monomer-resolved system shows anisotropic features that can not be accounted for in

the isotropic effective model. Also the correlation functions stemming from the isotropic effective model are markedly different from the microscopically derived ones. Anisotropy is particularly strong for rings with high bending stiffness or few monomers, as they have a strong tendency to orient with respect to other rings in their proximity. This motivates us to introduce an anisotropic effective model for the description of semiflexible ring polymers in this article. In this model, we will define the effective particles as soft disc-like molecules which are described not only by their center of mass but also by the direction in which their faces are oriented. An anisotropic effective model was already used successfully for the description of hard disc-like macromolecules[70], but to the best of our knowledge this approach was up to now never applied to penetrable macromolecules, where the centers of mass of the macro-particles can coincide. Penetrable particles are particularly interesting as they allow for clustering, which often leads to a rich phase behavior. For instance, point-particles interacting with a certain class of ultrasoft potentials form so-called cluster crystals[9, 10, 11]. Unlike in an ordinary crystal multiple soft particles can sit on top of each other at the same lattice site in a cluster crystal. Another peculiar feature of this state of matter is that by compressing it one only changes the occupation number of particles per lattice site, while the lattice constant remains invariant. Monomer-resolved simulations of semiflexible ring polymers on the other hand show the formation of the cluster glass phase[13, 12], which is an arrested-state that also contains some of the features found in the cluster crystal phase. In both cases the overall structure of the system is frozen, while individual particles can hop between the lattice sites of the cluster crystal or the stacks found in the cluster glass. Elongated dendrimers, which unlike hard rod-like particles exhibit local antinematic order[71], are another interesting example for a system of penetrable particles, which behaves distinctively different to its solid counterpart. By creating an anisotropic effective model for the semiflexible ring polymers, we aim at a model that is still computationally cheap, and that improves the description obtained by the isotropic model, especially for the case of high densities. In addition, the analysis of the interactions in the anisotropic effective potential allows us to get a better understanding for the interaction between the anisotropic, penetrable nanoparticles in systems of semiflexible RPs.

The remainder of this article is structured as follows. In Section 2.2 we first present the Hamiltonian of the monomer-resolved model which we use for the description of semi-flexible RPs and then introduce an anisotropic effective model for such a system. In Section A we give more details about the derivation of the effective interactions for such a model. We carried out Molecular Dynamics simulations of the monomer-resolved model and Monte Carlo simulations of the effective models; details concerning these simulations

are given in Section 2.3. In Section 2.4 we present the anisotropic effective potential and discuss its features. Results of Monte Carlo simulations with this potential, which show that the inclusion of anisotropy in the effective model can significantly improve the agreement with the monomer-resolved model, are presented in Section 2.5, whereas in Section 2.6 we briefly discuss the effects of truncation of the expansion of the potential on the quality of the results. Conclusions are given in Section 2.7. In the Appendix, we explain the expansion of the anisotropic pair-correlation function of a system of two RPs, which contains all the information for calculating the effective potential, as a sum of suitably chosen basis functions.

2.2 Anisotropic Effective Model

Monomer-resolved Model for Semiflexible Ring Polymers

The derivation of the anisotropic effective model is based on a microscopic model of semiflexible ring polymers, each consisting of N monomers. They are described with the bead-spring model by Kremer and Grest[72] and an additional rigidity term. Thus, any two-monomers interact via the truncated and shifted Lennard-Jones potential

$$V_{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & \text{if } r < 2^{1/6}\sigma; \\ 0 & \text{if } r \geq 2^{1/6}\sigma. \end{cases} \quad (2.1)$$

This potential is purely repulsive, accounting then for monomer excluded volume interactions. Bonded monomers also interact through a finitely extensible non-linear elastic potential (FENE)

$$V_{\text{FENE}}(r) = -\frac{kR_0^2}{2} \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right]. \quad (2.2)$$

Rigidity is introduced via the bending potential

$$V_{\text{bend}}(\theta) = \kappa(1 - \cos \theta)^2, \quad (2.3)$$

where θ is the angle between two consecutive bond vectors.*. The potential V_{bend} vanishes for $\theta = 0$, when the polymer chain does not bend at the respective angle. We choose $\epsilon = k_B T$, $k = 30k_B T/\sigma^2$, $R_0 = 1.5\sigma$ and $\kappa = 30k_B T$, where k_B is the Boltzmann constant and T the temperature. These are precisely the parameters employed in the simulation study of ref. [69]. The corresponding dynamics does not allow for chain crossings and thus topology is preserved.

*Note that this is not the Kratky-Porod model (linear in the cosine). We expect the same qualitative results for Kratky-Porod rings with the same N 's and persistence lengths as the model simulated here"

In ref.[12] the characteristic ratio[5] of this polymer model was estimated by carrying out simulations of isolated linear chains. Excluded volume interactions were switched off except for mutually connected monomers, in order to obtain long-range Gaussian statistics. C_∞ was obtained by analyzing the long- s limit of the ratio $\langle R^2(s) \rangle / s \langle b^2 \rangle$, where $R(s)$ is the distance between two monomers i, j with $s = |i - j|$, and b is the bond length ($\langle b^2 \rangle = 0.94$). The authors reported a value of $C_\infty \sim 15$, which is typical for stiff polymers[5]. We can give an estimate for the persistence length of the model by mapping it to the freely rotating chain model using the relation $\cos \theta = \frac{C_\infty - 1}{C_\infty + 1} \sim 0.875$, where θ is the bending angle of the freely rotating chain model[5]. The persistence length is then obtained as $s_p b = -b / \ln(\cos \theta) \sim 7.3$. We carried out simulations of ring polymers with $N = 20, 50$, and 100 monomers, which have the contour to persistence length ratio $N/s_p \sim 2.7, 6.7$ and 13.3 respectively.

The Anisotropic Effective Model

In earlier work[69], Bernabei *et al.* carried out extensive monomer-resolved simulations of stiff ring polymers to obtain the structure of concentrated solutions of the same. In an attempt to coarse-grain the system in the simplest possible way, they also derived and employed an isotropic effective potential for their effective description, reducing thereby stiff RP's into point-like effective particles, namely their centers of mass. At this level of approximation, the effective particles possess no other, internal (spin-like) degrees of freedom and thus the effective interaction is isotropic. The effective potential between these macro-particles was defined by calculating the pair correlation function $g^{\text{iso}}(r)$ in an infinitely dilute system and using

$$\beta V_{\text{eff}}^{\text{iso}}(r) \equiv -\ln [g^{\text{iso}}(r)] \quad (2.4)$$

to define the effective interaction potential between these point particles, where $\beta = 1/(k_B T)$. In the infinitely dilute case, the distribution of the centers of mass of the ring polymers in equilibrium is identical to the distribution of the point particles in the effective model. At higher densities, however, it turns out that multi-particle terms in the effective potential are necessary to obtain the correct equilibrium distribution of the centers of mass in the effective model. One of the reasons due to which multi-particle interactions become important is that two ring polymers that are sufficiently close and stiff, will prefer to align parallel to each other. A third ring polymer interacting with those two will not see them as two independent rings but as a system of two rings that are correlated. When using the potential $V_{\text{eff}}(r)$ calculated in Eq. (2.4) one assumes that the free energy penalty of one ring with respect to a second is independent of the presence

of another polymer in the vicinity of the second. If the ring polymers preferentially align parallel, this assumption is clearly violated and one has to correct the effective potential by introducing multi-particle terms. Bernabei *et al.* showed that already at moderate densities one can encounter strong correlations of the orientations of the semiflexible ring polymers, in particular if the chains contain only few monomers (e.g., $N = 20$)[69]. Therefore, a more accurate coarse-graining which takes into account the ring anisotropy is called for.

The easiest way to incorporate the correlations of the orientations of rings is to introduce them via additional degrees of freedom (d.o.f.) in the effective description. This is precisely what we do in this article. For this purpose, we need to first come up with a suitable definition for the orientation of a RP. To this end, we make use of the gyration tensor

$$S_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N r_{\alpha}^{(i)} r_{\beta}^{(i)}, \quad (2.5)$$

where $r_{\alpha}^{(i)}$ ($\alpha = x, y, z$, Cartesian components) denotes the position of the i -th monomer with respect to the center of mass of the ring to which this monomer belongs. The eigenvectors of $S_{\alpha\beta}$ are the principal axes of an ellipsoid that approximates the shape of the macromolecule: If a RP is flat, which means that all its monomers lie in one plane, the ellipsoid has one zero eigenvalue with a corresponding eigenvector that is perpendicular to that plane. Also in the more general case, where the monomers do not all lie in the same plane, we define the normalized eigenvector corresponding to the smallest eigenvalue of $S_{\alpha\beta}$ as the direction vector $\mathbf{d}$ of the RP. Note that $\mathbf{d}$ and $-\mathbf{d}$ are equivalent for reasons of symmetry. The ring polymers in the anisotropic effective model we propose are described via the position vectors of their centers of mass, $\mathbf{R}^{(i)}$, and their direction vector $\mathbf{d}^{(i)}$. Henceforth, we describe the stiff rings as soft circular discs and ignore differences in the other 2 eigenvectors of the gyration tensor $S_{\alpha\beta}$. This choice is motivated by the limit of infinite bending stiffness, where the rings assume flat and precisely circular conformations. Our model, therefore, amounts to the *minimal* anisotropic extension of the spherically symmetric effective interaction between the centers of mass. We emphasize, however, that there is no a priori guarantee that this will be an improvement over the isotropic model at finite densities and in particular at high concentrations: this depends on the degree in which the RP's at high concentration maintain their anisotropic shape and properties encoded in the high-dilution limit in which the anisotropic pair potential is derived. Accordingly, the introduction of such a potential is not a straightforward part of a systematic strategy of introducing more and more detail into the effective description of the system.

In order to determine the anisotropic effective potential V_{eff} , we carried out monomer-resolved simulations of two ring polymers inside a large simulation box. The effective pair potential is then defined such that it exactly reproduces the correlation functions of the effective degrees of freedom in this infinitely dilute, monomer-resolved simulation. In the effective model, two ring polymers are described by a total of 10 degrees of freedom, three for each center of mass and two for each direction vector of each ring polymer. However, due to translation, rotation and mirror symmetry the distinct configurations (those that cannot be related by symmetry transformations) of a system with two effective particles are reduced and can be specified by 4 parameters only.

A convenient choice for these variables is illustrated in figure 2.1 and reads as follows:

$$\begin{aligned} r &\equiv |\mathbf{r}|; \\ \cos \theta_1 &\equiv \mathbf{d}^{(1)} \cdot \hat{\mathbf{r}}; \\ \cos \theta_2 &\equiv \mathbf{d}^{(2)} \cdot \hat{\mathbf{r}}; \\ \varphi &\equiv \arccos \left(\frac{\mathbf{d}_{\perp}^{(1)} \cdot \mathbf{d}_{\perp}^{(2)}}{|\mathbf{d}_{\perp}^{(1)}| |\mathbf{d}_{\perp}^{(2)}|} \right), \end{aligned} \quad (2.6)$$

where $\mathbf{r} \equiv \mathbf{R}^{(2)} - \mathbf{R}^{(1)}$ is the connection vector between the centers of mass of the two rings, $\hat{\mathbf{r}} \equiv \mathbf{r}/r$ the unit vector in the direction of $\mathbf{r}$ and $\mathbf{d}_{\perp}^{(i)}$ the component of the director $\mathbf{d}^{(i)}$ perpendicular to $\mathbf{r}$; $0 \leq \varphi \leq \pi$ denotes the angle between vectors $\mathbf{d}_{\perp}^{(1)}$ and $\mathbf{d}_{\perp}^{(2)}$. By selecting the appropriate sign of $\mathbf{d}^{(i)}$ we can always choose $\cos \theta_i$ to lie in the interval $[0, 1]$.

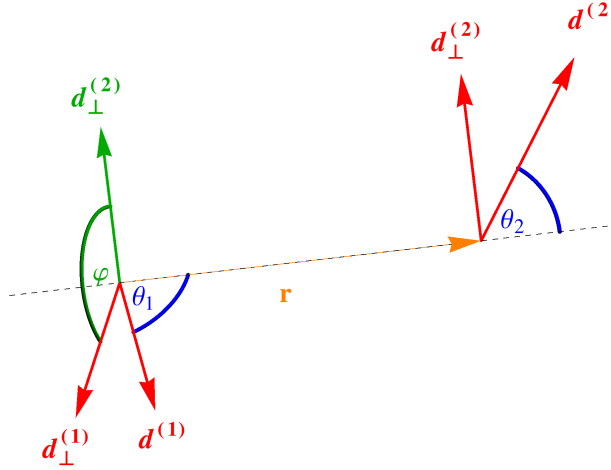


Figure 2.1: Illustration of the effective variables $r = |\mathbf{r}|$, θ_i and φ with which relative configurations of ring polymers are described.

Let us define the ideal case as the system where the effective particles do not inter-

act and thus every orientation and position of the effective particles occurs with equal probability, independently of the configuration of the other effective particle. With the effective coordinates defined in (2.6) the probability density in the ideal system, $P_{\text{id}}(r, \cos \theta_1, \cos \theta_2, \varphi)$ is proportional to r^2 and constant in both $\cos \theta_i$ as well as in φ . This simple behavior of $P_{\text{id}}(r, \cos \theta_1, \cos \theta_2, \varphi)$, makes (2.6) a particularly convenient choice of the effective coordinates. In the simulations with two ring polymers, we obtain a probability density $P(r, \cos \theta_1, \cos \theta_2, \varphi)$ that is different from the ideal distribution P_{id} . We define as a generalised version of the radial distribution function the anisotropic pair correlation function as

$$g(r, \cos \theta_1, \cos \theta_2, \varphi) = \frac{P(r, \cos \theta_1, \cos \theta_2, \varphi)}{P_{\text{id}}(r, \cos \theta_1, \cos \theta_2, \varphi)}. \quad (2.7)$$

Thus, the quantity $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ describes the factor by which configurations in the effective anisotropic model have to be enhanced or suppressed with respect to the ideal case, in order to obtain a distribution for the effective d.o.f. that is identical to the distribution obtained in a monomer-resolved simulation in the infinitely dilute case. As in the isotropic case (2.4) the relation to the associated effective potential reads

$$\beta V_{\text{eff}}(r, \cos \theta_1, \cos \theta_2, \varphi) = -\ln[g(r, \cos \theta_1, \cos \theta_2, \varphi)]. \quad (2.8)$$

From the anisotropic effective potential, we can deduce the isotropic pair-correlation function via

$$g^{\text{iso}}(r) = \frac{1}{\pi} \int_0^1 d \cos \theta_1 \int_0^1 d \cos \theta_2 \int_0^\pi d \varphi g(r, \cos \theta_1, \cos \theta_2, \varphi). \quad (2.9)$$

The associated isotropic effective potential is then given by (2.4).

The effective potential between two identical ring polymers remains invariant if we swap the orientations of their respective director with respect to the connection vector, i.e., if we swap the values of the polar angles θ_1 and θ_2 of the two rings:

$$V_{\text{eff}}(r, \cos \theta_1, \cos \theta_2, \varphi) = V_{\text{eff}}(r, \cos \theta_2, \cos \theta_1, \varphi). \quad (2.10)$$

This symmetry is violated for the effective potential between bidisperse ring polymers, e.g. for ring polymers with a different number of monomers. However, apart from this symmetry, there would be no differences in the procedure of calculating the effective potential between different types of ring polymers.

2.3 Simulation Details

Derivation of the effective interaction

To determine the effective potential, we carry out constant NVT molecular dynamics

simulations with two ring polymers. We simulate rings of $N = 20, 50$ and 100 monomers. For these simulations we use the LAMMPS simulation package[73]. The polymer rings are placed in a simulation box, which is large enough to prevent multiple interactions via the periodic boundary conditions. The temperature in the simulation is maintained by the use of Langevin-Dynamics. The corresponding equations of motion read as[74]:

$$m\ddot{\mathbf{r}}_i(t) = \mathbf{F}_i(t) - \gamma m\dot{\mathbf{r}}_i(t) + \boldsymbol{\eta}_i(t). \quad (2.11)$$

Here, $\mathbf{r}_i$ is the position of the i -th monomer, m its mass and $\mathbf{F}_i(t)$ the deterministic force acting on it, which includes the microscopic forces originating from potentials (2.1-2.3) and the force originating from a biasing potential. The bias potential $V_{\text{bias}} = (r - r_j)^2 k_j/2$ introduces a harmonic spring with spring constant k_j between the centers of mass of the ring polymers. The spring is relaxed for $r = r_j$. We carried out simulations for different values of r_j , starting at $r_j = 0$ and increasing it up to some maximum value r_C in steps of $\sigma/2$. For $N = 20, 50, 100$, r_C was chosen as $10\sigma, 20\sigma, 30\sigma$ respectively. These values for r_c are much bigger than the infinite-dilution diameters of gyration ($D_{g0} = 5.9\sigma, 13\sigma, 21.5\sigma$ for $N = 20, 50, 100$ respectively). For k_j we chose the values $2.5\epsilon/\sigma^2$ and ϵ/σ^2 for all ring sizes and for $N = 20$ we also carried out simulations with $k_j = 5\epsilon/\sigma^2$. The quantity $\boldsymbol{\eta}_i(t)$ is a random force, with $\langle \boldsymbol{\eta}_i(t) \rangle = 0$, which is related to the friction coefficient γ by the fluctuation dissipation relation $\langle \eta_i^\alpha(t) \eta_j^\beta(t') \rangle = 2\gamma m k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$, α and β denoting Cartesian components. Our unit of time is set by $t_0 = (m\sigma^2/\epsilon)^{1/2}$ and the friction coefficient γ is chosen as $1/t_0$. We integrate the equations of motion with a timestep of $\Delta t = 10^{-3}t_0$, and use 2×10^8 timesteps for equilibrating the system and collect data during another 2×10^9 timesteps.

We sample histograms $P^{(j)}(Q)$, where Q refers to a bin in the 4D space of the effective coordinates. $P^{(j)}(Q)$ gives the probability for a state in the j -th simulation to have effective coordinates in bin Q . The histograms have 128 bins in r and 16 bins in $\cos \theta_1$, $\cos \theta_2$ and φ direction. As discussed in appendix A we use the *Self-Consistent Histogram Method* by Ferrenberg and Swendsen[75, 76] to combine the $P^{(j)}(Q)$ histograms for simulations with identical ring sizes but different biasing potentials to arrive at an estimate for $P(Q)$ in the unbiased system.

Many-body effective fluid

Using the anisotropic effective potential we carry out standard Metropolis Monte Carlo (MC) simulations for the anisotropic effective model. The values of the anisotropic effective potential have been calculated on a discrete grid in the $(r, \cos \theta_1, \cos \theta_2, \varphi)$ space and we use linear interpolation to estimate the values of $\exp(-\beta V_{\text{eff}})$ in between the grid

points. Having in mind a comparison with both the monomer-resolved simulation results and the isotropic effective potential of ref.[69], we choose the same number of particles and effective densities that were used in those simulations. For rings with $N = 20, 50$ and 100 monomers we simulate systems of $n = 2400, 1600$ and 1200 rings, respectively, varying in each case accordingly the cubic box size L as to achieve the desired density $\rho = n/L^3$. As the effective potential V_{eff} is bounded, a random distribution of the particles in the simulation box can be used as initial condition. We have implemented two types of MC moves: the first one translates a randomly chosen particle in a random direction, and the second randomly rotates the particle's director by some angle. The distance by which the particles are displaced and the angle by which they are rotated is randomly selected in an interval starting at 0 and going up to some maximum value. For both moves, this maximum value of the interval is chosen such that the acceptance ratio is approximately 15%. We use 9×10^6 MC moves to equilibrate the system. During this equilibration period the individual soft particles diffuse to several times their own diameter. Afterwards, during 15×10^6 MC moves equilibrium configurations are generated. We store the configurations every 20×10^3 moves and use them to compute the physical observables that are presented in the section 2.5.

The gain in computational efficiency for the simulations in going from a monomer resolved to a coarse grained simulation is considerably. The relevant quantity to consider here, would be the velocity through phase-space. This can conveniently be characterized by means of the mean square displacement of the rings per unit of CPU time. If one ignores the detailed implementation aspects, the CPU time spend on a single sweep over all monomers in the former and a run over all effective ring particles in the latter, which strictly speaking depend on both the number of monomers N per ring and the overall density of rings, are of similar magnitude. However, the diffusion per sweep in the coarse grained simulation is significantly larger than that for the monomer resolved simulation, i.e., for the case of $N = 50$ and $\rho^* = 20$ this results in a factor of approximately 10^4 . The reason for this dramatic improvement is two-fold. First of all the translation/rotation of an effective ring corresponds to a much more time-consuming collective movement of the constituents. The second even more important contribution arises from the steric interaction that are present in the monomer resolved simulations and prevent the unphysical crossing of chain segments. In the coarse grained simulations such a restriction is absent, i.e., the effective rings are penetrable and can move apparently through each other. On this level of description this effect is not an unphysical process, but should be interpreted as a short-cut connecting initial and final configurations that are connected by a much more time-consuming and physically realizable pathway of folding and collective

monomer movements.

2.4 The Anisotropic Effective Potential

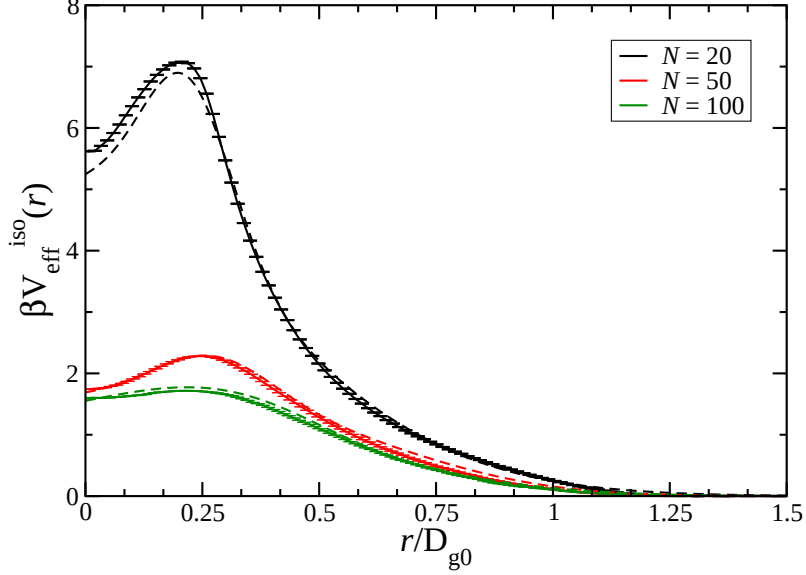


Figure 2.2: The effective, center-of-mass pair potential in the isotropic effective model for rings with different numbers of monomers N . The center-of-mass separation r is scaled with D_{g0} , the average diameter of gyration of a free ring polymer. The solid line shows the angularly-averaged effective pair potential, while the dashed lines are results of ref. [69].

We commence by recalculating the *isotropic*, i.e., angularly-average effective pair potential $V_{\text{eff}}^{\text{iso}}(r)$ between the stiff rings, as a way of comparison with the previously derived results in ref. [69]. Results are summarized in figure 2.2, reproducing indeed the previously derived ones[69]. The potential for $r = 0$ is finite, as the rings are allowed to overlap. It also features a local minimum there, whereas its maximum is located at $r \approx 0.25D_{g0}$ for all ring types investigated. Here, D_{g0} is the average diameter of gyration of a free ring polymer. The height of the potential barrier at small distances of r decreases by increasing the number of monomers N on the ring polymers.

Going over to the anisotropic effective model, we proceed with computing the aforementioned pair correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ for a system of two ring polymers. As the latter depends on 4 effective coordinates and is therefore difficult to visualize, we

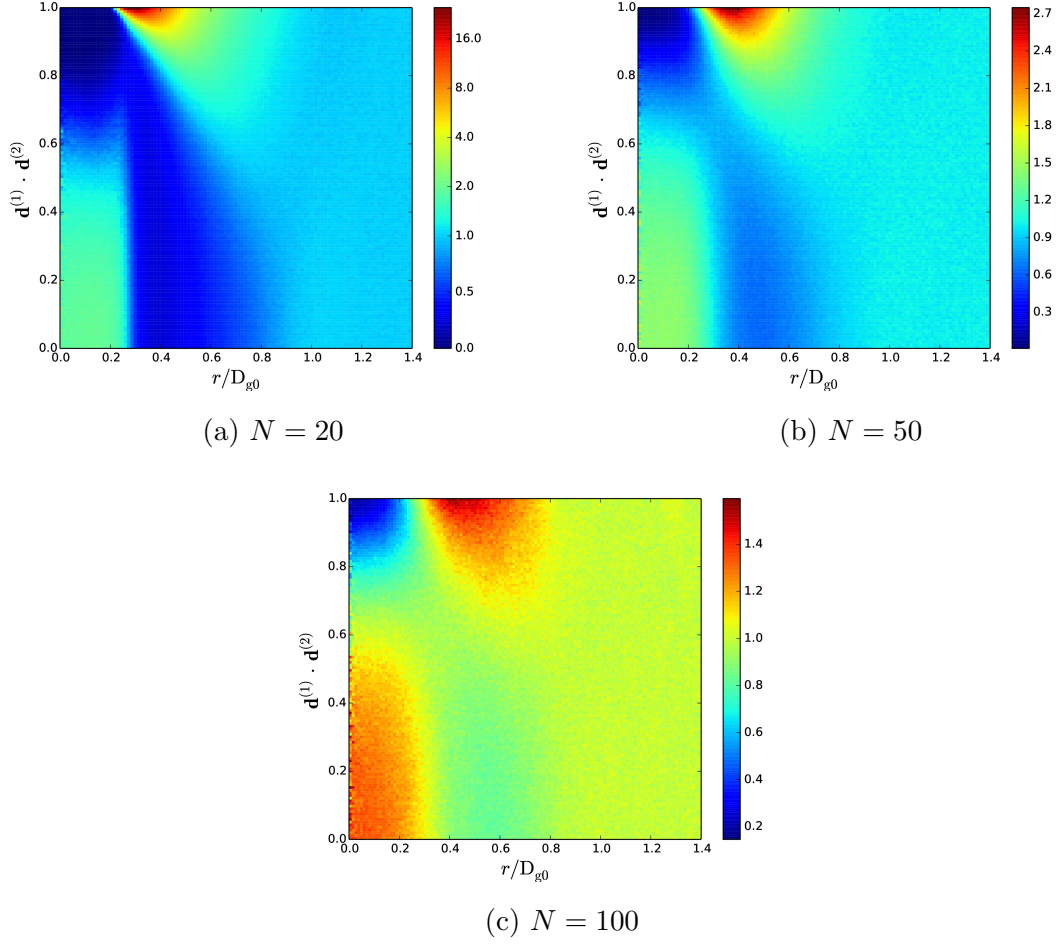


Figure 2.3: Infinite-dilution limit of the quantity $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$, which quantifies the distribution of the scalar product between directors for different values of r . We visualize this distribution for the ring sizes $N = 20$, $N = 50$ and $N = 100$.

first introduce a reduced pair correlation function $g(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$, which expresses the relative joint probability density of observing the two ring polymers at a distance r and with the directors mutually oriented at the value given by their scalar product, $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$, over the same quantity for noninteractive rings. Moreover, we introduce a reduced version of this function, $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$, by dividing over its isotropic counterpart, i.e.,

$$G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}) = \frac{g(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})}{g^{\text{iso}}(r)}. \quad (2.12)$$

Results are summarized in figure 2.3. One can see that the angular distribution of the directors changes significantly for $r \approx 0.25D_{g0}$, which is approximately the position of the maximum of $V_{\text{eff}}^{\text{iso}}(r)$. For $r < 0.25D_{g0}$ the angle between the directors is biased towards $\pi/2$, while for $0.25D_{g0} < r < D_{g0}$ they prefer to align parallel with respect to each other. The position of the maximum of $V_{\text{eff}}^{\text{iso}}(r)$ coincides approximately with the distance r where interpenetrated configurations of the rings become sub-dominant and where they are more likely to align parallel to each other. The transition between these two domains is particularly steep for $N = 20$ and becomes smoother for rings with a larger number of monomers. When the rings interpenetrate each other, the distribution of angles between the directors is rather wide, while it gets narrow after the transition where the bias towards parallel alignments of the rings is very strong in particular for the smallest rings with $N = 20$. It is readily visible from figure 2.3 that anisotropy is particularly important for smaller rings. For $r > D_{g0}$, the distribution of the angle between the directors becomes flat, as the rings are then well separated and hence do not interact. Note that by definition, Eq. (2.12), the quantity $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ is a normalized probability distribution for *fixed* r , and in figure 2.3 it is therefore meaningless to compare the plotted function at different r values.

The relative orientation between the vectors $\mathbf{r}$, $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ is of course not completely determined by the scalar product $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$; the function $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ contains less information than the full correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$. In particular, when the directors are parallel, i.e., $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)} = 1$, the angle between the connection vector $\mathbf{r}$ and the directors $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ is still arbitrary. We denote a configuration with $\mathbf{d}^{(1)} \parallel \mathbf{d}^{(2)} \parallel \mathbf{r}$ as $--$ and a configuration with $\mathbf{d}^{(1)} \parallel \mathbf{d}^{(2)} \perp \mathbf{r}$ as $||$. From the reduced pair correlation function $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ alone, we cannot say which of these two configurations is more probable, as the scalar product $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$ is identical to 1 in both cases. Using the full anisotropic pair correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ we can compare the corresponding effective potentials:

$$\begin{aligned} \beta V_{--}(r) &= -\ln [g(r, \cos \theta_1 = 1, \cos \theta_2 = 1, \varphi)] \\ \beta V_{||}(r) &= -\ln [g(r, \cos \theta_1 = 0, \cos \theta_2 = 0, \varphi = 0)]. \end{aligned} \quad (2.13)$$

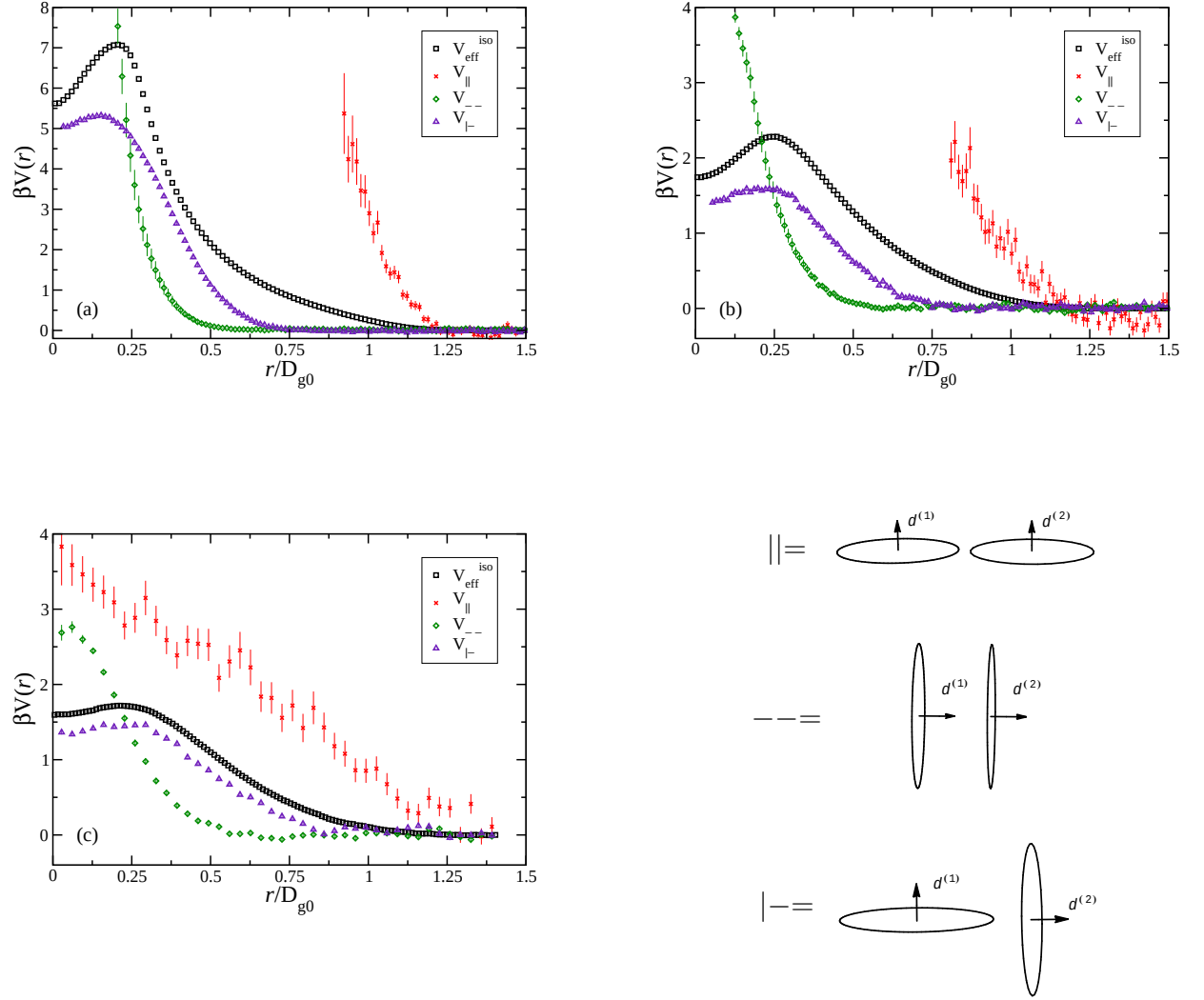


Figure 2.4: The effective potential for three different, fixed configurations of the directors and the connecting vector. As a comparison we also plot the pair potential in the isotropic effective model. (a) $N = 20$; (b) $N = 50$; (c) $N = 100$. The effective potentials are shown only for r values for which we have relatively good statistics. We also show a sketch of the $||$, $--$ and $|-$ configurations.

For the $--$ case the value of the φ coordinate is immaterial. However, due to the finite bin size of the grid on which we have calculated $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ the choice of φ makes a small difference, even for $V_{--}(r)$. We compute $V_{--}(r)$ from the average of $g(r, \cos \theta_1 = 1, \cos \theta_2 = 1, \varphi)$ in φ .

In figure 2.4 we see that $V_{||}(r)$ increases significantly when r approaches D_{g0} , while V_{--} stays close to 0 until much smaller distances r . We can understand this results if we imagine the rings as discs with diameter D_{g0} . In the $||$ configuration, the rings lie in the same plane and will therefore start to overlap as soon as $r \leq D_{g0}$. Since the rings are not perfect circles and their shape fluctuates, they can feel each other also for distances r which are slightly larger than D_{g0} . In the $--$ configuration two discs overlap only if the distance between their centers of mass is smaller than their thickness. These results tell us that the peak in the reduced pair correlation function $g(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ for $r \approx 0.25D_{g0}$ and $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)} \approx 1$ is mostly due to $--$ like configurations. However, as soon as the rings can overlap in $--$ type configurations the effective potential increases very fast for smaller r and we come to a regime where other configurations of the directors are more favorable. As a comparison we also consider a configuration with $\mathbf{d}^{(1)} \perp \mathbf{d}^{(2)} \parallel \mathbf{r}$, which we denote by $|-$. The corresponding effective potential is given by

$$\beta V_{|-}(r) = -\ln [g(r, \cos \theta_1 = 0, \cos \theta_2 = 1, \varphi)]. \quad (2.14)$$

As in the $--$ case, the value of the φ coordinate is irrelevant for calculating $V_{|-}(r)$, which we compute from the arithmetic mean of $g(r, \cos \theta_1 = 0, \cos \theta_2 = 1, \varphi)$ in φ .

For small distances r one ring interpenetrates the other in microscopic configurations of type $|-$. While $V_{|-}(r)$ starts to increase at larger r values than $V_{--}(r)$, the increase is slower and converges to a constant for $r \rightarrow 0$. This is intuitive to understand since it requires only a finite amount of bending energy to deform two rings such that one can fit into the other. The required bending energy is smaller if the rings are larger. The $|-$ becomes dominant over the $--$ configuration at an r value below the threshold $r \approx 0.25D_{g0}$. This is also the r value at which we find the transition in the reduced pair correlation function $g(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ between a regime where configurations with parallel directors, as in $--$, are preferred, to a regime where they are suppressed and other configurations like $|-$ become dominant.

In the Appendix we explain how one can expand the angular part of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ into a series of suitably chosen basis functions $f_{l_1, l_2, m}(\cos \theta_1, \cos \theta_2, \varphi)$. The expression for this expansion is given in Eq. (B.7) and the corresponding coefficients $c_{l_1, l_2, m}(r)$ can be determined by calculating particular ensemble averages as shown in Eq. (B.10). We plot these coefficients $c_{l_1, l_2, m}(r)$ for $l_1, l_2 \leq 2$ in figure 2.5. From the fast change of

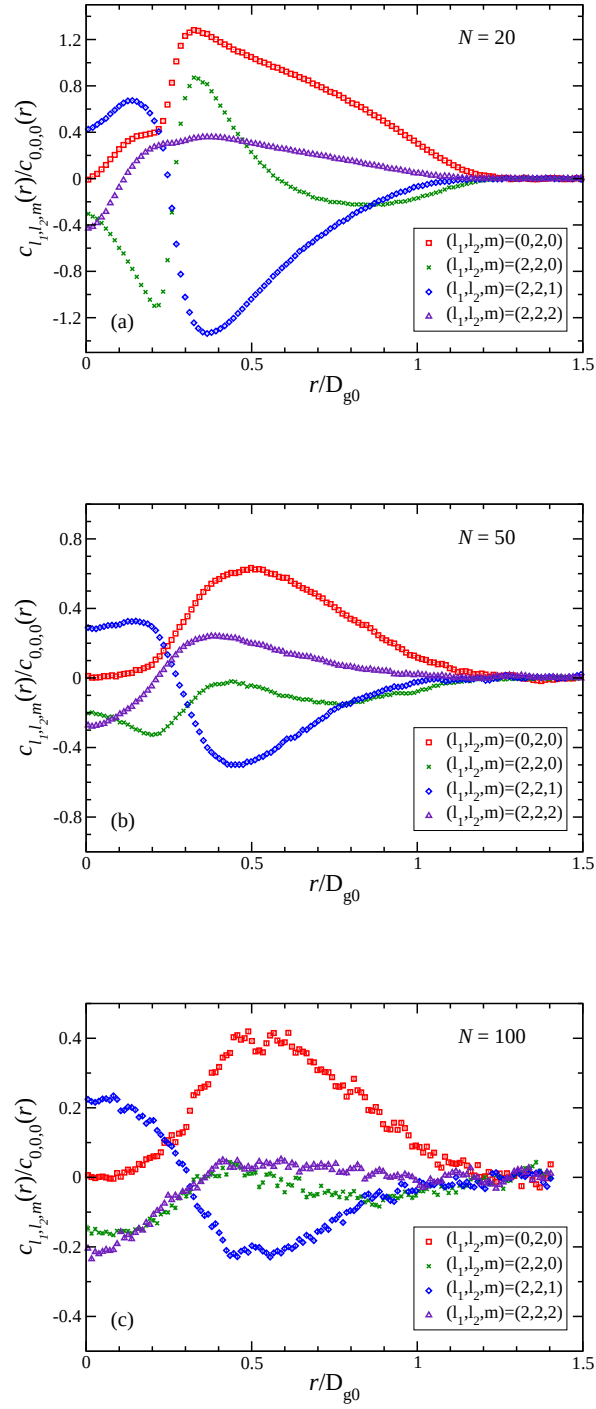


Figure 2.5: The first coefficients in the expansion of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ divided by the coefficient $c_{0,0,0}(r)$. (a) $N = 20$; (b) $N = 50$; (c) $N = 100$.

$c_{l_1, l_2, m}(r)$ for $r \approx 0.25D_{g0}$ one can once more see the transition between two regimes for r in which the distribution of the directors of the ring polymers is very different. We can again see that this transition is smoother for larger rings. The magnitude of coefficients $c_{l_1, l_2, m}(r)/c_{0,0,0}(r)$ with $(l_1, l_2) \neq (0, 0)$ tells us about the significance of the corresponding anisotropy in $g(r, \cos \theta_1, \cos \theta_2, \varphi)$. Anisotropy is more important for smaller rings and becomes more pronounced after the transition at $r \approx 0.25D_{g0}$, where the rings prefer parallel configurations.

2.5 Monte Carlo Simulations of the Anisotropic Effective Model

We carried out Monte Carlo simulations of systems of effective particles described by the anisotropic effective model for different ring sizes N and various densities. We define the reduced density in our simulation as $\rho^* \equiv nD_{g0}^3/L^3$, where n is the number of rings in the sample. In order to assess the quality of the anisotropic effective model, we compare our results to results of full monomer-resolved simulations from ref. [69] and the results of simulations using the isotropic effective model. As we can see in figure 2.6 for all choices of the number of monomers N the effective models are in good agreement with the full monomer-resolved simulations at low densities ρ^* . This is an important consistency check for the effective models, in which the interactions have been chosen such that the distribution of the effective degrees of freedom agrees with their distribution in the full monomer-resolved simulations, in the limit of small densities.

In figure 2.7, we present results for the smallest rings with $N = 20$ monomers at higher densities. There is a dramatic improvement of the accuracy as one compares the isotropic with the anisotropic model. While the former fails for $\rho^* > 2$ the anisotropic effective model works up to $\rho^* \cong 5$ and even gives a semi-quantitatively correct description of the system at $\rho^* = 5.97$. At the highest densities, we see the development of a peak in $g(r)$ at $r \cong 0.3D_{g0}$. This peak in the pair correlation function is associated with the emergence of stacks of parallel rings and its position describes the typical distance of rings in these stacks[69]. Interestingly, the isotropic effective potential has a *maximum* for $r \approx 0.25D_{g0}$ which is close to the typical distance of the rings in the stacks and one could wonder why the rings prefer to align at a distance which seems to have a very high free energy penalty according to the isotropic effective potential. The answer to this apparent paradox lies in the strongly peaked nature of the anisotropic effective interaction, which we could observe in figures 2.3, 2.4 and 2.5. While the average configuration of the angular degrees of freedom at distances $r \approx 0.3D_{g0}$ has a high free energy penalty, a certain class of configurations, where the directors of the rings are almost parallel, is much more favorable. Obviously, stacking can not be observed in the isotropic effective

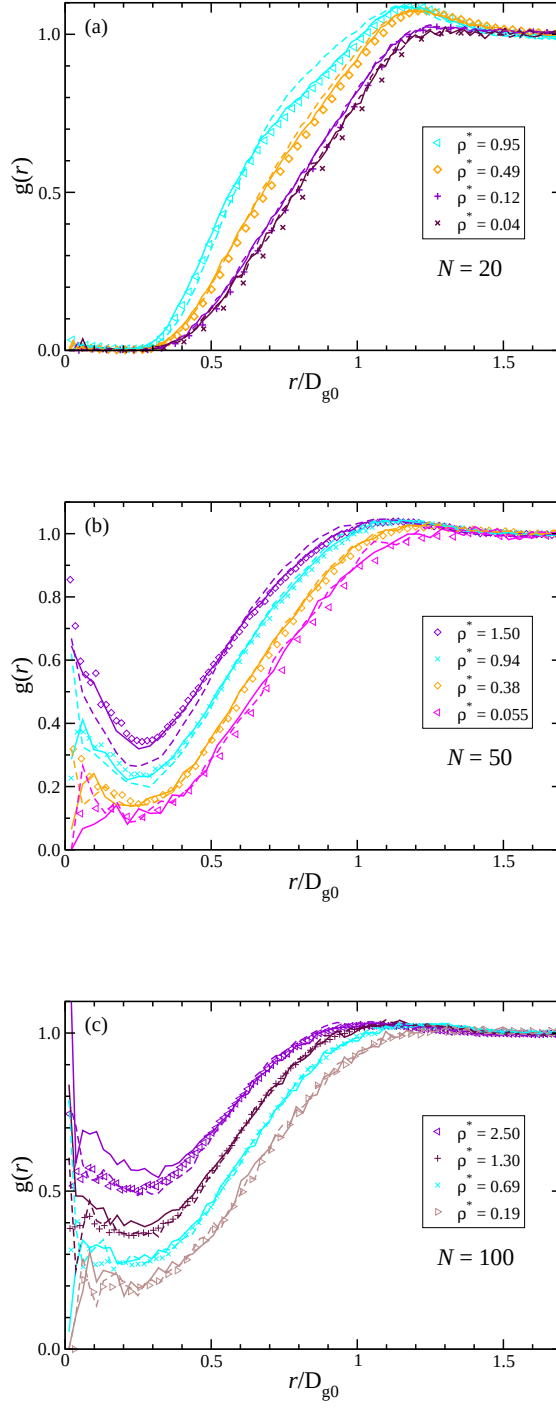


Figure 2.6: The pair correlation function $g(r)$ at low reduced densities ρ^* for a simulation of many ring polymers in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid line) and the isotropic effective model (dashed line).

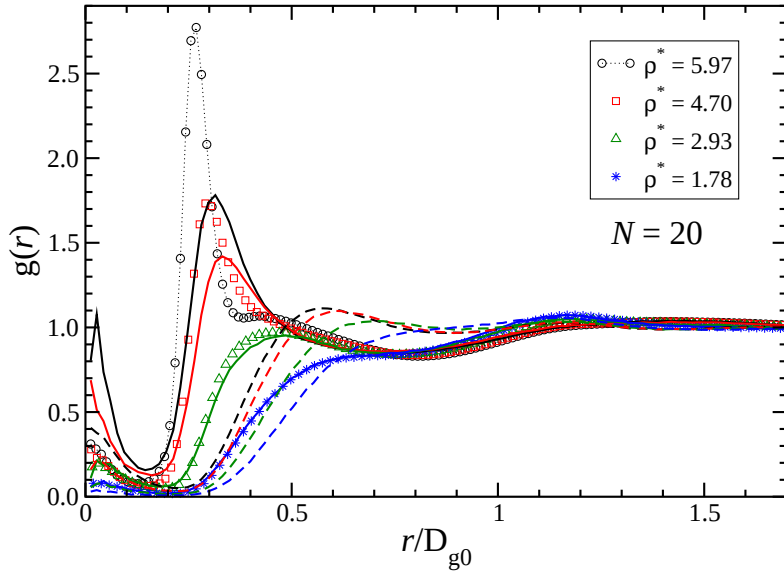


Figure 2.7: The pair correlation function $g(r)$, at high densities, for a simulation of many ring polymers with $N = 20$ monomers in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid line) and the isotropic effective model (dashed line).

model, where particles possess no directional degrees of freedom.

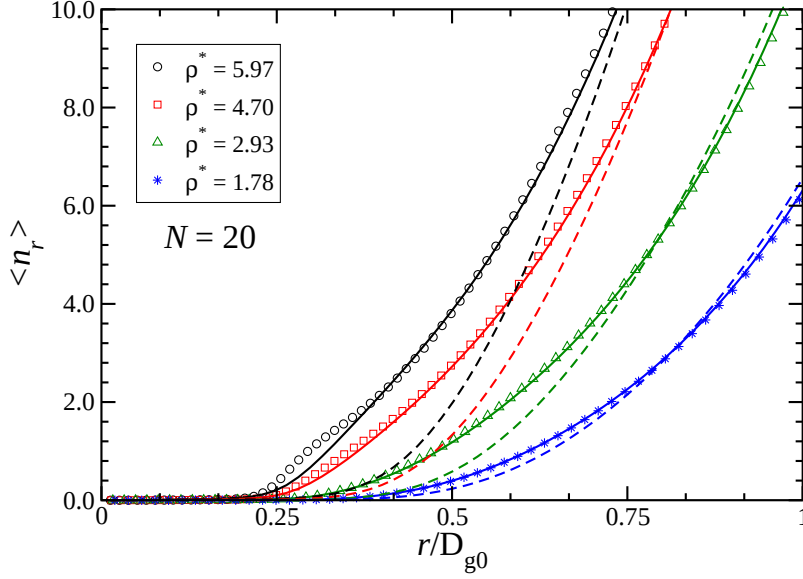


Figure 2.8: $\langle n_r \rangle$ in a simulation of many ring polymers with $N = 20$ monomers in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid line) and the isotropic effective model (dashed line).

As a further characteristic of the short-range coordination of the rings, we consider the average number $\langle n_r \rangle$ of neighbors within a distance r from the center of mass of a randomly chosen ring. This is expressed as

$$\langle n_r \rangle = 4\pi\rho \int_0^r dx x^2 g(x). \quad (2.15)$$

For the rings with $N = 20$ monomers we present results for $\langle n_r \rangle$ in figure 2.8. Once more, the good agreement between the full monomer-resolved and the anisotropic effective model, even at the highest densities investigated, is confirmed: small differences appear only for $0.25D_{g0} \leq r \leq 0.4D_{g0}$. Evidently, $\langle n_r \rangle$ does not contain more information than the $g(r)$ plot in figure 2.7, but it nevertheless clarifies the meaning of the disagreement between the $g(r)$ curves in the monomer-resolved and the anisotropic effective model. At the highest densities in the full simulation, the centers of mass move a bit closer to each other than they do in the anisotropic effective simulation. This manifests itself as a shift of the peaks in the $g(r)$ curves. The difference in the height of the peaks is partly a consequence of the shift, since a peak in $g(r)$ has to be higher at smaller distances if it amounts to the same amount of average neighbours as a peak at a larger distance r .

The fact that the $\langle n_r \rangle$ curves for the anisotropic effective and the full simulation in figure 2.8 agree for $r \geq 0.4D_{g0}$ shows us that the peaks in the $g(r)$ curves indeed correspond to the same amount of average nearby particles that are simply accumulated at slightly different distances.

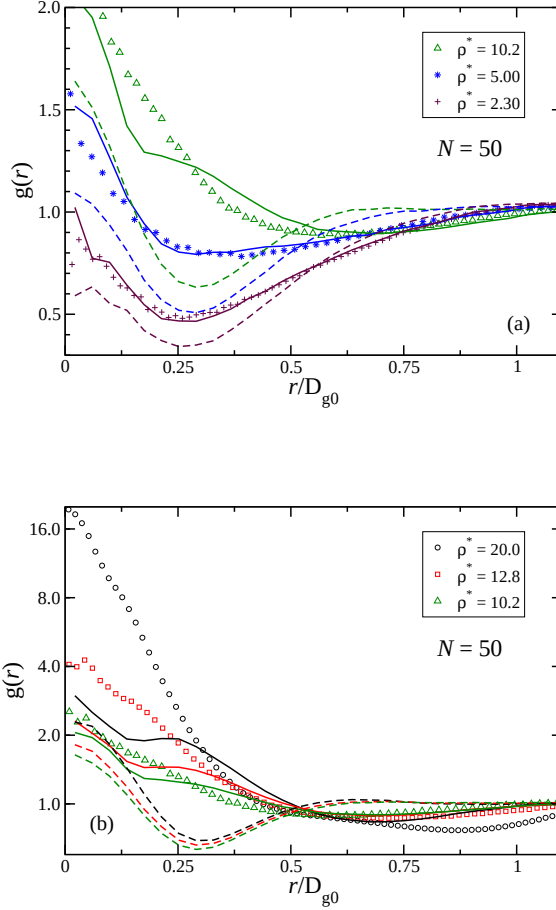


Figure 2.9: The pair correlation function $g(r)$ for a simulation of many ring polymers with $N = 50$ monomers in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid line) and the isotropic effective model (dashed line). The two plots show different reduced density ρ^* ranges.

We proceed now with the longer rings, $N = 50$. As can be seen by the pair correlation curves in figure 2.9(a), also in this case the inclusion of anisotropy improves the agreement with the monomer-resolved simulations significantly for densities ρ^* from 2.3 to 10.2. In figure 2.9(b) we present $g(r)$ for higher ρ^* . In the full monomer-resolved simulations we can see a peak emerging in the pair correlation function $g(r)$ at $r = 0$ on increasing the density. As described in ref. [69, 12] the monomer-resolved system forms stacks of

quasi-parallel oblate rings that are fully penetrated by bundles of elongated rings. In this phase, the deformation of the penetrating rings is particularly strong. The effective description, on the other hand, breaks down if the internal configurations of the rings in the monomer-resolved system differ significantly to the internal configurations in the system with only 2 ring polymers. Therefore, the anisotropic effective model should not be expected to be a quantitative description at the high densities in which this phase is formed. Agreement with the monomer-resolved model here is less satisfactory but the improvement over the isotropic model is still spectacular.

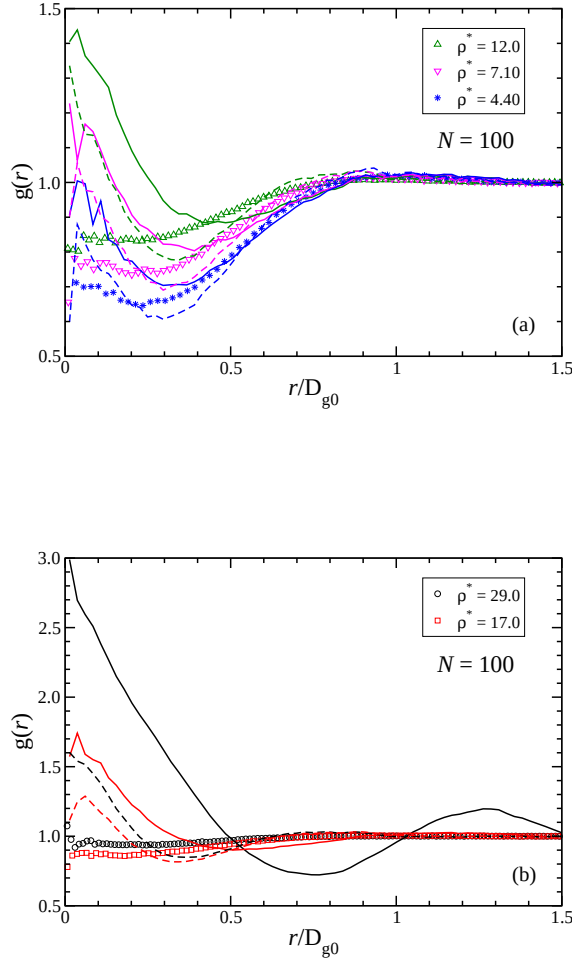


Figure 2.10: The pair correlation function $g(r)$ for a simulation of many ring polymers with $N = 100$ monomers in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid line) and the isotropic effective model (dashed line). The two plots show different reduced density ρ^* ranges.

For the rings with $N = 100$ we find that anisotropy does not play a key role any more, at least not for the full model at the investigated densities. This had to be expected, as we could already see in figure 2.3 and 2.5 that anisotropy is less pronounced for larger ring sizes. As we saw in figure 2.6(c) both the isotropic and the anisotropic model give good results for $g(r)$ up to $\rho^* \approx 2.5$. In figure 2.10, we see that for higher densities the inclusion of anisotropy does not yield results that are in better agreement with the full monomer-resolved simulations. The results in the isotropic effective model even seem to be in better agreement with the full model, which is attributed to multi-particle interactions that can change the configurations of the large and therefore more deformable rings significantly. The already small correlation between the directors, which is present in the dilute case, might therefore be even smaller at high densities. In the anisotropic effective model, we then overestimate the angular correlations between the directors and arrive at results that can be slightly worse than those of the isotropic model. Interestingly at $\rho^* = 20.0$, which is the highest density investigated, the anisotropic model appears to crystallize. At this density we see the emergence of columns that are closed over the periodic boundary conditions and organize in a hexagonal 2D lattice structure.

Finally, let us focus exclusively on orientational correlations. We define $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ as the probability density distribution for the scalar products between the directors $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ of two ring polymers which are a distance $r < 0.6D_{g0}$ away from each other. In figure 2.11, we present results for $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ for simulations in the monomer resolved and in the anisotropic effective model. If the directors were uncorrelated $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ would be equal to 1. For low densities ρ^* we obtain good agreement for all ring sizes investigated. Since we only look at the directional correlation of close by ring polymers, $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ can show strong anisotropic features even for $\rho^* \rightarrow 0$. As expected the anisotropy in $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ is stronger for smaller rings. When the density is increased, the distribution always shifts towards parallel configurations in the effective model. This happens because less volume per ring is available for higher ρ^* and by aligning parallel the rings occupy less space. Typically one observes the same trend in the monomer resolved simulation, only for the $N = 100$ rings we find more parallel rings for $\rho^* = 2.5$ than for $\rho^* = 17.0$. In contrast to the effective model the rings in the monomer-resolved simulation can deform and their interaction with other rings can therefore be more isotropic at higher densities ρ^* . This explains why for the large rings with $N = 100$ monomers, which deform more easily than the smaller rings, the correlation between the directors is much weaker than in the effective model and can even decrease with density. For $N = 50$ one can see that the number of orthogonal rings in the monomer-resolved model at high densities is significantly larger than in the effective simulation. As described in ref. [69, 12] for

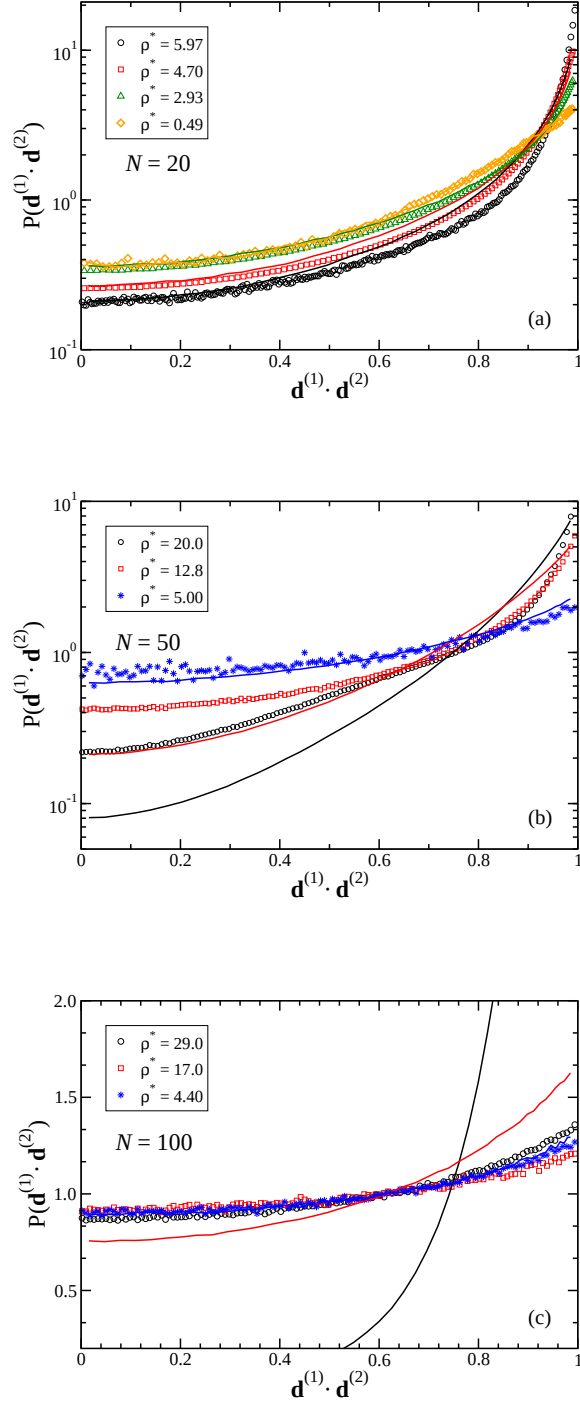


Figure 2.11: $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ is the probability density to find the scalar product $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$ between the directors of two close by rings ($r < 0.6D_{g0}$). Here we show $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ for a simulation of many ring polymers in the full monomer-resolved simulation (symbols) and the anisotropic effective model (solid line). (a) $N = 20$; (b) $N = 50$; (c) $N = 100$.

$N = 50$ and $\rho^* \geq 12.8$ one observes that oblate rings are interpenetrated by elongated prolate rings. Since the directors of the oblate and the interpenetrating prolate rings can be orthogonal to each other, one observes perpendicular directors for $N = 50$ even at the highest densities investigated. In the anisotropic effective model on the other hand, this interpenetration is disfavoured and we observe almost no orthogonal close-by rings at $\rho^* = 20$ for $N = 50$.

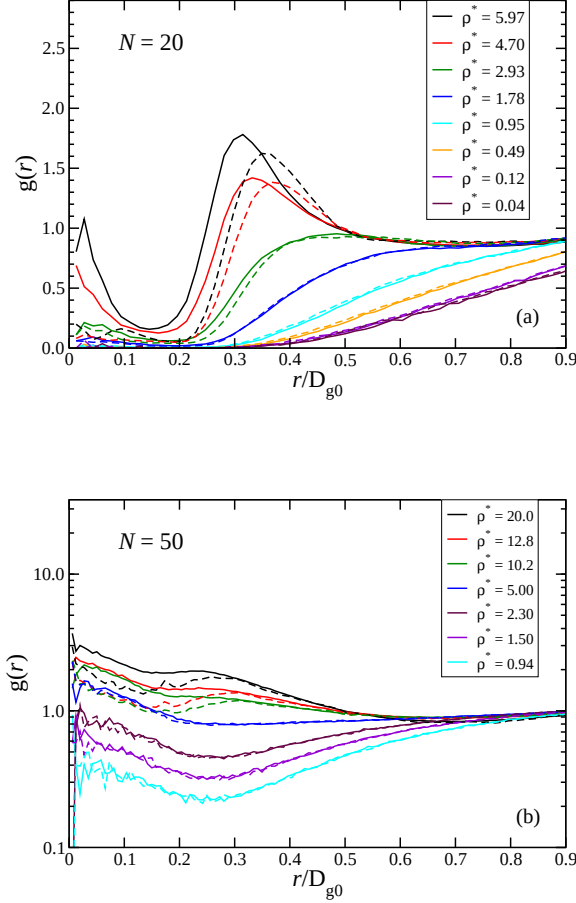


Figure 2.12: The pair correlation function $g(r)$ for a simulation of many ring polymers in the anisotropic effective model. For the dashed line we expanded the pair-correlation function g before computing the associated effective pair-potential. For the expansion we took the 14 coefficients for which $l_1, l_2 \leq 4$ into account. The solid line shows results of a simulation with the unexpanded effective pair interaction. (a) $N = 20$; (b) $N = 50$.

2.6 Truncation of the Expansion of the Anisotropic Potential

Instead of working with a fully tabulated effective potential on a four-dimensional grid, it can be advantageous to use the analytical expansion on basis functions presented in the Appendix. Such expansions are truncated after some term, and here we shortly discuss the quality of such truncations for the problem at hand. To test the quality of the expansion of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ we also carried out Monte Carlo Simulations, where we used the effective potential associated to the expanded correlation function as the pair-interaction between our effective particles. We took the 14 coefficients $c_{l_1, l_2, m}(r)$ for which $l_1, l_2 \leq 4$ into account and truncated the rest of the expansion. While $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ can never be negative, the truncated expanded version of g can accidentally become smaller than zero. Wherever this happens $g = 0$ and $V_{\text{eff}} = \infty$ is used in the simulation. In figure 2.12 the pair correlation function $g(r)$ obtained in this simulation is shown in comparison with the $g(r)$ function, which we computed previously employing the full anisotropic effective potential. For both $N = 20$ and $N = 50$ we obtain reasonable results with the truncated effective interaction, given by only 14 expansion coefficients. For the full effective interaction, which we store on a 4D grid, we save $16^3 = 4096$ entries for each value of r (see section 2.3). At intermediate densities the results obtained with the expanded effective interaction are a significant improvement with respect to the isotropic effective model. However, one has to be aware that for $N = 20$ the coefficients of higher order modes can still be quite high, especially for r between $0.2D_{g0}$ and $0.7D_{g0}$. In figure 2.5 we see that the coefficient for the mode with $(l_1, l_2, m) = (0, 2, 0)$ can be larger than the coefficient of the isotropic expansion mode. The reason for the high contribution of higher order modes for $N = 20$ is of course the strongly peaked nature of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ for these small rings, which we can also observe in figure 2.3. The convergence of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ is poor for the $N = 20$ rings due to the strong anisotropy of their effective interaction. However our results show that the expansion modes up to $l_1, l_2 \leq 4$ already capture the main features of the effective interaction. For $N = 50$ the degree of anisotropy is weaker and therefore the convergence of the expansion of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ is better.

2.7 Conclusions

We have introduced a minimal anisotropic model to coarse-grain ring polymers with a finite bending rigidity as soft, penetrable disks. For the shortest ($N = 20$) and the intermediate ($N = 50$) sized rings, this model represents a dramatic improvement over the isotropic coarse-graining, in which the relative orientations between the rings are

all integrated upon and a radially symmetric interaction results instead. The approach is capable of distinguishing between the relative orientations at infinite dilution and it carries this distinction also to highly concentrated systems, where it reproduces well the salient features of the structure as seen in the full, monomer-resolved simulations. Whereas this is valid more for $N = 20$ and $N = 50$, which have a contour length to persistence length ratio of $N/s_p \sim 2.7$ and 6.7 respectively, some important features, such as the penetration of elongated rings in columns formed by oblate rings (found for $N = 50$), are suppressed or even lost in the effective description, as genuine many-body effects come into play. For the largest rings, $N = 100$, for which we obtain $N/s_p \sim 13.3$, the contour length is much larger than the persistence length and they thus resemble more flexible objects. In this case the anisotropic potential at high concentrations fails to describe the structural correlations. This indeed reflects the fact that such rings undergo, at high concentrations, conformational changes (shrinking, interpenetration) that are quite distinct from the assumptions that go into the anisotropic, soft disc-model, rendering it thereby very inaccurate. We therefore expect that our anisotropic model yields quantitative results over a broad density range, for systems of polymer rings with a contour to persistence length ratio of $N/s_p \lesssim 10$.

Our work provides, thus, an accurate and efficient general scheme for the coarse-graining of semiflexible ring polymers, as it allows for a very dramatic reduction of their degrees of freedom, while at the same time introducing a realistic class of systems for which anisotropic generalizations of the ultrasoft, penetrable effective interactions are physically meaningful. Future work will focus on the investigations of the structural and phase behavior of mixtures of stiff rings and of the dynamics of the structure formation in the same.

3 Anisotropic Effective Interactions and Stack Formation in Mixtures of Semiflexible Ring Polymers

Submitted for publication*

*By means of extensive computer simulations, we investigate the formation of columnar structures (stacks) in concentrated solutions of semiflexible ring polymers. To characterize the stacks we employ an algorithm that identifies tube-like structures in the simulation cell. Stacks are found both in the real system and in the fluid of soft disks interacting through the effective anisotropic pair potential derived for the rings [P. Poier et al., Macromolecules, 2015, **48**, 4983-4997]. Furthermore, we investigate binary mixtures of cluster-forming and non-cluster-forming rings. We find that monodispersity is not a requirement for stack formation. The latter is found for a broad range of mixture compositions, though the columns in the mixtures exhibit important differences to those observed in the monodisperse case. We extend the anisotropic effective model to mixtures. We show that it correctly predicts stack formation and constitutes a significant improvement with respect to the usual isotropic effective description based only on macromolecular centers-of-mass.*

*Some results from the underlying monomer-resolved simulations shown in Figs 3.1, 3.3, 3.4, 3.8, 3.9, 3.10, 3.11, 3.12, 3.13, 3.14, 3.16, 3.17, 3.18, 3.19, 3.21 have been produced by P. Bačová and A. J. Moreno.

3.1 Introduction

A rapidly growing body of research has been devoted to polymer rings over the last years, in different fields of mathematics, physics, chemistry and biology. The simple operation of joining permanently the two ends of a linear chain to form a topologically different object — a ring — has a dramatic effect on the properties of the former. A well-known example is their different scaling behaviour. Linear chains in θ -solvent or in polymer melts behave as ideal chains (no excluded-volume interactions) and adopt random-walk conformations [5]. Thus, their size scales with their polymerization degree N as $D_g \sim N^{1/2}$, with D_g the diameter of gyration. However, the size of isolated ideal rings (keeping the topological constraints; i.e., bond uncrossability) scales as [35, 36, 37, 38, 39, 40, 41, 42] $D_g \sim N^{\nu_F}$, with $\nu_F \approx 0.588$ the Flory exponent. In the melt state, strongly entangled ring polymers adopt crumpled globular conformations, with an effective scaling exponent showing a crossover from $\nu \sim 0.4$ to $\nu \sim 0.33 - 0.36$ in the limit of large N [46, 47, 77]. Topological constraints have also a deep impact on the rheological properties of entangled ring polymer melts. Thus, the stress relaxation displays a long power-law decay with time, instead of the entanglement plateau followed by exponential decay observed in entangled linear chains [48, 49]. Moreover, the viscosity of entangled rings exhibits a weaker dependence on the polymerization degree than their linear counterparts [49, 78, 79]. Static and dynamic properties of rings have been much less explored in the intermediate concentration regime between dilute solutions and melts. This regime is of practical relevance because of its implications in, e.g., biophysics (living cells contain concentrated solutions of biomacromolecules). Accordingly, topological interactions between ring polymers — a simple picture for chromatin loops — have been invoked for explaining the creation of chromosome territories [44, 50, 51, 52, 80, 81].

The investigation of ring polymer properties in the semidilute regime can be facilitated by using a coarse-graining approach. In this methodology the internal degrees of freedom of the polymer (i.e., the monomer coordinates) are replaced by a reduced set of suitably-chosen effective coordinates. In this way, each real macromolecule is substituted by a single-particle (represented by the effective coordinates) interacting with the others through an effective potential. The microscopic information of the real macromolecule determines the form of the effective potential. This potential is generally *ultrasoft* [53] since, unlike hard or quasi-hard objects, macromolecules can interpenetrate at a moderate energetic cost. Simulation of the fluid of ultrasoft particles provides an economical route to investigate properties of the real macromolecular solution. Indeed, by using the effective coordinates, most of the degrees of freedom are removed and the computational effort is largely reduced.

The methodology of coarse-graining is well-established and has found successful application in, e.g., polymer chains [54, 55, 56], star polymers [57, 58, 59, 60], star-shaped polyelectrolytes [61, 62], dendrimers [63, 64, 65], block copolymers [66, 67, 68] and rings [45, 69], among others. The dramatic effect of the ring topology on the polymer properties with respect to those for the case of linear chains becomes again evident in the effective potential. Linear chains interact through effective Gaussian potentials [54, 55]. However, for ring polymers a non-Gaussian potential is found, which can even show a minimum at zero distance [45, 69] and includes a contribution from the *topological-potential* [82]. The effective attraction associated to this minimum is a direct consequence of the usual configurations of two rings with coincident or very close centers-of-mass: in such configurations one of the rings ‘opens up’ to be threaded by the other one [45, 83]. The effective interaction can lead to a striking feature in rings with, *purely repulsive*, excluded volume interactions between the monomers. Namely, a cluster phase can emerge in the case of *semiflexible* rings [69], which unlike flexible rings [45, 77], only show a weak shrinkage with increasing concentration, facilitating full interpenetration [69].

The identification of the relevant degrees of freedom is an essential part in the design of an effective model [1, 53]. In many situations of interest, the macromolecule is represented as a point particle at the position of a selected monomer (e.g., the central one in a star polymer) or more generally the position of the macromolecular center-of-mass. If the latter is chosen as the effective coordinate, the effective ultrasoft potential is *bounded*, since the centers-of-mass of two macromolecules can coincide at a finite energetic cost. Hence the ultrasoft particles are fully penetrable. Because of their simplicity, this family of ultrasoft particles has motivated a huge amount of theoretical and computational investigations, leading to the discovery of new structural and dynamic scenarios with potential realization in solutions of real macromolecules [84, 85, 86, 87, 88, 89, 90, 9, 91, 92, 93, 13, 10, 94, 11, 95, 96, 12].

The choice of the center-of-mass position as the single relevant effective coordinate results by construction in, rotationally-averaged, *isotropic* effective potentials. However, this approach is not justified for every macromolecule, as e.g., in the case of *semiflexible* ring polymers. In ref. [69] semiflexible rings were coarse-grained to ultrasoft particles interacting by an isotropic potential, dependent only on the relative distance between centers-of-mass. In an intermediate range of N -values, corresponding to ratios of contour-to-persistence length $N/s_p \sim 6.7$, clustering of the rings was observed both in the real monomer-resolved system and in the isotropic effective model. This was recognized by a peak at distance $r = 0$ in the radial distribution function $g(r)$ of the centers-of-mass. However, clustering in the real system was markedly *anisotropic*. The cluster phase in the

real system was formed by disordered columns (‘stacks’) of oblate rings, penetrated by bundles of elongated prolate rings. Though for small N , $N/s_p \sim 2.7$, interpenetration and clustering was negligible ($g(r \rightarrow 0) \ll 1$) due to excluded volume, anisotropic stacking of the rings was still observed. These features were not captured by the effective isotropic potential, which indeed did not take into account the orientation-dependent character of the real interactions, and led to the formation of isotropic clusters. Rings with high bending stiffness or few monomers have a strong tendency to orient with respect to other rings in their proximity. Thus, the energetic cost paid for mutually approaching two stiff rings to a fixed (small) separation between their centers-of-mass is highly dependent on their relative orientation. The absence of this feature in the effective isotropic model did not only result in the failure to predict the anisotropic character of the stacks and clusters. It also resulted in a poor description, in dense solutions, of rotationally-averaged static correlation functions as $g(r)$.

In order to improve the description of the real monomer-resolved system, an *anisotropic* effective model for semiflexible ring polymers has been introduced[97]. In that model, the effective particles are defined as soft disk-like molecules. These were represented not only by the positions of their centers-of-mass, but also by the direction in which their faces were oriented. A considerable improvement in the description of the monomer-resolved system was achieved by the effective anisotropic model for small- N (non cluster-forming) and intermediate N (cluster-forming). Namely, in comparison to the isotropic model, it provided a much better description of $g(r)$, and was applicable over a broader density range. It also accounted for the orientational correlations between neighbouring rings. The isotropic model provided, however a better description than the anisotropic one in the case of (non cluster-forming) long rings (large N , $N/s_p \sim 13.3$). This was attributed to the overestimation of the orientational effects in the interactions between long rings, which are much more deformable than those with small or intermediate N and the same stiffness. In ref. [70, 98] Heinemann et al. follow a similar approach showing that the anisotropy in the effective interactions of the molecule coronene plays a crucial role in its structural properties.

In this article we investigate whether stacking is reproduced by the anisotropic effective model, and how the results compare with respect to the real monomer-resolved system. To this end, we introduce an algorithm to define a stack of ring polymers, and compare the distribution of stack sizes in the effective and monomer-resolved systems. Furthermore, we examine whether monodispersity is required for the occurrence of stacks, by investigating binary mixtures of rings of different sizes. In particular, we simulate mixtures of rings with intermediate and small N , which form and do not form,

respectively, cluster phases in the monodisperse case. We find that stacking is resilient to polydispersity, persisting even in mixtures with 50 % of non cluster-forming rings. The article is organized as follows. In Section 2 we summarize model and simulation details [69] of the monomer-resolved and monodisperse effective system. In Section 3 we introduce the algorithm for identifying stacks. In Section 3.4 we summarize the method to derive the effective potentials [97]. In Section 3.5 we characterize stacks in the monodisperse systems. In Section 3.6 we show results for effective potentials corresponding to the cross-interactions between small and intermediate rings. In Sections 3.7 and 3.8 we show results for the binary mixtures and characterize, respectively, static correlations and stacks. We compare the obtained results for the real mixtures and the effective systems. Conclusions are given in Section 3.9.

3.2 Model and Simulation Details

The monomer-resolved system consists of bead-spring rings. Non-bonded interactions between monomers are given by the cut-and-shifted Lennard-Jones (LJ) potential [72]:

$$V_{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & \text{if } r < 2^{1/6}\sigma; \\ 0 & \text{if } r \geq 2^{1/6}\sigma. \end{cases} \quad (3.1)$$

This potential is purely repulsive, accounting then for monomer excluded volume interactions. Bonded monomers also interact through a FENE potential [72]:

$$V_{\text{FENE}}(r) = -\frac{kR_0^2}{2} \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right]. \quad (3.2)$$

Rigidity is introduced via the bending potential

$$V_{\text{bend}}(\theta) = \kappa(1 - \cos \theta)^2, \quad (3.3)$$

where θ is the angle between two consecutive bond vectors. We choose $\epsilon = k_B T$, $k = 30k_B T/\sigma^2$, $R_0 = 1.5\sigma$ and $\kappa = 30k_B T$, where k_B is the Boltzmann constant and T the temperature. All simulations are done at $k_B T = 1$. In what follows absolute distances will be given in units of the LJ diameter σ . The characteristic ratio C_∞ and persistence length bs_p of the model are estimated [97] as $C_\infty \sim 15$ and $bs_p \sim 7.5$, where b is the bond length ($b \sim 0.97$). We performed standard Langevin dynamics simulations to investigate solutions of the monomer-resolved rings at different densities. We define the reduced density as $\rho^* = nV^{-1}D_{g0}^3$, with n the number of rings, V the volume of the simulation box, and D_{g0} the diameter of gyration of the ring at infinite dilution ($\rho^* = 0$). The overlap density is defined as $\rho^* = 1$ and represents the concentration at which the periphery of

the rings start to overlap. The investigated solutions covered a broad range of densities from high dilution to several times the overlap density.

The effective isotropic and anisotropic potentials were derived (see below) from the distribution functions of the relative distances (in both cases) and the relative orientations (in the anisotropic case). Such distributions were sampled from simulations of two isolated rings at different relative distances. Bias Monte Carlo and molecular dynamics methods were used for efficient sampling [69, 97]. The solutions of the ultrasoft particles, interacting through the effective isotropic or anisotropic potentials, were simulated by standard Langevin and Monte Carlo dynamics. As in the monomer-resolved case, they covered a broad range of densities from high dilution to several times the overlap density. Further simulation details are given in refs. [69, 97].

3.3 Algorithm for the Identification of Stacks

Now we describe the algorithm to identify the stacks of rings. Defining a condition for two rings to be neighbour particles in a stack is sufficient to identify all the stacks in the system. To identify a stack we randomly choose some ring A and start with a set that contains only this ring as a member. We continue to extend the set by the neighbours of its members until no new rings are added, and the set thus corresponds to the stack which contains the ring A . We repeat the procedure for the rings that are not part of any stack yet and thus gradually identify the stacks in the system.

We will formulate the condition for two rings to be neighbours in a stack in terms of the effective coordinates of the rings, defined in ref. [97], which are accessible in both the effective and the monomer-resolved simulations. Let us consider two rings with the effective coordinates $(\mathbf{R}^{(1)}, \mathbf{d}^{(1)})$ and $(\mathbf{R}^{(2)}, \mathbf{d}^{(2)})$. $\mathbf{R}^{(i)}$ refers to the center-of-mass of the respective ring and $\mathbf{d}^{(i)}$ to its normalized director ($|\mathbf{d}^{(i)}| = 1$). The director is defined along the direction of the smallest eigenvalue of the gyration tensor of the ring. Thus, for an ideally flat ring the director is perpendicular to the plane of the ring. We define $\mathbf{r} \equiv \mathbf{R}^{(2)} - \mathbf{R}^{(1)}$ as the relative vector between the centers-of-mass of the rings. We formulate our criteria for identifying stacks such that they contain rings that form tube-like structures. While it is possible that other rings interpenetrate these tubes, we will not aim at identifying them as members of the stack. Therefore, the first condition for two rings to be neighbours in a stack is that their directors are almost parallel:

$$|\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}| > 1 - \Delta\gamma, \quad (3.4)$$

where the parameter $\Delta\gamma$ is fixed to some value (see below) and quantifies how much the directors of two neighbours in a stack can deviate from a perfectly parallel orientation

($\Delta\gamma = 0$). Furthermore, the centers-of-mass of neighbours in a stack must be close to each other. We differentiate between the distance in the $\mathbf{d}^{(1)}$ direction, which is given by $|\mathbf{r} \cdot \mathbf{d}^{(1)}|$, and in the direction orthogonal to it, which can be computed as $|\mathbf{r} - \mathbf{d}^{(1)}(\mathbf{r} \cdot \mathbf{d}^{(1)})|$. We restrict both of these distances independently:

$$|\mathbf{r} \cdot \mathbf{d}^{(1)}| < v_{\parallel}, \quad (3.5)$$

$$|\mathbf{r} - \mathbf{d}^{(1)}(\mathbf{r} \cdot \mathbf{d}^{(1)})| < v_{\perp}. \quad (3.6)$$

For perfectly parallel rings $v_{\parallel}$ controls the maximum distance between the ring surfaces, while $v_{\perp}$ sets how much misalignment between the centers-of-mass of the two rings is accepted. Conditions (3.4) - (3.6) must be simultaneously fulfilled.

It is arbitrary which ring has the label 1 and therefore the result of whether the two rings are neighbours in a stack must not depend on it. However, conditions (3.5)-(3.6) have an explicit dependence on $\mathbf{d}^{(1)}$. In order to restore the $1 \leftrightarrow 2$ symmetry, we also classify rings 1 and 2 as belonging to the same stack if the conditions in (3.5)-(3.6) are satisfied for $\mathbf{d}^{(1)} \rightarrow \mathbf{d}^{(2)}$. Since, for small $\Delta\gamma$, the condition (3.4) requires $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ to be similar, the change $\mathbf{d}^{(1)} \rightarrow \mathbf{d}^{(2)}$ just slightly modifies the numerical values of the left sides of conditions (3.4)-(3.6), which are still fulfilled.

The parameters $\Delta\gamma$, $v_{\parallel}$ and $v_{\perp}$ have to be set by hand. If one only wants the algorithm to identify a stack if the rings form perfect tubular structures, one has to choose $\Delta\gamma, v_{\perp} \rightarrow 0$, with some finite $v_{\parallel}$, quantifying by how much the rings forming the tube can be separated. We have chosen finite values for $\Delta\gamma$ and $v_{\perp}$, since the stacks formed by the rings in simulations always exhibit imperfections with respect to a perfect tube-like arrangement. We use $v_{\parallel} = 3\sigma$, $v_{\perp} = 2.5\sigma$, $\Delta\gamma = 0.1$ for the identification of stacks of rings with $N = 50$ monomers, and $v_{\parallel} = 5\sigma$, $v_{\perp} = 5\sigma$, $\Delta\gamma = 0.1$ in the case of larger rings with $N = 100$ monomers. This choice of parameters is justified a posteriori, since it has resulted in the identification of stacks that are compatible with our intuitive notion of tube-like structures. The stack-identification algorithm together with this choice of parameters therefore provides an unambiguous definition of stacks of ring polymers. We have to emphasize that this definition is not the only sensible one, and that the results obtained with a 10% variation in the parameters $\Delta\gamma$, $v_{\parallel}$ and $v_{\perp}$ were qualitatively identical.

Using this algorithm we can determine the stacks in configurations of anisotropic effective, as well as monomer-resolved systems. As shown below, for both levels of description we observe the formation of long columns at sufficiently high densities. On the other hand, in the isotropic effective model stacks are never observed, confirming that in order to describe the system at high densities, at least at a qualitative level, the introduction of

anisotropy is essential. It is interesting to note that the absence of stacks in the isotropic effective model is not self-evident, since there exist other systems where the interactions between particles are also isotropic and *stacks*, i.e. linear clusters, are formed[99, 100].

3.4 Derivation of the Effective Potentials

In refs. [69, 97] we derived isotropic and anisotropic effective potentials for the description of *monodisperse* systems of semiflexible ring polymers. One can extend these models for the description of mixtures, by introducing interaction potentials between different ring types. In this work, we will limit ourselves to mixtures of rings with $N = 20$ and $N = 50$ monomers, but an extension to other binary, or multicomponent mixtures is straightforward. As discussed in ref. [97] this corresponds to rings with a contour to persistence length ratio N/s_p of ~ 2.7 and ~ 6.7 respectively (rings of $N = 100$ to be discussed below have $N/s_p \sim 13.3$). The diameter of gyration at infinite dilution of the rings with $N = 20, 50$ and 100 monomers is $D_{g0} = 5.9\sigma, 13\sigma$ and 21.5σ respectively.

To determine the effective interaction potential between different ring types, we follow a similar procedure to that reported in ref. [97] for the case of identical rings. In particular, we carry out simulations of a system of two ring polymers. We then determine $P(r, \cos \theta_1, \cos \theta_2, \varphi)$, which is the probability density to find the two rings at a certain distance and relative orientation with respect to each other. The arguments of P refer to the effective coordinates defined in Eq. (6) in ref. [97]. Namely, r is the distance between the centers-of-mass of the two rings (denoted as 1 and 2), and θ_i is the angle between the vector $\mathbf{r}$ joining the centers-of-mass and the director $\mathbf{d}^{(i)}$ of the i -ring. The angle φ is the angle between $\mathbf{d}_\perp^{(1)}$ and $\mathbf{d}_\perp^{(2)}$, which are the components of $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ perpendicular to $\mathbf{r}$. It is important to note at this point that if the two rings are not identical (different N), the distribution P is not invariant under the exchange of $\cos \theta_1$ and $\cos \theta_2$, since these now refer to directors of nonequivalent rings. For this reason also the effective interaction between different ring types loses the $\cos \theta_1 \leftrightarrow \cos \theta_2$ symmetry. We then compute the anisotropic pair correlation function as

$$g(r, \cos \theta_1, \cos \theta_2, \varphi) = \frac{P(r, \cos \theta_1, \cos \theta_2, \varphi)}{P_{\text{id}}(r, \cos \theta_1, \cos \theta_2, \varphi)}, \quad (3.7)$$

where $P_{\text{id}} \sim r^{-2}$ is the probability density for an ideal gas of (non-interacting) effective particles. To determine $P(r, \cos \theta_1, \cos \theta_2, \varphi)$ we employed umbrella sampling. Details of the simulations were explained in section 3 in ref. [97]. The effective anisotropic potential is obtained as

$$\beta V_{\text{eff}}(r, \cos \theta_1, \cos \theta_2, \varphi) = -\ln [g(r, \cos \theta_1, \cos \theta_2, \varphi)]. \quad (3.8)$$

with $\beta = (k_B T)^{-1}$. In the isotropic case, the procedure to obtain the effective potential between different types of rings is identical to the former. As in the monodisperse case, one can deduce the radial distribution function $g^{\text{iso}}(r)$ by averaging over $\cos \theta_{1,2}$ and φ in the anisotropic pair correlation function, and obtains the isotropic interaction potential as $\beta V_{\text{eff}}^{\text{iso}}(r) = -\ln g^{\text{iso}}(r)$.

3.5 Formation of Stacks in Monodisperse Systems

Using the previously described algorithm for the identification of stacks, we have analyzed configurations of monomer-resolved and effective simulations of monodisperse systems of ring polymers with $N = 50$ and $N = 100$ monomers. In figure 3.1 we present simulation snapshots of a monomer-resolved monodisperse system containing rings with $N = 50$ monomers. The snapshots are both at high densities, namely $\rho^* = 16.3$ and 20.0 respectively. In the snapshots, rings belonging to the same stack have identical colors. Rings which are not part of any stack or part of a stack that contains less than 5 rings are painted in turquoise. For every density, we display two snapshots, where in the first all the rings are shown while in the second the turquoise rings are hidden for clarity. It can be seen that already at the lower density the majority of the stacks contain more than 5 rings and at the larger density one can spot several long columns that extend throughout the whole simulation box. For clarity, rings are always depicted as a whole and therefore individual monomers can lie outside of the periodic boundaries of the simulation box, while the center-of-mass of a ring is always within the boundaries. Some of the columns continue over the periodic boundary conditions. Columns can grow very long at large densities, however they do not display any orientational order within the simulation time.

In figure 3.2 analogous snapshots of the anisotropic effective system are shown. At the density $\rho^* = 20$ one can see some stacks containing 20 or more rings, but the length of the columns is reduced with respect to the corresponding monomer-resolved system. Comparing the snapshots of the effective model with the ones in figure 3.1 one sees that the interpenetration of the rings is disfavored in the effective case. The reason for this might be that in the effective simulation an individual ring, which is squeezed within a stack that stands orthogonal to it, pays a very high free energy penalty, since one adds up pair terms of effective potential for every interpenetrated ring in the stack. However, in the monomer-resolved simulation the deformation energy to squeeze a ring within one or several rings does not differ by such a big amount and the energy barrier for the interpenetration of stacks is therefore lower. This feature was already indirectly observed in figure 11(b) in ref. [97], where it was found that the directors of neighboring rings are more likely to be orthogonal in the monomer-resolved than in the effective simulation.

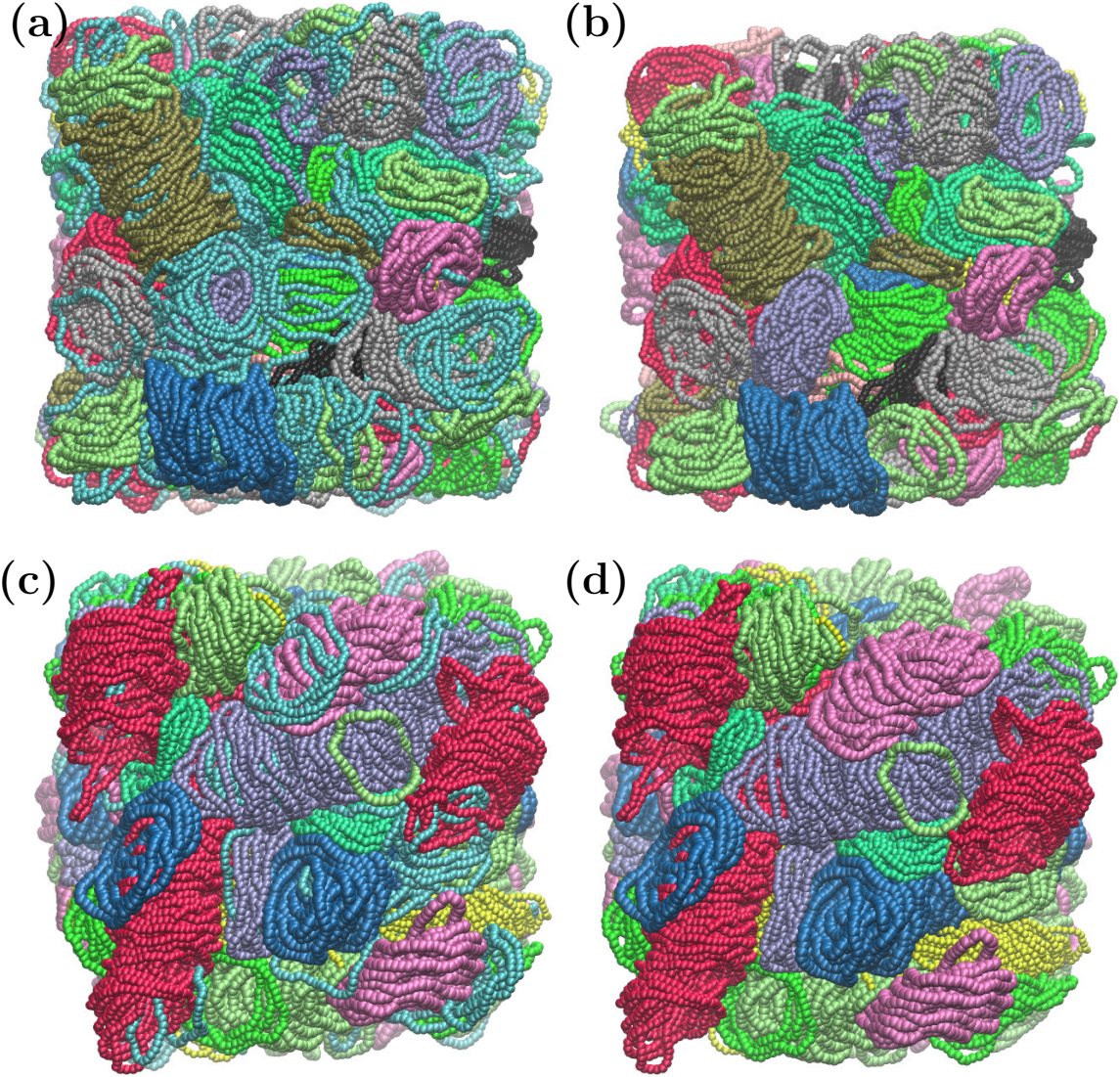


Figure 3.1: Snapshots of a monomer-resolved system of ring polymers with $N = 50$ monomers. Rings belonging to the same stacks are dyed with identical colors. Turquoise polymers belong to a stack with less than 5 members. Snapshots (a), (b) are taken from a simulation at density $\rho^* = 16.3$, while (c), (d) are for the density $\rho^* = 20.0$. The snapshots (a), (c) contain all the particles simulated, while turquoise rings are not shown in (b), (d).

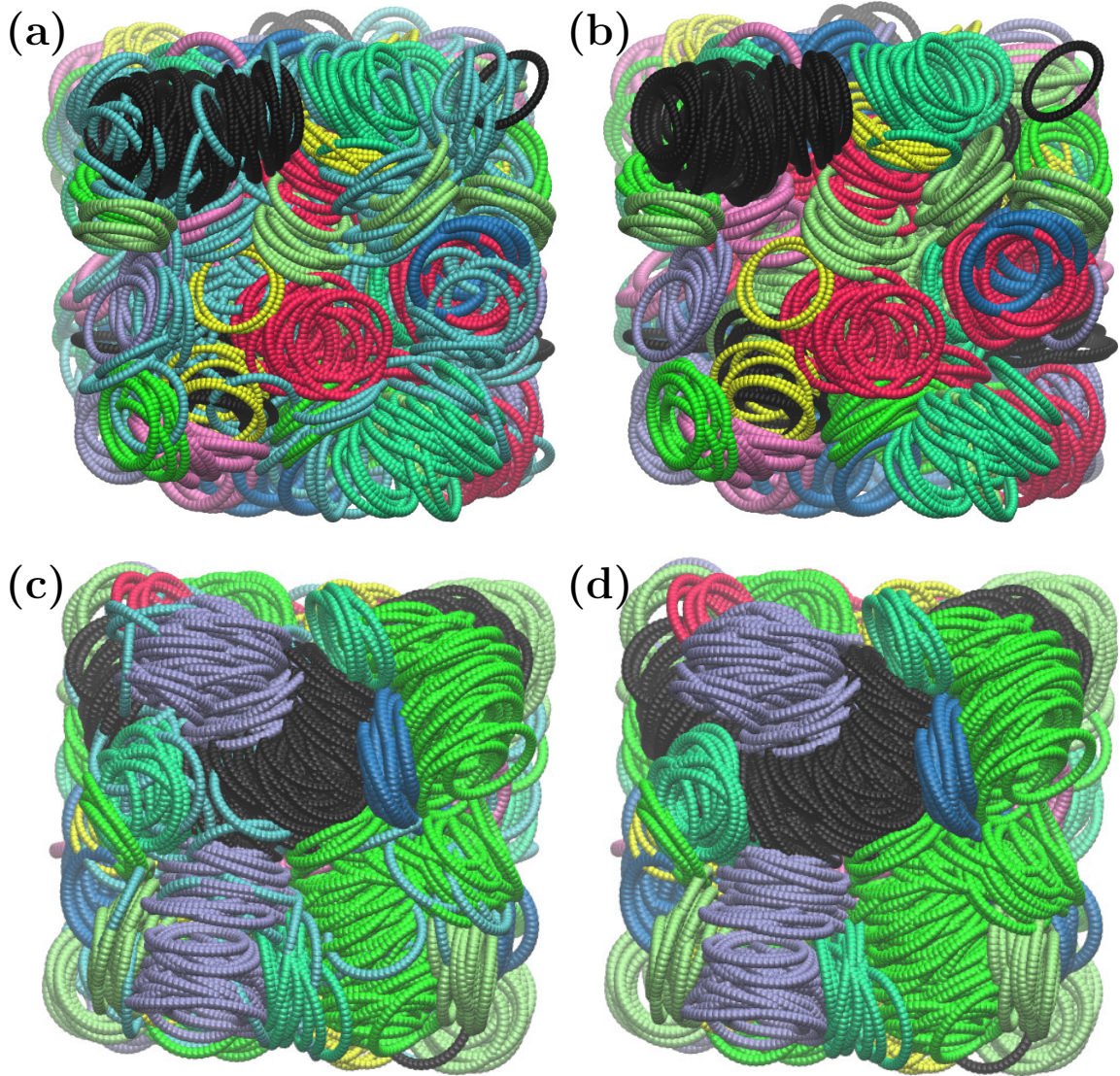


Figure 3.2: Snapshots of a simulation of soft disks, representing ring polymers with $N = 50$ monomers. The effective particles are visualized by perfect circles of radius $R_{g0} = 6.5\sigma$, with director vectors and centers-of-mass identical to those of the corresponding effective particles. R_{g0} is the radius of gyration of the represented rings at zero density. Rings belonging to the same stack are dyed with identical colors. Turquoise rings belong to a stack with less than 5 members. Snapshots (a), (b) are taken from a simulation at density $\rho^* = 20.0$, while (c), (d) are for the density $\rho^* = 30.0$. The snapshots (a), (c) contain all the particles simulated, while turquoise rings are not show in (b), (d).

This can also be related to the enhanced stack size in the monomer-resolved simulation, since interpenetration enhances the directionality of the stacking and therefore also the formation of long columns. In addition, interpenetration should enhance the alignment of the centers-of-mass of the stacked rings, and one can indeed see that the columns in the monomer-resolved snapshots are straighter than in the effective ones. By increasing the density to $\rho^* = 30$, the length of the columns formed by the soft disks increases significantly and the stack length distribution becomes comparable to the one observed at $\rho^* = 20$ in the monomer-resolved simulation, while the center-of-mass alignment of the disks within a stack is still reduced with respect to the monomer-resolved simulation.

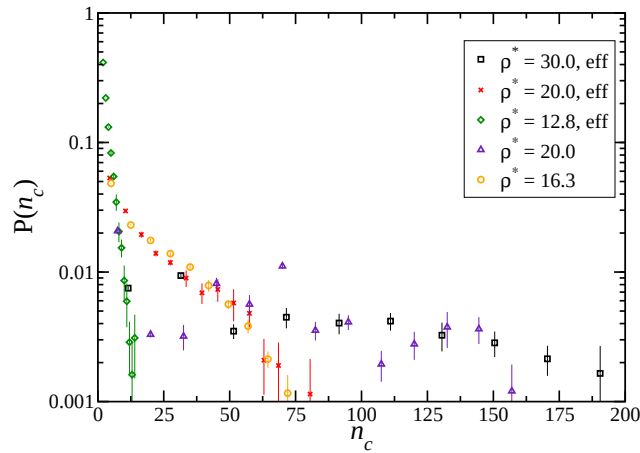


Figure 3.3: Probability distribution, $P(n_c)$, for a ring to be part of a stack with n_c members for different densities in anisotropic effective and monomer-resolved simulations. Results for the former are indicated by *eff* in the legend, on which the density ρ^* is also quoted.

In figure 3.3 we have compared the distribution of stack lengths at different densities. The plotted function $P(n_c)$ gives the probability that a randomly chosen ring is part of a stack with n_c members. To compute $P(n_c)$ we have analyzed several configurations, which are separated by 10^6 MD steps in the case of the monomer-resolved system and by 2×10^4 MC steps for the anisotropic effective system. Errorbars have been computed assuming that the $P(n_c)$ distributions of different configurations are uncorrelated. The small errorbars for the $P(n_c)$ distribution evaluated for the highest simulated densities might underestimate the *real* error, since the cluster dynamics becomes glassy at high densities (for more details see ref. [12]) and the assumption that the analyzed configurations are uncorrelated is therefore not valid. While the formation of stacks is obviously enhanced

in the monomer-resolved simulation, the effective model eventually shows the same stack length distribution at higher densities. One can for instance see that the stack size distributions for the soft disk model at $\rho^* = 20$ and $\rho^* = 30$ are almost identical to those obtained for the monomer-resolved model at $\rho^* = 16.3$ and $\rho^* = 20.0$, respectively. These results demonstrate that the anisotropic effective model is a significant improvement over an isotropic model, where the formation of stacks is excluded in first place. Although quantitative agreement with the monomer-resolved simulation cannot be achieved, the formation of stacks is correctly predicted and even the stack-size distribution is similar to that of a monomer-resolved simulation at a lower density.

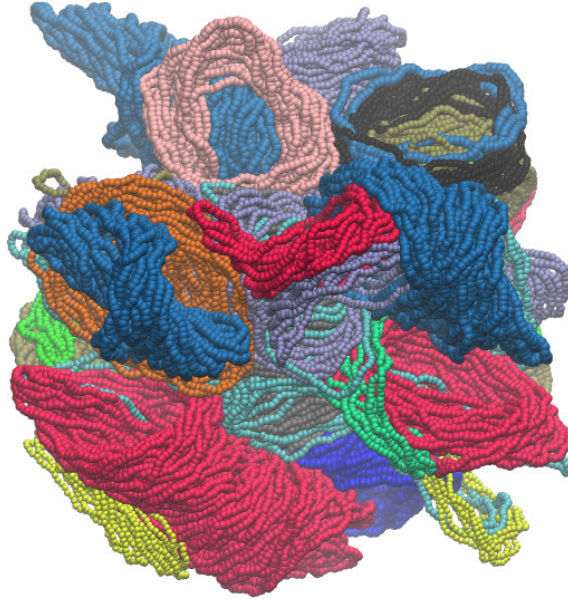


Figure 3.4: Snapshot of a monomer-resolved system of ring polymers with $N = 100$ monomers at density $\rho^* = 44.2$. Rings belonging to the same stack are dyed with identical colors. Turquoise polymers belong to a stack with less than 5 members.

Analogously we have analyzed configurations of systems with $N = 100$ monomers. In ref. [97] we found that for these long rings the agreement of the soft disk model with the real system was worse than in the case of the smaller ring sizes $N = 20$ and $N = 50$. The anisotropic model even provided a worse description than the isotropic one for the correlation functions of $N = 100$. We attributed this to the fact that the long rings have a larger ratio between contour and persistence length, and are thus more easily deformed. At higher densities, they therefore acquire collapsed configurations that significantly deviate from the most probable ones in the infinitely dilute limit, at which the effective interactions have been derived. In this work we have performed new simulations of the real system for $N = 100$, investigating higher densities than in ref. [97]. As can

be seen in figure 3.4, if one continues to increase the density in the monomer-resolved simulations, the rings again favor configurations which are expanded and much closer to disk-like shapes than those found at lower densities. The reason for this might be that if the volume per ring becomes very small, the system prefers a more optimally packed state, where individual rings have more space to fluctuate. At some density a configuration of expanded rings, which are packed within columns, is apparently the best compromise for the system, and in this state the individual rings are again more disk-like.

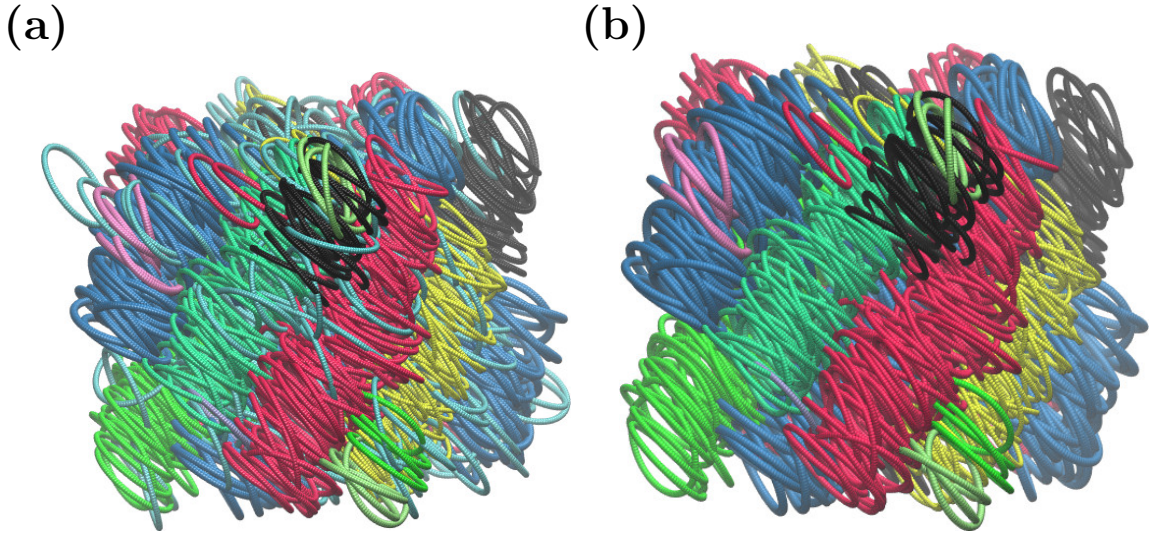


Figure 3.5: Snapshots of the soft-disk model for rings of $N = 100$, at density $\rho^* = 29.0$. The effective particles are visualized by perfect circles of radius $R_{g0} = 10.8\sigma$, with director vectors and centers-of-mass identical to those of the corresponding effective particles. R_{g0} is the radius of gyration of the represented rings at zero density. Rings belonging to the same stack are dyed with identical colors. Turquoise rings belong to a stack with less than 5 members. Snapshot **(a)** contains all the particles simulated, while turquoise rings are not shown in **(b)**.

As a consequence the configurations of the anisotropic and the monomer-resolved system at high densities are qualitatively similar, and long columns are formed in both cases. For the effective system, the stacks also orient themselves with respect to each other, while this does not happen to the same extent in the monomer-resolved simulation. Therefore, for high densities the disk-like nature of the effective model is again an appropriate description for the long rings, at least at a qualitative level.

3.6 Effective Model for Binary Mixtures

We have computed the anisotropic effective correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ between two stiff ring polymers containing $N = 20$ and $N = 50$ monomers at infinite dilution, which is related to the interaction potential between effective particles of different types via equation (3.8). The four-dimensional pair correlation function is difficult to visualize, however we can consider a reduced version of this function:

$$g(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}) = \frac{P(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})}{P_{\text{id}}(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})}. \quad (3.9)$$

Here $P(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ is the probability distribution to find two isolated rings separated by a distance r and with a scalar product $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$ between their directors, while $P_{\text{id}} \sim r^2$ gives the same distribution for two non-interacting rings. In figure 3.6 we present results for the function

$$G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}) = \frac{g(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})}{g^{\text{iso}}(r)}, \quad (3.10)$$

which gives the probability distribution of the scalar product between the directors of two isolated rings at a fixed mutual distance r . The abscissa in the plot is given by r/D_{g0} ,

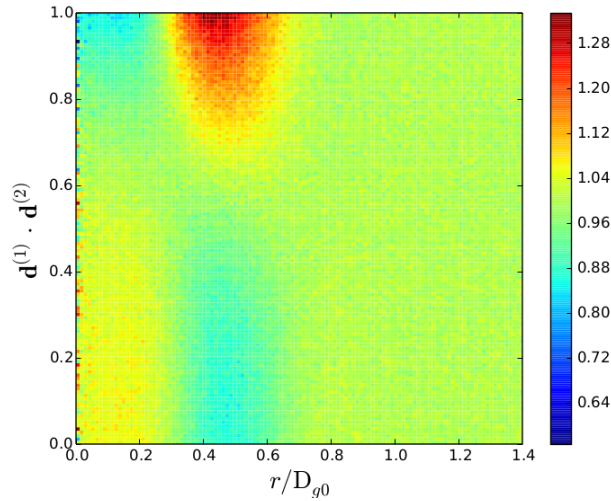


Figure 3.6: Infinite-dilution limit of the quantity $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$, which quantifies the distribution of the scalar product between directors for different values of r . We visualize this distribution between rings of size $N = 20$ and $N = 50$.

where D_{g0} refers to the diameter of gyration of the $N = 50$ rings at infinite dilution. In the following, r/D_{g0} will always refer to the distance normalized by the diameter of gyration of the larger rings in the mixture. Compared to the $G(r, \mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ of identical ring polymers [97], the anisotropy is significantly reduced. In particular the distribution

of $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$ is almost flat for small distances r , where the directors had a tendency to be orthogonal with respect to each other in the case of identical rings. For $r \approx 0.4D_{g0}$ the directors do have a tendency to orient parallel, but the extent of this is much weaker than for identical $N = 50$ and even $N = 100$ rings.

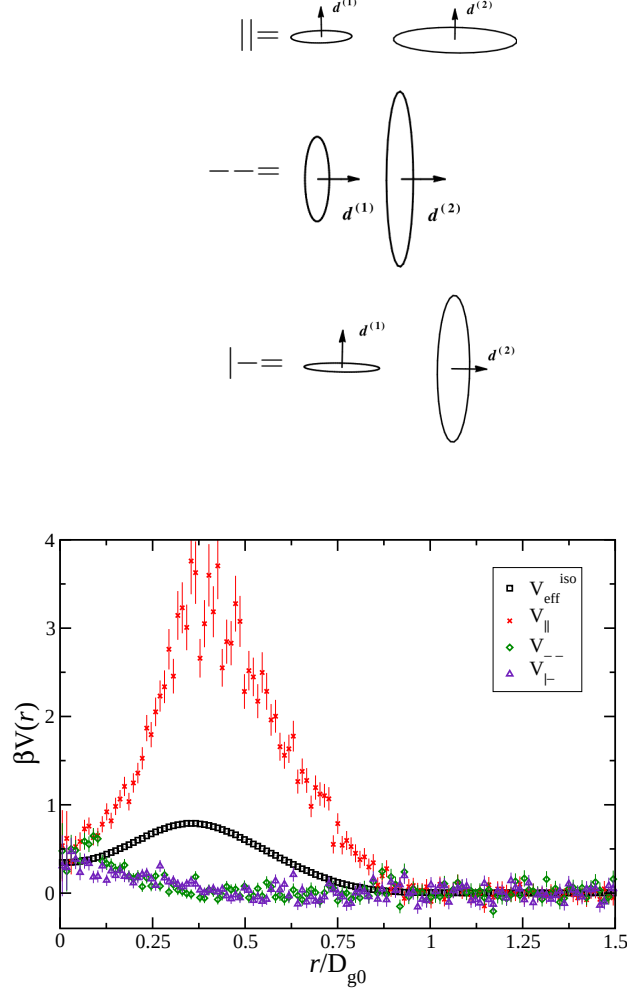


Figure 3.7: The pair potential in the isotropic effective model ($\beta V_{\text{eff}}^{\text{iso}}(r) = -\ln g^{\text{iso}}(r)$) and for three different, fixed orientational degrees of freedom (through eq 3.8). These are potentials between rings with $N = 20$ and $N = 50$ monomers. A sketch illustrates the $||$, $--$ and $|-$ configurations.

In figure 3.7, we present the rotationally averaged, isotropic effective potential, and the anisotropic potentials evaluated for three fixed orientations of the rings (see legend). The analogous plots for the interactions between identical rings have been displayed in figure 4 in ref. [97], where also the precise meaning of the three fixed orientations is described in more detail. There is now almost no difference between $V_{|-}$ and V_{--} , which both remain very low for all distances r . As in the case of identical rings, $V_{||}$ rises

significantly at intermediate distances, when the contours of the rings start to overlap, but different to the case of identical rings, $V_{|-}$ is as low as the other potentials for small distances r . This is quite intuitive since the smaller ring can easily fit inside the larger one, irrespective of its orientation. In general, the interaction potentials between different rings are significantly weaker than for identical rings.

3.7 Correlation functions in binary mixtures

We have carried out simulations of binary mixtures of rings with $N = 20$ and $N = 50$ monomers, employing the methods described in Refs. [97, 69]. For the reduced density in a mixture of rings, we use the following definition:

$$\rho^* \equiv \frac{\sum_i n^{(i)} \left(D_{g0}^{(i)}\right)^3}{V}, \quad (3.11)$$

where V is the volume of the simulation box, $n^{(i)}$ the number of rings of type i , and $D_{g0}^{(i)}$ the diameter of gyration of the respective rings at infinite dilution. We first concentrate on a system with 1143 $N = 20$ and the same number of $N = 50$ rings, to which we will refer to as the 1:1 mixture. Radial distribution functions of such a system at density $\rho^* = 1.2$ are presented in figure 3.8. The plot shows that at the density $\rho^* = 1.2$ both the anisotropic as well as the isotropic effective model (derived at infinite dilution [97]) are in excellent agreement with the monomer-resolved simulation results, which implies that many-body effects are very small and that orientation-specific correlations are weak.

In figures 3.9, 3.10 and 3.11 we show the same correlation functions at the higher densities $\rho^* = 3.9$, 10.0 and 15.7. At $\rho^* = 3.9$ the results for $g_{20,20}$ and $g_{50,50}$ are still in good agreement with the monomer-resolved simulations, while the results of the isotropic model deviate significantly. The correlation function between different rings ($g_{20,50}$) on the other hand, shows that the anisotropic model overestimates the extent of interpenetration of the small within the large rings. For $\rho^* = 10.0$ there is good agreement between the monomer-resolved and the anisotropic effective results for the correlation functions between different rings ($g_{20,50}$) and also between $N = 50$ rings ($g_{50,50}$). The isotropic model on the other hand misses important features for all correlation functions, both for different and identical rings. In the case of the monomer-resolved simulation, the correlation function between $N = 20$ rings, $g_{20,20}$, exhibits a characteristic peak similar to that observed in the monodisperse system of $N = 20$ rings (figure 7 in ref. [97]). For the anisotropic effective system on the other hand the peak in $g_{20,20}$ is missing at $\rho^* = 10$ and looks similar to the correlation function measured in a monodisperse system of $N = 20$ rings at a lower density. For the higher density, $\rho^* = 15.7$, the peak in $g_{20,20}$

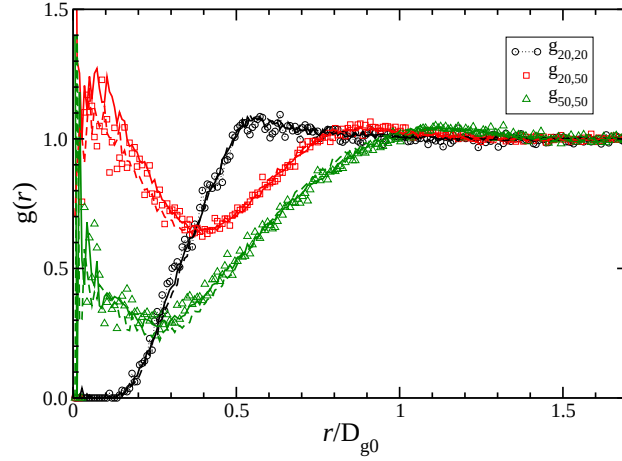


Figure 3.8: Pair correlation functions, at density $\rho^* = 1.2$, for the 1:1 mixture, in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid lines) and the isotropic effective model (dashed lines). Different colors refer to the pair correlation function between different types of rings (see legend).

emerges also in the anisotropic effective model, but it is much less pronounced than in the monomer-resolved system at the same density. The peak of the $g_{50,50}$ correlation function at $r \rightarrow 0$ is an indication of the formation of clusters, and the corresponding stacks are found both in the anisotropic effective and in the monomer-resolved systems. However, in the monomer-resolved case the peak is much more pronounced and correspondingly also the length of the stacks is increased (see below). Additionally, the $g_{20,50}$ curve exhibits a pronounced peak in the monomer-resolved system for $r \rightarrow 0$, which reflects that the clusters are formed both by $N = 50$ and $N = 20$ rings. In the anisotropic effective system this maximum is also visible but much less pronounced, indicating that there are less small rings locked within the columns than in the monomer-resolved system.

We introduce the function $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$, defined as the probability density distribution for the scalar product between the directors $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ of two ring polymers that are separated by a distance $r < 0.6D_{g0}$. Therefore, this function provides information about orientational correlations in the system. Figure 3.12 shows the former distribution, computed both for the monomer-resolved system and the anisotropic effective model, at the densities $\rho^* = 3.9$ and 15.7 . For the smaller density the anisotropic effective model and the monomer-resolved system are in very good quantitative agreement. For the larger density the rings in the monomer-resolved system are more likely to orient parallel with respect to each other, and correspondingly orthogonal orientations of the

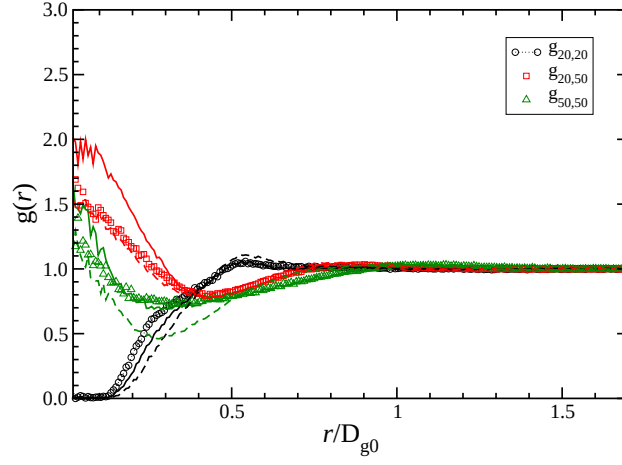


Figure 3.9: Pair correlation functions, at density $\rho^* = 3.9$, for the 1:1 mixture, in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid lines) and the isotropic effective model (dashed lines). Different colors refer to the pair correlation function between different types of rings (see legend).

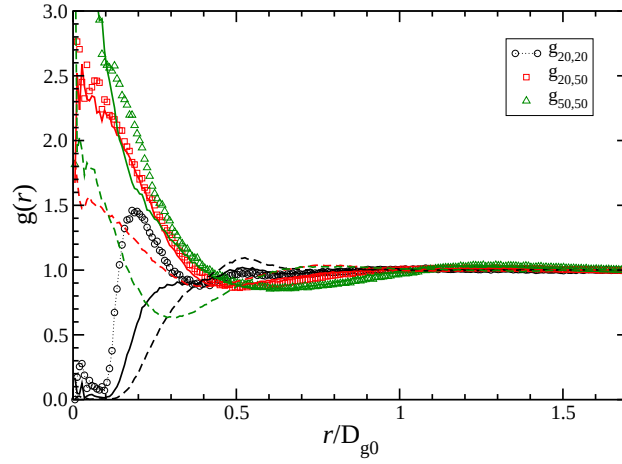


Figure 3.10: Pair correlation functions, at density $\rho^* = 10.0$, for the 1:1 mixture, in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid lines) and the isotropic effective model (dashed lines). Different colors refer to the pair correlation function between different types of rings (see legend).

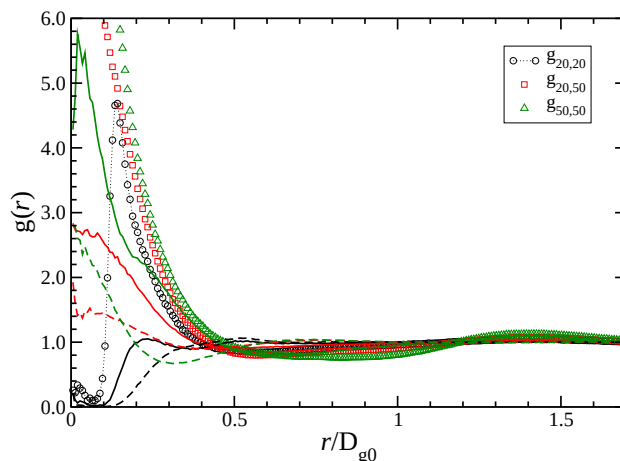


Figure 3.11: Pair correlation functions, at density $\rho^* = 15.7$, for the 1:1 mixture, in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid lines) and the isotropic effective model (dashed lines). Different colors refer to the pair correlation function between different types of rings (see legend).

directors are largely suppressed. This is consistent with the fact that the large rings in the monomer-resolved system are often part of long stacks, and are therefore almost parallel oriented with respect to each other. We will further elaborate on this in the next section. At the higher density, $\rho^* = 15.7$, the rings in the soft-disk mixture also exhibit an enhanced probability to orient parallel with respect to each other, but while the qualitative behavior is correct, this enhancement is much weaker than in the monomer-resolved case. Correspondingly, we will show in the next section that the rings also form stacks in the anisotropic effective model, though their length is reduced with respect to the monomer-resolved mixture at the same density.

Finally, we also carried out simulations of an asymmetric binary mixture, where 364 chains contained $N = 20$ and the other 1454 rings consisted of $N = 50$ monomers, we will call this system the 1:4 mixture in the following. The partial radial distribution functions for this solution are shown in figure 3.13 for the representative densities $\rho^* = 11.9$ and 18.6. The qualitative trends of the correlation functions, both for the monomer-resolved and the effective anisotropic model, are the same as those displayed in figure 3.11 for the symmetric mixture at a similar density $\rho^* = 15.7$. This finding suggests that there is a broad range of compositions in mixtures of small and intermediate rings that will present the qualitative scenario presented above.

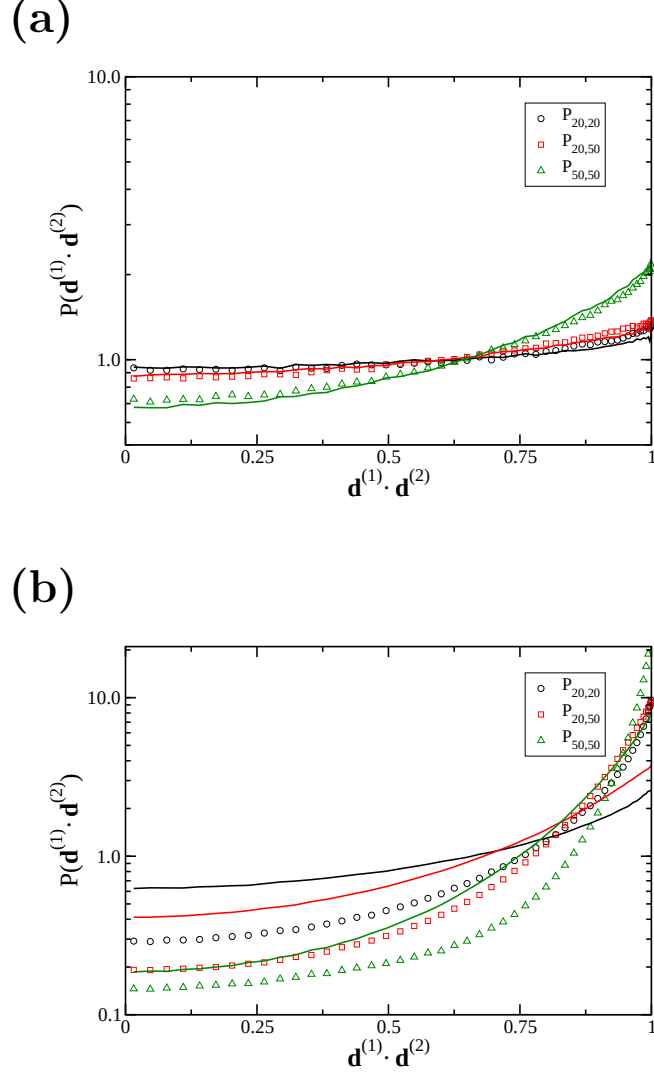
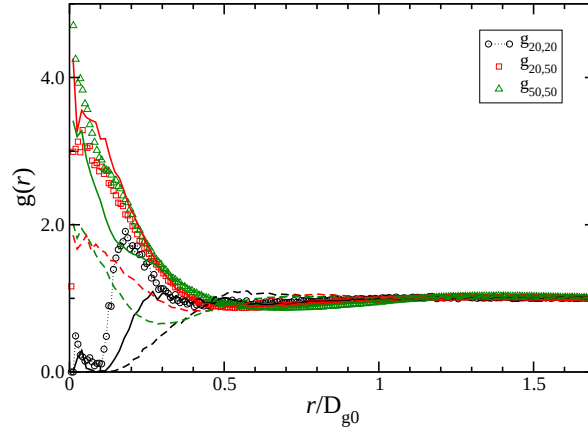


Figure 3.12: Probability density $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ for the scalar product $\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)}$ between the directors of two close-by rings ($r < 0.6D_{g0}$). The presented results are computed for the 1:1 mixture. Different data sets correspond to distributions for pairs of rings with identical or different N (see legend). Panels (a) and (b) show results for $\rho^* = 3.9$ and $\rho^* = 15.7$, respectively. Symbols correspond to monomer-resolved simulation data and lines to results obtained in simulations of the effective soft disks.

(a)



(b)

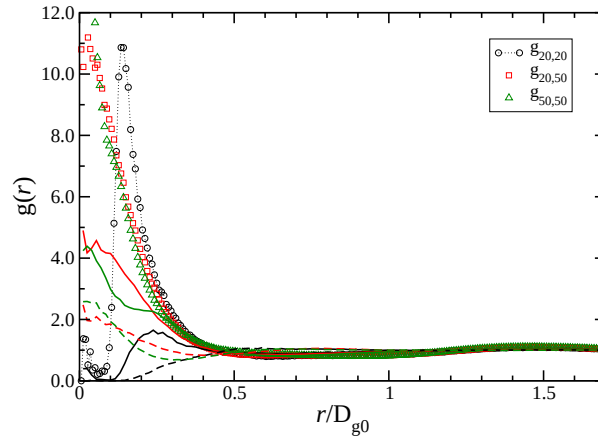


Figure 3.13: Pair correlation functions, at densities $\rho^* = 11.9$ (a) and 18.6 (b), for the 1:4 mixture in the full monomer-resolved simulation (symbols), the anisotropic effective model (solid lines) and the isotropic effective model (dashed lines). Different colors refer to the pair correlation function between different types of rings (see legend).

3.8 Formation of Stacks in Binary Mixtures

Finally, we characterize formation of stacks in binary mixtures of rings, to clarify whether monodispersity is a requirement for the formation of long columns, and to test if the anisotropic effective model for mixtures is able to capture the essential features of stacking at high densities. To this end, we have applied the algorithm described in section 3.3 to identify stacks of the large rings in configurations taken from simulations of the mixtures. First we concentrate on the 1:1 mixture, which contains the same number of rings with $N = 20$ and $N = 50$ monomers.

In figure 3.14 we show the same configuration of a monomer-resolved simulation at density $\rho^* = 15.7$ in four different representations (see caption). It can be seen that most rings are part of stacks containing 5 or more rings, which are interpenetrated by the small rings. The large rings are not only parallel with respect to each other, but their centers-of-mass are also aligned, which allows for an unblocked view through the columns if the small rings are not shown and the column stands along your view.

Figure 3.15 displays configurations of the soft-disk mixture at the densities $\rho^* = 15.7$ and 24.9. We can see that stacks are formed in the anisotropic effective system, but at the same density they are shorter than for the monomer-resolved case. The reason for this could be that the free energy penalty for a small ring which interpenetrates a column is overestimated because the effective potential is pairwise additive and we thus add up contributions due to interactions with many large rings. Analogously, a large ring can be interpenetrated by many small rings and the same interaction penalty is summed up for each additional interpenetration. In the monomer-resolved model on the other hand the free energy penalty could be smaller, since for instance the entropy of a large ring that is interpenetrated by a small one is restricted in first place and it might not reduce by the same amount if a second small ring is locked in. In figure 3.14, we can indeed see that in the full simulation it is common that large rings are simultaneously pierced by several small rings, while this hardly ever happens in configurations of the effective system displayed in figure 3.15. By increasing the density in the effective system we eventually encountered systems with a similar probability distribution $P(n_c)$ as observed in the monomer-resolved simulation at a smaller density. An example of this fact is illustrated in figure 3.16, where a configuration of the monomer-resolved mixture ($\rho^* = 10.8$) and of the effective soft-disk mixture ($\rho^* = 12.7$) are displayed. In both cases the small rings, as well as large rings not being part of a stack of at least 5 members are not shown. Both snapshots are qualitatively similar. The similarity observed in these snapshots at this and other densities suggests that the anisotropic effective model is at least qualitatively able to reproduce the formation of stacks also for the case of binary mixtures.

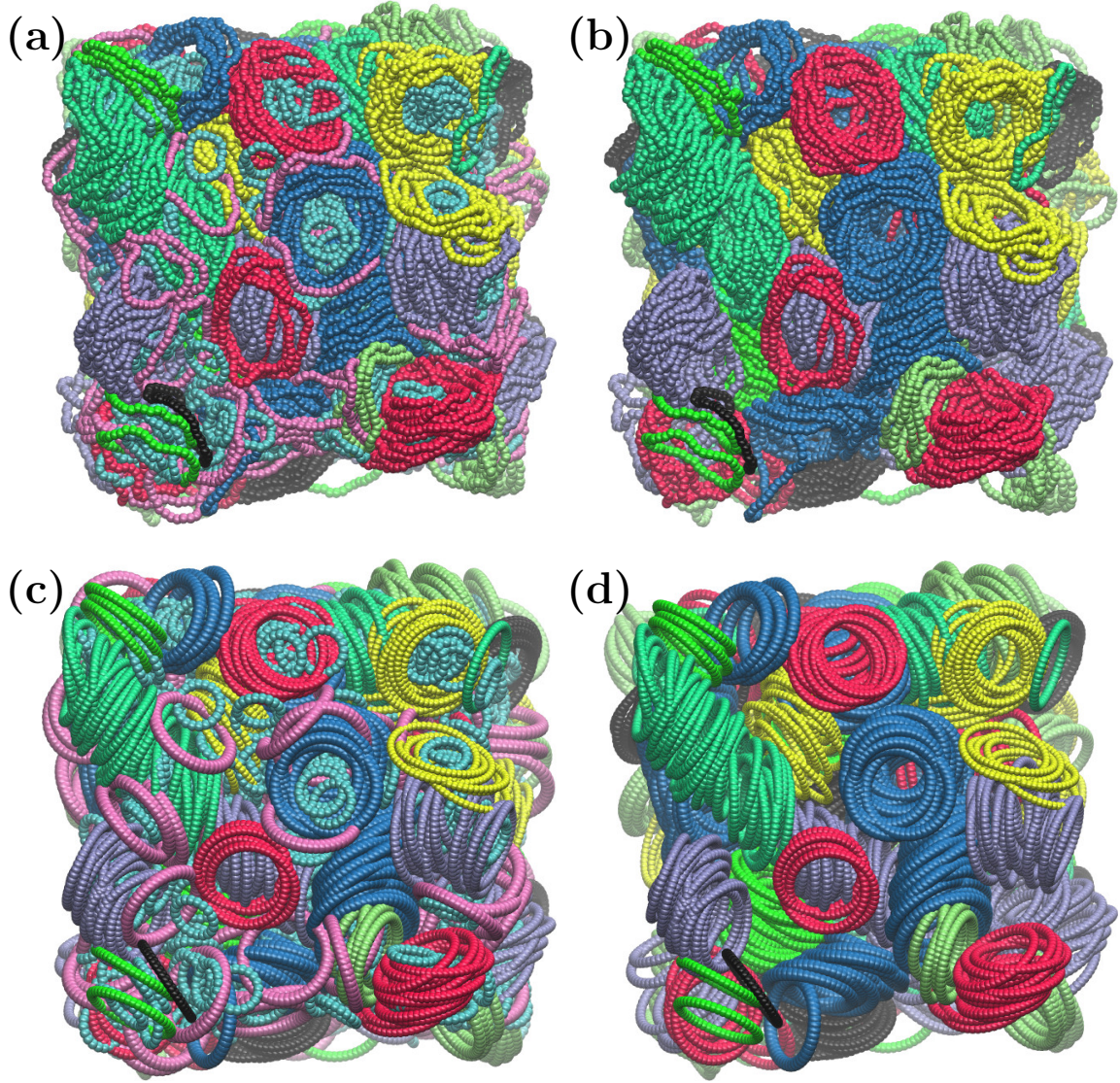


Figure 3.14: Visualizations of the same configuration of a monomer-resolved simulation for the 1:1 mixture at density $\rho^* = 15.7$. Large rings which are part of the same stack have identical colors. If the stack has less than 5 members they are colored pink. All small rings are colored turquoise. In (a) we show a snapshot with all the rings, while in (b) the pink and turquoise rings are not shown. For displaying the snapshots (c), (d) we have first computed the effective coordinates (centers-of-mass and directors) of the *monomer-resolved rings* (not to be confused with the soft disks of the simulations of the effective model). Then we have represented the real rings by perfect circles with the same centers-of-mass and directors as the corresponding real rings. Moreover the circles have a radius R_{g0} (different for $N = 20$ and $N = 50$) identical to that of the corresponding real rings at zero density. The representation of the snapshots (c), (d) in terms of the effective coordinates facilitates visualization of the internal structure of the stacks. In (c) all the rings are displayed. The pink and turquoise rings are not shown in (d).

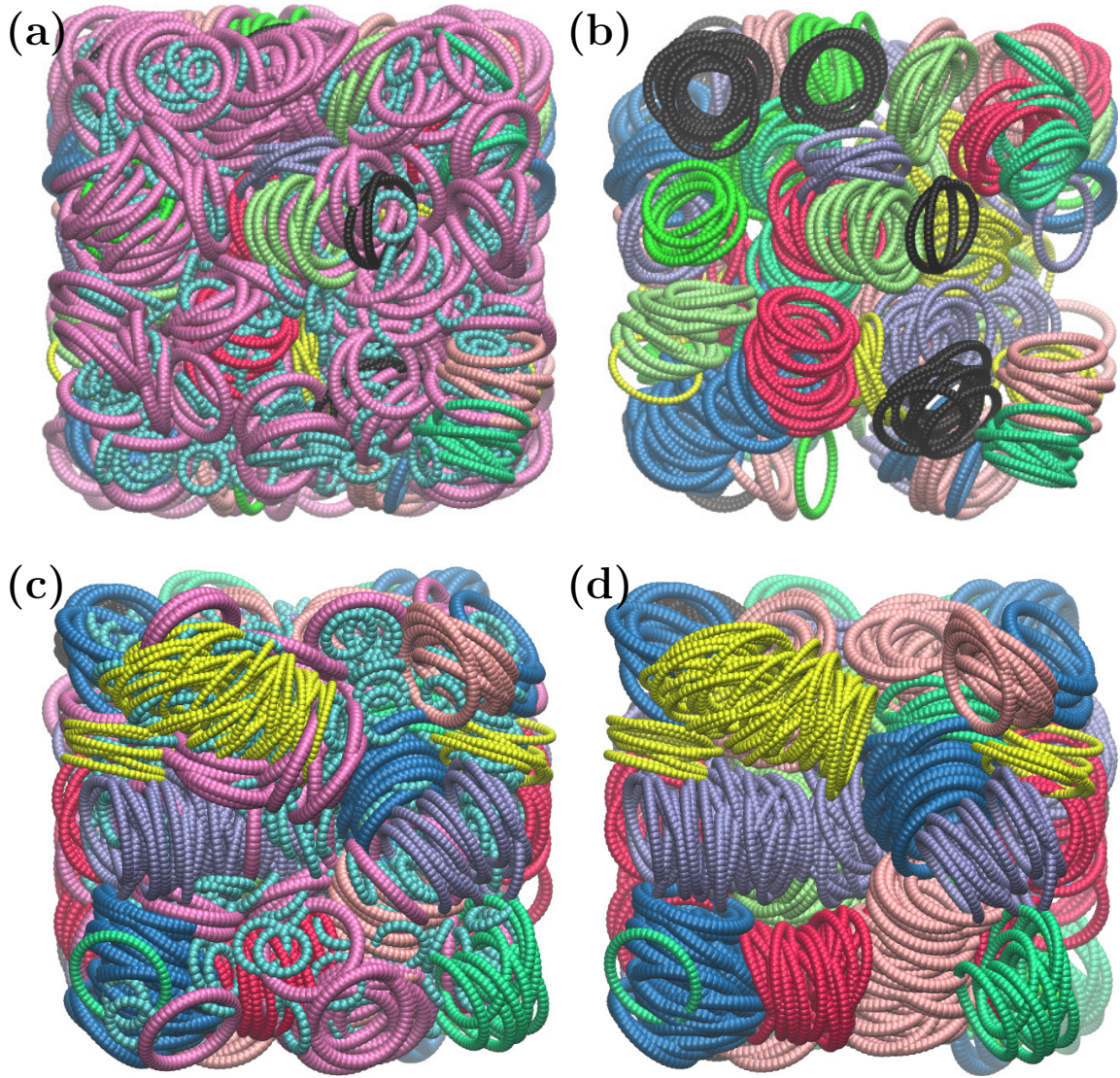


Figure 3.15: Snapshots of a simulation of effective soft disks, representing the 1:1 mixture. The effective particles are visualized by perfect circles, with centers-of-mass and directors identical to those of the effective particles. Large rings which are part of the same stack have identical colors. If the stack has less than 5 members they are colored pink. All small rings are colored turquoise. The snapshots (a), (b) are taken from a simulation at density $\rho^* = 15.7$, while (c), (d) are for the density $\rho^* = 24.9$. The snapshots in (a), (c) contain all particles simulated, while the turquoise and pink particles are not shown in (b), (d).

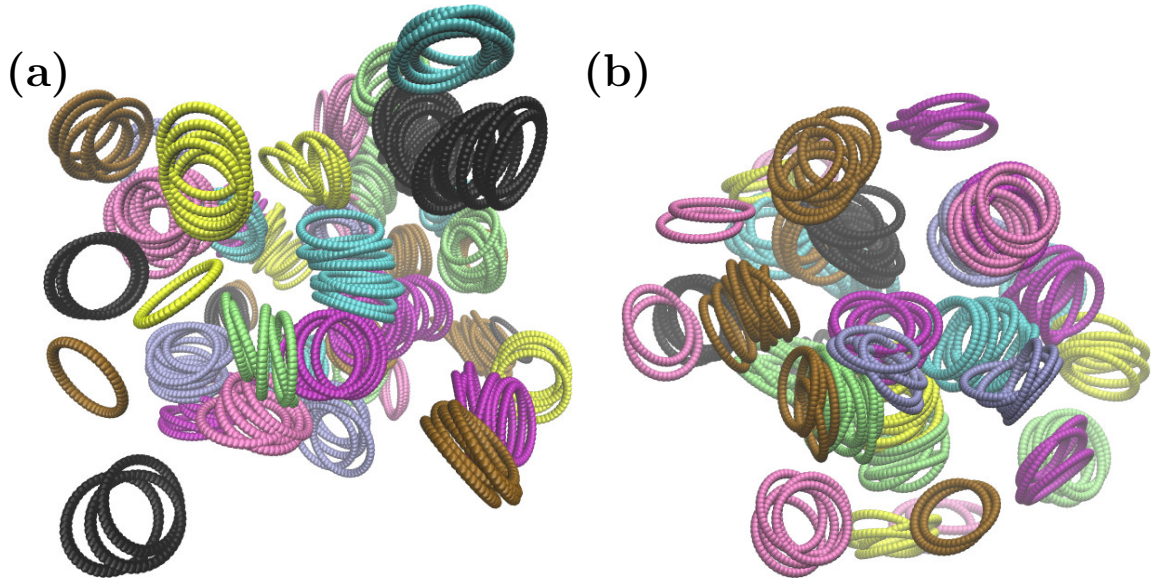


Figure 3.16: Snapshot (a) represents a visualization of the effective degrees of freedom in a configuration taken from a monomer-resolved simulation at density $\rho^* = 10.8$, while (b) represents a configuration from a simulation of the anisotropic effective model at $\rho^* = 12.7$. In both cases the small rings, as well as large rings which are not part of a stack with at least 5 members, are not shown.

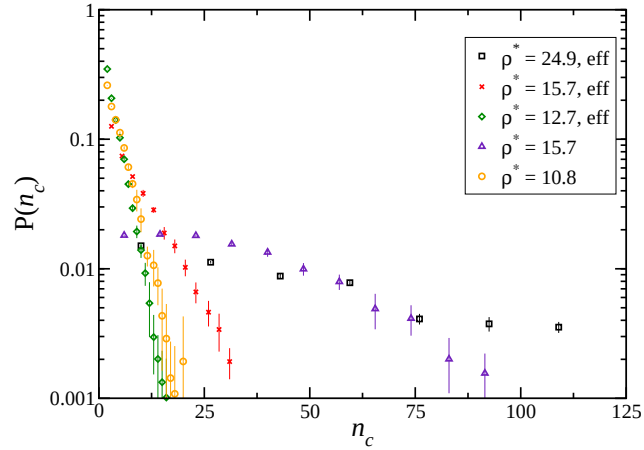


Figure 3.17: Probability distribution, $P(n_c)$, for a large ring to be part of a stack with n_c members, in simulations of the 1:1 mixture.

Figure 3.17 shows the probability $P(n_c)$ for an individual large ring to be part of a stack with n_c members. As in the monodisperse case, we find that for a given monomer-resolved system there exists an effective soft-disk system, at a higher density, with a similar stack size distribution. The formation of stacks is typically accompanied by a

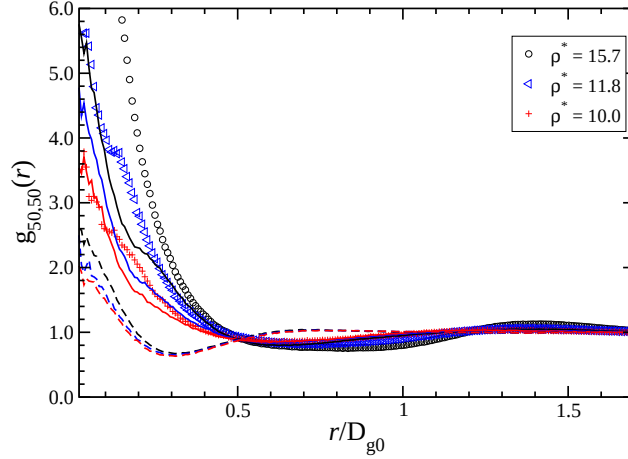


Figure 3.18: Radial pair distribution function of the large rings for a simulation of the 1:1 mixture. Data is shown for the monomer-resolved simulation (symbols), the anisotropic effective model (solid lines) and the isotropic effective model (dashed lines).

high maximum at $r \rightarrow 0$ in the radial distribution function of the large rings. This can be seen in figure 3.18 where we plot this correlation function for the monomer-resolved and the anisotropic effective models. While the maximum is lower in the soft-disk model than in the monomer-resolved one, it also increases with the density.

Finally, we have also characterized stacks in simulations of the 1:4 mixture. Figure 3.19 shows two representations of the same configuration, for density $\rho^* = 18.6$, of the monomer-resolved 1:4 mixture. We can see that the system still forms long columns of large rings penetrated by small ones. In snapshot 3.19a all the rings are displayed, while in 3.19b only the small rings are shown. Interestingly, the small rings do not fill all the columns formed by the large ones. Moreover, the columns in which the small rings are present are not filled homogeneously; the small rings agglomerate within some tubes formed by the large rings, while others remain hollow of small rings. This agglomeration is consistent with the sharp peak observed in the radial distribution function of the small rings $g_{20,20}$ (see figure 3.13 above). The fact that the small rings aggregate within the large rings could mean that the free energy penalty of many small rings interpenetrating a few large ones is smaller than that of many large rings being interpenetrated by

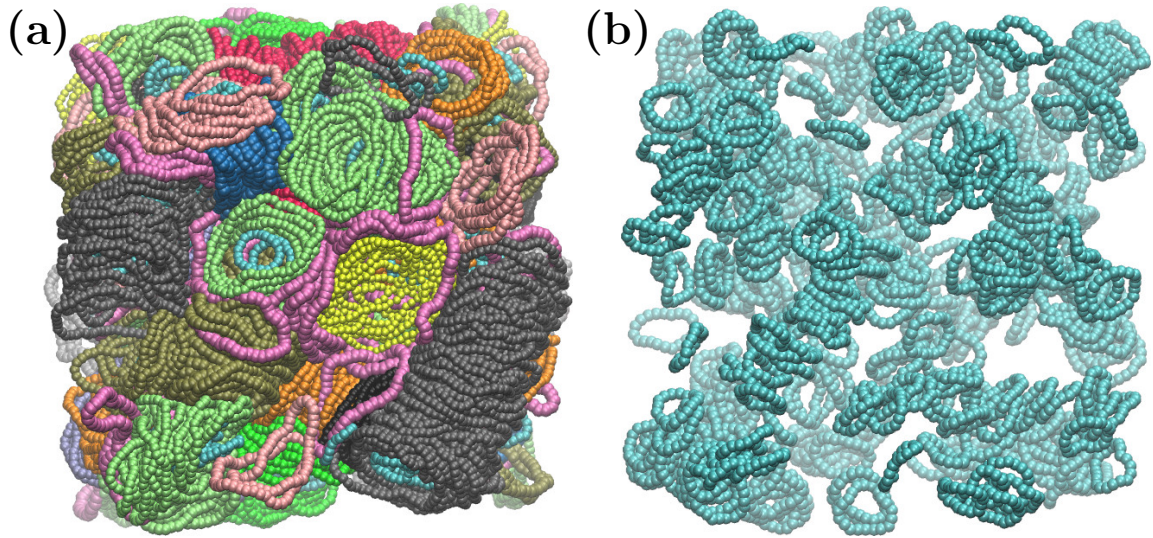


Figure 3.19: Visualizations of a configuration from a monomer-resolved simulation of the 1:4 mixture at density $\rho^* = 18.6$. In **(a)** we show a snapshot with all the rings, while in **(b)** only the small rings are shown.

individual small rings. This interpretation is also consistent with the reduced amount of interpenetration observed in the anisotropic effective model. This only includes pair interactions and therefore does not take into account that, for the real rings, the energy penalty of inserting an additional small ring inside a large one is not necessarily identical to the free energy penalty due to the interpenetration of the first small ring. A snapshot of the asymmetric effective soft-disk mixture at the former density $\rho^* = 18.6$ is displayed in figure 3.20. Again, columns are formed in the effective system but the stacks are smaller than in the monomer-resolved case. Finally, figure 3.21 shows the probability distribution $P(n_c)$ for the asymmetric mixtures in the monomer-resolved and effective soft-disk models. We find the same qualitative features as in figure 3.17 for the symmetric mixtures.

3.9 Conclusions

We have presented extensive simulations of concentrated solutions of semiflexible ring polymers. These systems form phases containing columnar, tube-like structures of quasi-parallel rings (stacks). This feature, which cannot be captured by the standard isotropic effective interactions, is qualitatively reproduced by an anisotropic effective model. In this model the effective interactions do not only depend on the distance between macro-molecular centers-of-mass, but also on the relative orientations. We have introduced a

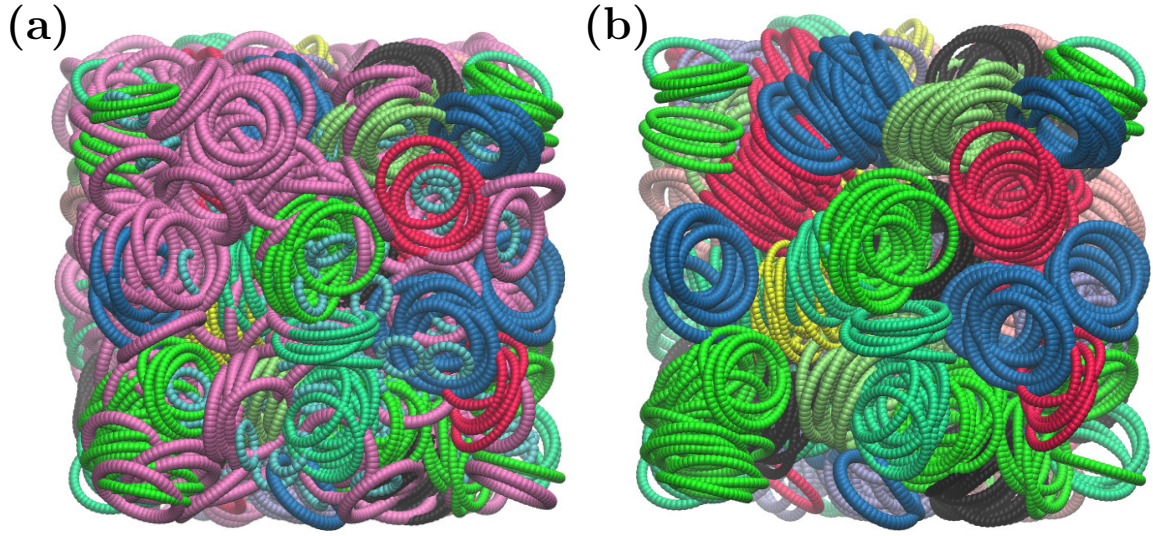


Figure 3.20: Snapshots of a simulation of effective soft disks, representing the 1:4 mixture at density $\rho^* = 18.6$. The effective particles are visualized by perfect circles with centers-of-mass and directors identical to those of the corresponding effective particles. The snapshot in (a) displays all particles simulated. The small rings (turquoise), as well as the large rings that are not part of a stack with at least 5 members (pink), are not shown in (b).

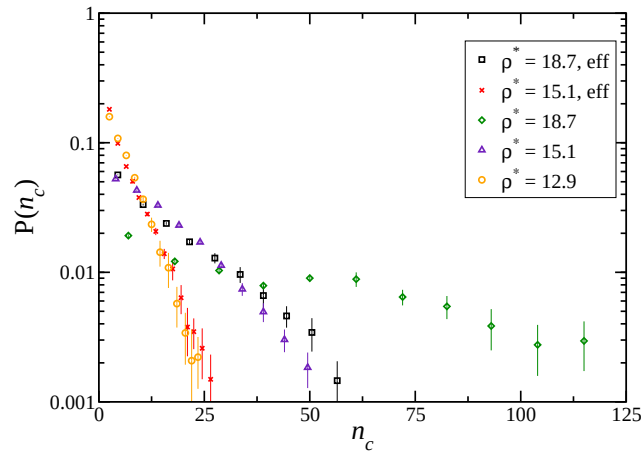


Figure 3.21: Probability distribution, $P(n_c)$, for a large ring to be part of a stack with n_c members in simulations of the 1:4 mixture.

simple algorithm to identify and characterize the stacks. Though, for the same density, the stacks are longer in the monomer-resolved system than in the effective anisotropic model, long stacks can be formed in both models at sufficiently high concentrations. The anisotropic model is, in general, clearly superior to the isotropic model. However, in ref. [97] it was shown that, for semiflexible rings with a significant degree of deformability, the isotropic effective model provided a better description of the real system than the anisotropic model in the range of density investigated there. This was attributed to the overestimation of the orientational effects in the interactions between such deformable rings. However, by further increasing the density, we have found that such rings expand themselves to optimize packing, stacks are formed and the anisotropic model provides again a superior description over the isotropic model.

We have extended the effective model to the case of binary mixtures of ring polymers, and compared it with simulations of the corresponding monomer-resolved mixtures. The simulations reveal stack formation in both models for a broad range of mixture compositions, demonstrating that stacking is highly resilient to polydispersity. As expected, the stacks in asymmetric mixtures are mostly constituted by columns of large rings. The small rings tend to be located inside of such columns. However, they do not fill them homogeneously but form agglomerates within the columns.

4 Density Functional Theory for Isotropic and Anisotropic effective models of Semiflexible Ring Polymers in the bulk and under confinement

4.1 Introduction

In the early days of computer simulations, the famous physicist Eugene Wigner playfully criticized the attitude that it is sufficient to solve problems with the help of massive computations by saying: *"It is nice to know that the computer understands the problem. But I would like to understand it too"*. While there is of course also great value in the brute-force application of computer simulations to numerically obtain the predictions of physical laws which would often be impossible to obtain otherwise, they can in addition be useful to establish the validity of simplified pictures for complex systems, that allow us humans to better understand these models by pen and paper. Likewise computer simulations can often show us where our simple minded pictures of the complex systems start to fail. By applying density functional theory (DFT) to the effective models for the coarse-grained description of semiflexible ring polymers, developed in chapter 2, we want to establish in how far the simplified pictures offered by mean field theory and the so-called hypernetted chain approximation are valid for the description of the effective models.

There are plenty of examples for the application of DFT for systems with isotropic interaction potentials [101], where the theory results in self-consistent equations that can be solved numerically by an iterative scheme. Often it is computationally less demanding to solve these self-consistent equations than to carry out molecular simulations of the system and the theory therefore allows for an efficient exploration of a wide range of parameters of the model. However, the theory can also offer additional physical insights into the system, since it provides a simplified description and is therefore in a way also a coarse-graining of the studied system. So even for systems that have already been simulated for a wide range of parameters it can be useful to study them with density functional theory. If the theory is able to successfully reproduce the results of simulations this motivates the validity of the assumptions that it makes about the system and allows us to think about the physics involved in terms of the transparent picture offered by the theory. With this physical picture in mind, it is sometimes possible to obtain understanding for results observed in computer simulations. A good example for this is Ref. [8], where the authors show why a wide range of models with particles interacting via a purely repulsive soft isotropic potential form cluster-crystals under sufficiently high

densities. They established that models with an interaction potential from the so-called $Q^\pm$ -class, which consists of the functions that have both positive and negative Fourier components, do form cluster crystals. Carrying out computer simulations they could have found that each individual model of that class forms a cluster crystal, but only by the application of the simplified picture offered by mean field theory, they were able to see the reason why this criterion is important for the formation of cluster crystals. In addition DFT allows to treat homogeneous and inhomogeneous systems on equal footing, to transparently separate the various contributions (energy, entropy, ideal and excess free energy) to the free energy and to examine the stability of different candidate structures.

In this chapter, we will also look at systems of ring polymers close to a wall and between two walls. To this end, we have carried out additional Monte Carlo Simulations to which our predictions from density functional theory can be compared and we will show that the behavior of the effective particles under confinement by itself is interesting. We will limit ourselves to the effective models presented in chapter 2 for the rings with $N = 50$ monomer units. We will first concentrate on density functional theories of the effective models in the bulk and then look at the anisotropic effective system in the presence of one or two walls. In appendix C we discuss the foundations of the theoretical methods applied in detail.

4.2 Density Functional Theory for the Isotropic Effective System in the Bulk

In appendix C.1 we have described how to use density functional theory (DFT) to derive several approximate self-consistent equations for the radial distribution function $g(\mathbf{r})$ of a system of identical particles that interact via a pair potential $v(\mathbf{r})$. We now apply these equations to the isotropic effective model we have derived in chapter 2, where rings are represented by point particles interacting via a spherically symmetric interaction potential $v(r)$, which is visualized in figure 2.2. In chapter 2 we have also carried out Monte Carlo simulations of the isotropic effective model and have measured the radial distribution function $g(r)$ in these simulations. We will compare the results for the pair correlation function $g(r)$ measured in simulations with the predictions obtained using the self-consistent equation from mean field theory (MFT) given in Eq. (C.42) and the Hypernetted chain (HNC) closure (C.33) in combination with the Ornstein-Zernike equation (OZE) (C.24). For the spherically symmetric potential $v(r)$, the self-consistent equation from MFT simplifies to

$$g(r) = \exp \left[-\beta \rho \int d\mathbf{r}' [g(r') - 1] v(|\mathbf{r} - \mathbf{r}'|) - \beta v(r) \right], \quad (4.1)$$

and the OZE together with the HNC closure read

$$c(r) = g(r) - 1 - \rho \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) [g(r') - 1], \quad (\text{OZE}) \quad (4.2)$$

$$g(r) = \exp[-\beta v(r)] \exp[g(r) - c(r) - 1]. \quad (\text{HNC})$$

Here ρ corresponds to the bulk density and $c(r)$ to the direct correlation function. We have solved these equations using the numerical methods discussed in appendix C.1.7 for the isotropic effective model with the boundary condition that $g(r) = 1$ for $r > 2.0D_{g0}$. In figure 4.1 we show results for the reduced densities $\rho^* = 1, 2, 5, 10$ and 20 . The agreement between theory and simulation is excellent up to the highest density of $\rho^* = 20$. In general the HNC approximation works slightly better than MFT at low densities, while the predicted $g(r)$ curves from MFT and HNC at the higher densities are practically identical. This indicates that the mean field theory assumption works particularly well at high densities. If one considers a spherical shell of thickness Δr around a selected particle, where the shell contains all its neighbors which have a distance $r \in [R_S, R_S + \Delta r]$, then this shell will of course always contain an integer amount of particles for every single configuration. In MFT we approximate the amount of particles in the shell by its average over all configurations. The more particles there are in the system, the less the actual amount of particles in the shell fluctuates around this average for different configurations and the better the MFT approximation therefore becomes. Our results therefore confirm that the HNC as well as the MFT approximations are an excellent tool to investigate the isotropic effective system, even at very high densities, where simulations require more computational resources. However, the isotropic effective model itself does not describe semiflexible rings well at densities $\rho^* \gtrsim 2$.

4.3 Density Functional Theory for the Anisotropic Effective System in the Bulk

While the anisotropic effective system is at higher densities more truthful to the underlying monomer resolved model, it is also more challenging to apply density functional theory for it. In appendix C.2 we have discussed how the density functional approach for point-particles can be generalized for disks, which are described by their center of mass $\mathbf{r}$ and their director $\mathbf{d}$. In the resulting theory, it is again possible to derive an Ornstein-Zernike equation, which we have displayed in Eq. (C.69), the well known closure relations like the HNC closure, which is given in Eq. (C.70). Alternatively one can also apply MFT to obtain the self-consistent equation (C.72). While the extension of density functional theory to disk like particle follows naturally, the resulting equations

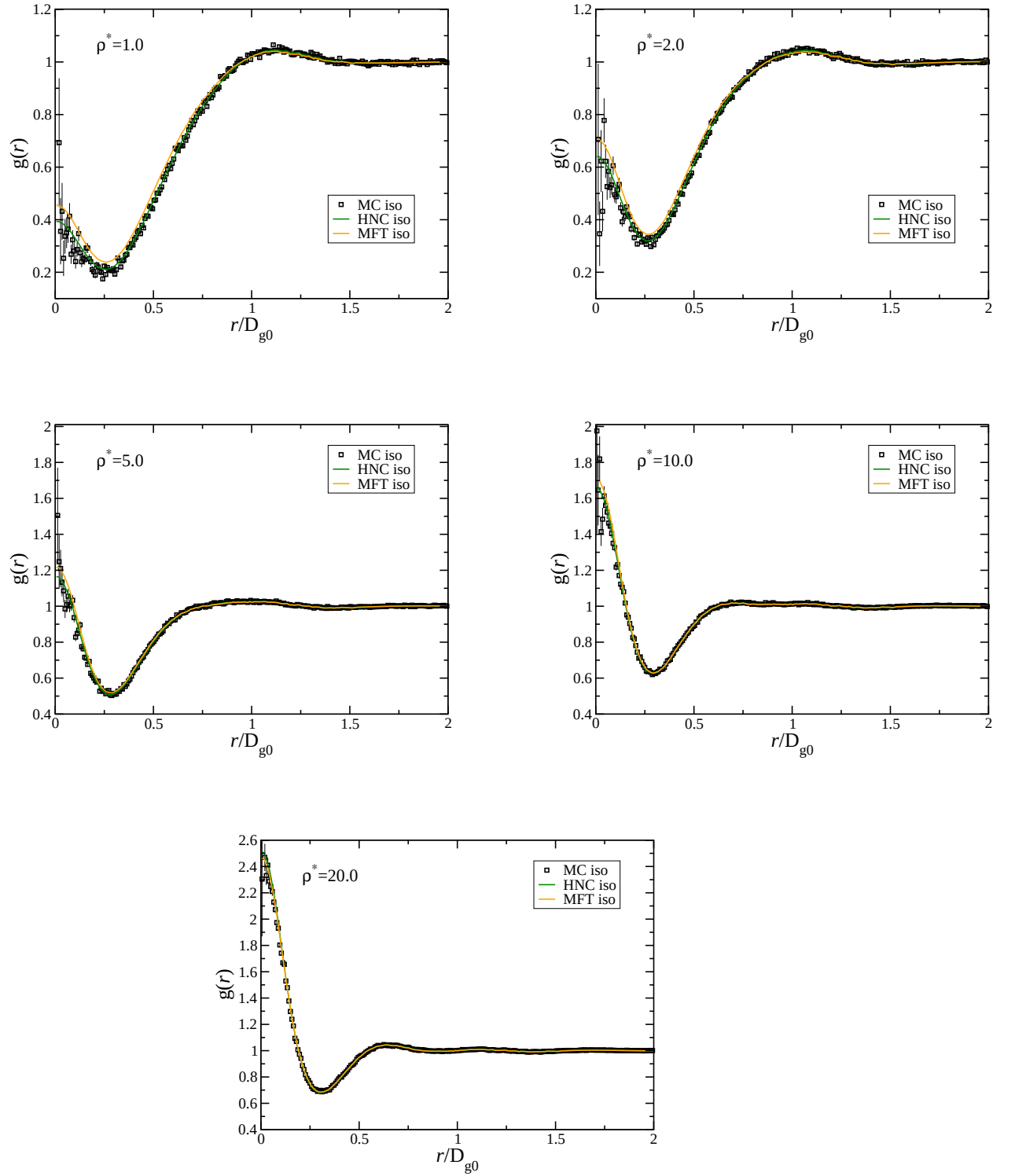


Figure 4.1: Pair correlation function $g(r)$ for a system of particles interacting via the isotropic effective interaction potential $v(r)$ for rigid rings. The plots show results at various reduced densities ρ^* obtained in Monte Carlo simulations (MC iso), with the HNC closure (HNC iso) and the MFT approximation (MFT iso).

are more challenging. We have solved the equations with the same iterative schemes we have employed in the case of the isotropic effective model, however the three dimensional convolutions of spherical symmetric functions which we had to solve in every iteration step are now replaced by integrals of the type

$$\int d\mathbf{r}' d\Omega f(\mathbf{r}, \mathbf{d}_1, \mathbf{d}) h(\mathbf{r} - \mathbf{r}', \mathbf{d}, \mathbf{d}_2). \quad (4.3)$$

This corresponds to a 5 dimensional integration, which we need determine for every choice of $(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$. As discussed in appendix C.2.3, we can use the rotational symmetry of the functions f, h and apply the fast Fourier transformation algorithm to make the evaluation of such integrals feasible, but nevertheless every iteration steps now takes several minutes instead of fractions of a second, depending also on the resolution of the grids on which one tabulates the functions f and h . In appendix C.2.3, where our algorithm for the computation of the integral (4.3) is described, we parametrize the coarseness of the grids with $\{N_{\cos\theta_2}, N_{\cos\theta}, N_\varphi, N_r\}$, which correspond to the number of grid points in different variables. For this work we have used $N_{\cos\theta_2}, N_{\cos\theta}, N_\varphi = 8$ and $N_r = 32$. We have solved the self-consistent equations for the HNC and the MFT approximation with the boundary condition $g(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = 1$ for $r > 1.7D_{g0}$, where D_{g0} is the diameter of gyration of a ring in the infinitely dilute system. From the anisotropic pair-correlation function $g(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$, which we obtain as the result of the iteration schemes, we have computed the isotropic pair correlation function $g(r)$, which we have also determined in Monte Carlo simulations of the system of disk-like particles in chapter 2. In figure 4.2 we present the prediction for $g(r)$ from DFT at densities up to $\rho^* = 5$ and compare them with the corresponding simulation results. While MFT was quite successful in predicting the pair correlation function $g(r)$ in the effective model with isotropic interactions, its results are now much worse than those obtained via the HNC approximation for all investigated densities ρ^* . One reason why MFT is unsuccessful in making accurate predictions is that the anisotropic interaction potential is in fact not soft everywhere, but can become very high and steep for certain relative orientations of the rings, as we have seen in figure 2.4. This renders MFT less accurate because it assumes that for every configuration the distribution of other particles around a selected one is given by the anisotropic pair correlation function $g(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$. This however leads to big interaction energies between particles in the vicinity of the selected one, since according to the MFT approximation they can assume orientations with respect to each other that involve very high energies. For this reason, we should expect MFT to overestimate the strength of the interaction between the particles, and we can indeed see from our results that at given density ρ^* MFT predicts a $g(r)$ that looks similar to the result which the MC simulation obtains at

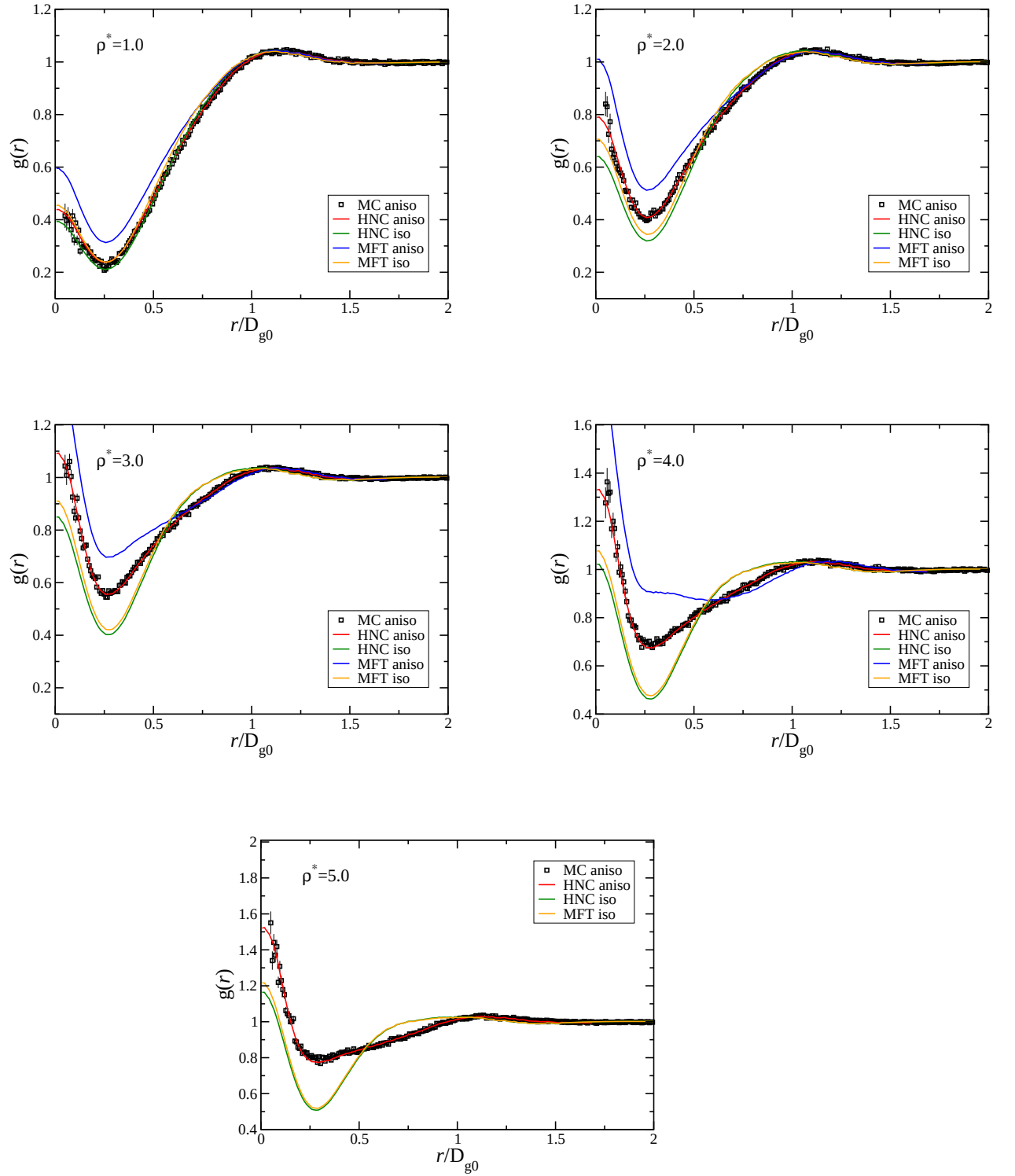


Figure 4.2: Pair correlation function $g(r)$ from a MC simulation of the effective system with anisotropic interactions (MC aniso), density functional theory of the anisotropic and isotropic system employing the HNC closure (HNC aniso/iso) and the MFT approximation (MFT aniso/iso). The plots show results at various reduced densities ρ^* .

a higher density. Another reason why MFT might be in general worse for systems that involve multiple particle types* is that we now not only assume that the overall number of particles in a thin spherical shell around a reference particle is always identical but that this is true for the number of each particle type individually. This is of course an even stronger statement than the assumption of MFT in the isotropic system, where there is only one particle type and the assumption seemed to be very accurate at $\rho^* = 5$, which of course was also facilitated by the softness of the interaction potential. For $\rho^* = 5$ we do not show results for the MFT of the anisotropic system, because the numerical iteration scheme did not converge there. The good news, however, is that the HNC approximation gives us a $g(r)$ result which is virtually indistinguishable from the result obtained in MC simulations for all densities investigated. This means that we should be able to use the HNC approximation to understand the anisotropic effective model at least up to densities $\rho^* = 5$. There is no indication of a breakdown of the HNC approach at higher densities; we just stopped somewhere. In figure 4.2 we have also plotted the results from the isotropic density functional theories, which give good agreement for $\rho^* = 1$, but the effect of anisotropy is already significant at $\rho^* = 2$.

From the anisotropic pair correlation function $g(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$ we can also predict $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$, which we have defined in section 2.5 as the probability distribution for the scalar products between the directors $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ of two effective particles which are a distance $r < 0.6D_{g0}$ away from each other. In figure 2.11 we have compared results for $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ obtained in the monomer-resolved and the effective systems. To compute $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ from the anisotropic pair correlation function, we have iterated through the whole grid on which we have tabulated $g(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$. For each grid point we have randomly generated 20 effective variables within the bin around that grid point and for each of these points in effective variable space we have computed $\mathbf{d}_1 \cdot \mathbf{d}_2$, provided that $r < 0.6D_{g0}$. We have thus obtained a list of $\mathbf{d}_1 \cdot \mathbf{d}_2$ values, which we have then weighted by the pair correlation function at the respective grid point to obtain a histogram for $\mathbf{d}_1 \cdot \mathbf{d}_2$. After the normalization this histogram is the prediction for $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ from the DFT approach by which the respective anisotropic pair correlation function was computed.

Results for $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ from density functional theory and MC simulations of the effective system with anisotropic interaction are shown in figure 4.3. As for the isotropic pair correlation function $g(r)$ the results of MFT overestimates the change of the $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ distribution function with respect to the infinitely dilute case. The HNC approximation on the other hand stays very close to the result from MC simulations and correctly

*In appendix C.2.2 we have argued that a system with anisotropic interactions can be understood as a system of point particles of multiple types corresponding to the different orientations of the directors.

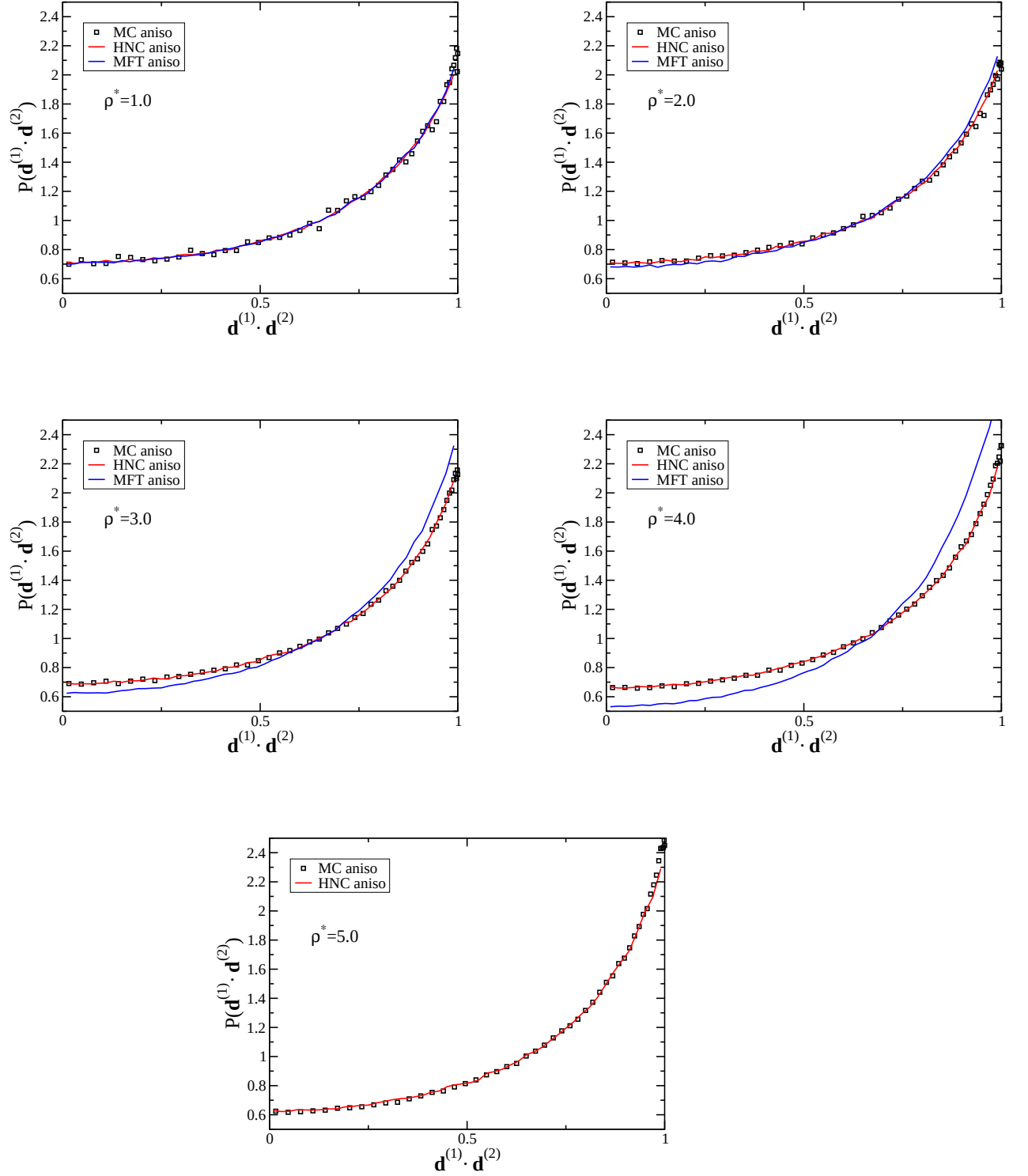


Figure 4.3: Probability distribution for the scalar product between directors of nearby particles $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ from a MC simulation of the effective system with anisotropic interactions (MC aniso), density functional theory of the anisotropic system employing the HNC closure (HNC aniso) and the MFT approximation (MFT aniso). The plots show results at various reduced densities ρ^* .

predicts the small change of $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ from density $\rho^* = 1$ to $\rho^* = 5$.

We have therefore seen that the HNC approximation is able to accurately predict the two observables $g(r)$ and $P(\mathbf{d}^{(1)} \cdot \mathbf{d}^{(2)})$ for the system with anisotropic effective interactions. In the next section we will follow up on these promising results from density functional theory to make predictions for the distribution of disks in the presence of a wall.

4.4 System of Effective Particles in Confined Geometries

We have carried out Molecular Dynamics simulation of a monomer-resolved ring in the presence of a wall to determine the effective ring-wall potential. To this end, we have employed the same methods and the same underlying model for the monomer resolved rings as in section 2.2. For the monomer-wall interaction potential we have used

$$V_{\text{wall}}(z) = \begin{cases} \epsilon \left[\frac{2}{15} \left(\frac{\sigma}{z} \right)^9 - \left(\frac{\sigma}{z} \right)^3 + \frac{\sqrt{10}}{3} \right] & \text{if } z < \left(\frac{2}{5} \right)^{1/6} \sigma; \\ 0 & \text{if } z \geq \left(\frac{2}{5} \right)^{1/6} \sigma, \end{cases} \quad (4.4)$$

where z denotes the distance of the monomer to the wall. The energy scale ϵ and the length σ also appear in the Lennard-Jones interaction between monomers in Eq. (2.1). If the space for $z < 0$ was homogeneously filled with Lennard Jones interaction sites, $V_{\text{wall}}(z)$ without the cutoff would describe the force that a particle feels for $z > 0$. We have introduced the cutoff such that the wall potential is purely repulsive. For a system containing only one wall and a single ring polymer we have obtained a distribution function $P_{\text{wall}}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ that is proportional to the probability that the center of mass of the ring is found a distance z away from the wall, and that the scalar product of its director $\mathbf{d}$ with the vector normal to the wall is $\mathbf{d} \cdot \hat{\mathbf{z}}$. We have chosen the normalization such that $P_{\text{wall}} = 1$ for $z \rightarrow \infty$, and have visualized this function in figure 4.4.

The behavior of P_{wall} is quite intuitive: The center of mass of rings with a director orthogonal to the wall can come closer to the wall than rings with a director parallel to the wall. For rings with a director parallel to the wall, the range where P_{wall} is between 0 and 1 is larger than for rings with an orthogonal director. The reason for this is that rings with their surface standing orthogonal to the wall can be squeezed which makes it possible for their center of mass to come closer to the wall. However the squeezing also costs energy and thus the probability for these squeezed states is suppressed. Therefore there is a range of wall-distances, corresponding to squeezed states of the rings, for which P_{wall} is between 0 and 1. While individual monomers can approach the wall up to the distance $\left(\frac{2}{5} \right)^{1/6} \sigma \approx 0.066D_{\text{g0}}$ without feeling any energy penalty from the wall, even rings with a surface parallel to the wall have a very small probability to approach the wall closer than $0.2D_{\text{g0}}$, because the entropy of the allowed configurations of the monomers of a ring

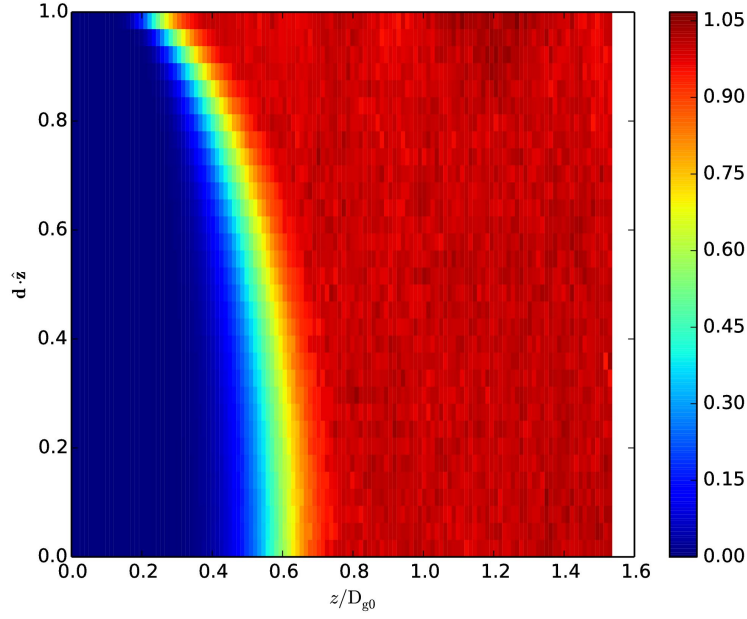


Figure 4.4: Visualization of P_{wall} , which is proportional to the probability that a single ring polymer is located a distance z away from the wall and that the scalar product of its director $\mathbf{d}$ with the vector normal to the wall is $\mathbf{d} \cdot \hat{\mathbf{z}}$.

is significantly affected if its center of mass is held very close to the wall. The wall is purely repulsive, and thus P_{wall} values are, within numerical accuracy, lower or equal to unity. In the anisotropic effective model we then use the potential

$$\Phi_{\text{wall}}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) \equiv -k_B T \log(P_{\text{wall}}) \quad (4.5)$$

to effectively describe the interaction between a ring polymer and the wall.

For a small Δz and $\Delta \cos \theta$, the one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ allows us to compute the average number of rings with a distance $z \in [Z, Z + \Delta z]$ to the wall and a director $\mathbf{d}$ that has a scalar product $\mathbf{d} \cdot \hat{\mathbf{z}} \in [\cos \theta, \cos \theta + \Delta \cos \theta]$ with the unit vector $\hat{\mathbf{z}}$ that stands orthogonal to the wall, as $\rho^{(1)}(Z, \cos \theta) \Delta z \Delta \cos \theta$. In this work, we have studied $\rho^{(1)}$ in the presence of a wall and between two walls. To this end, we have carried out Monte Carlo (MC) simulations, where we have directly measured $\rho^{(1)}$ and we also determined $\rho^{(1)}$ by applying Density Functional Theory (DFT). In appendix C.3, we have discussed two different self-consistent equations for $\rho^{(1)}$. Eq. (C.85) was derived employing the MFT approximation, while Eq. (C.82) corresponds to a first order expansion of the direct correlation function $c^{(1)}$ in density deviations $\Delta \rho^{(1)}$ with respect to the homogeneous system in the absence of the wall. The derivation of the latter equation follows the same approach that we have used to derive the HNC approximation for the

bulk system in appendix C.1.4 and we have also used the results from the HNC approximation to provide the direct pair-correlation function $c^{(2)}$ of the bulk system which is required to apply Eq. (C.82). For these reasons, we will refer to the solutions of the self-consistent Eq. (C.82) as results obtained via the HNC approach. We want to point out that the direct pair-correlation function $c^{(2)}$ of the bulk system is of course density dependent and since we have only solved the HNC equation for the bulk up to density $\rho^* = 5$ we can strictly speaking not apply Eq. (C.82) at higher densities. However we will nevertheless try to apply this approach at slightly higher densities using the direct pair-correlation function $c^{(2)}$ computed at density $\rho^* = 5$.

To solve the self-consistent equations we have used the iterative approach described in appendix C.1.7 and have carried out all the integrations numerically in real space without the use of the convolution theorem. This was possible because the required integrations were computationally much simpler than the ones of the type (C.74) that we have faced in the preceding section. In the case of the computations with one wall, we have set $\rho^{(1)}$ equal to the bulk density ρ for $z > 4.0D_{g0}$ and for the computations between two walls we simply set $\rho^{(1)} = 0$ outside the walls*.

For the MC approach, we have always simulated 3200 particles between two walls. To compare to the density functional results obtained for a single wall, we have set the two walls apart by a distance of $L_z = 7.7D_{g0}$, which was far enough to obtain the bulk phase in the middle of the simulation box. We have then superimposed the density distributions measured for $z \in [0, L_z/2]$ and $z \in [L_z/2, L_z]$ to predict $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ for $z \in [0, L_z/2]$ in the presence of one wall. We have always started the simulations with initial configurations where the positions and the directors of the particles were generated randomly and have used 20×10^8 MC moves to equilibrate the system.

In figures 4.5 and 4.6, we present results for the densities $\rho^* = 1.0$ and 3.0 respectively. At these densities all the results are qualitatively consistent and show a system where $\rho^{(1)}$ has a maximum close to the wall, where in addition the rings prefer to orient such that their director stands perpendicular to the wall. However, as we have expected from our results in the bulk, the MFT overestimates the strength of the interaction between the rings and thus overrates the strength of the tendency for rings to orient. The results from the HNC approach and MC simulations on the other hand are also numerically in good agreement. The agreement between the results from HNC and the simulations can be better appreciated in figures 4.7 and 4.8, where the one-particle densities are only shown for $z < D_{g0}$ and where the distribution close to the wall is thus better visible.

At higher densities, the picture changes also qualitatively. In figure 4.9 we have

only for the MFT computations at the densities $\rho^ = 4.5, 5.0$, we have set $\rho^{(1)} = \rho$ for $z > 6.2D_{g0}$

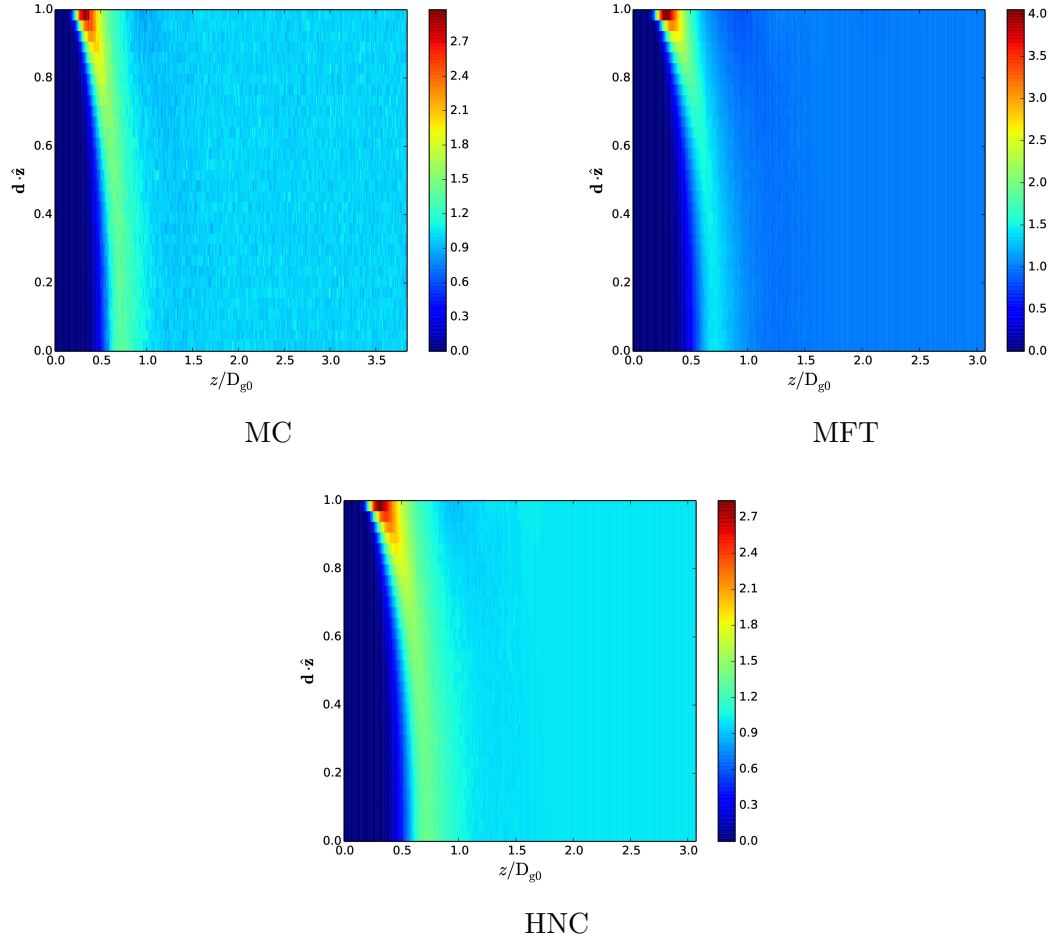


Figure 4.5: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ in the presence of a wall for the effective system with a reduced density of $\rho^* = 1.0$, determined in a MC simulation and with density functional theory employing the HNC or the MFT approximation.

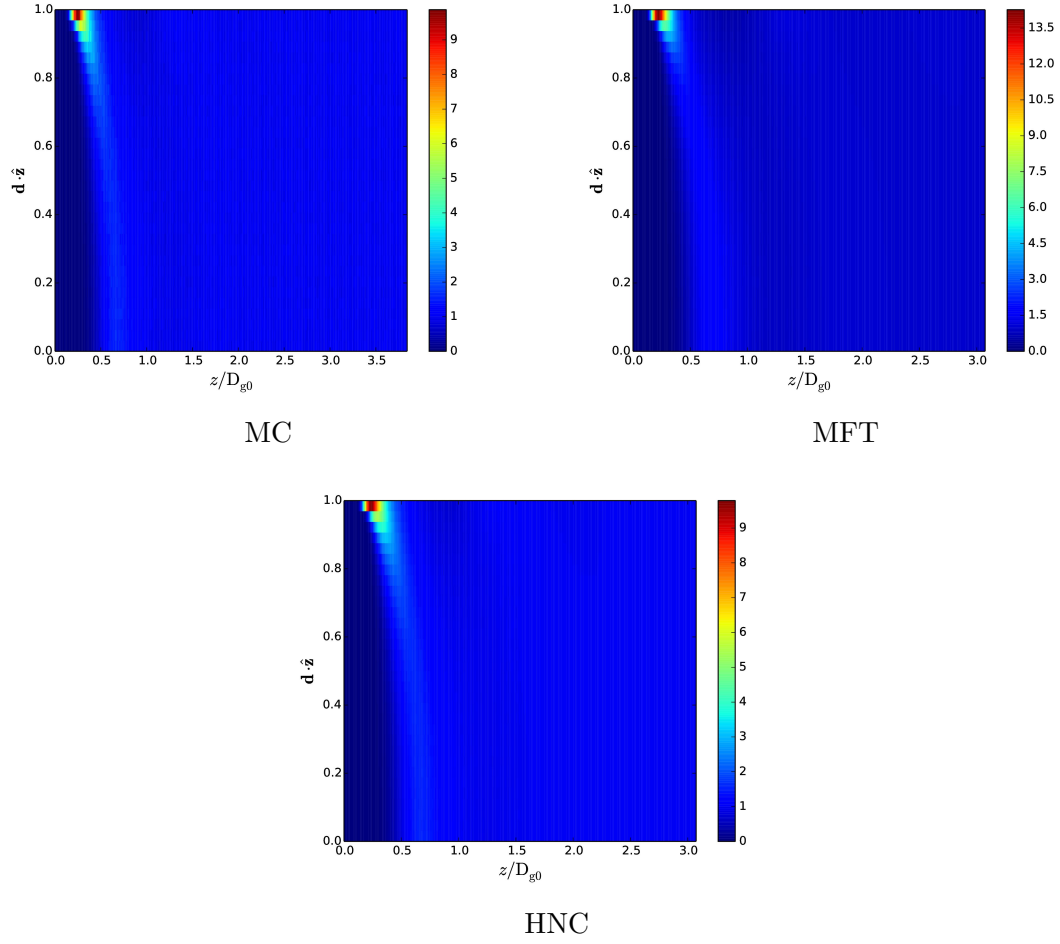


Figure 4.6: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ in the presence of a wall for the effective system with a reduced density of $\rho^* = 3.0$, determined in a MC simulation and with density functional theory employing the HNC or the MFT approximation.

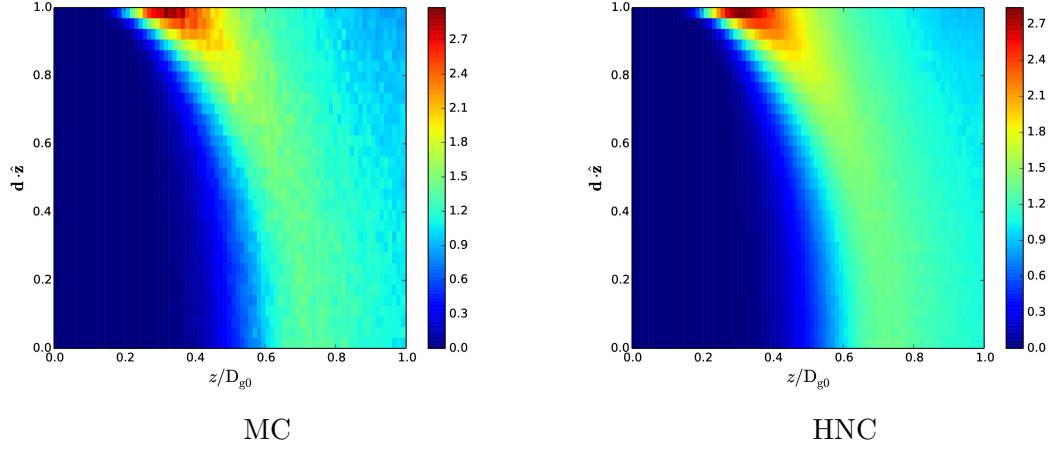


Figure 4.7: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ close to the a wall for the effective system with a reduced density of $\rho^* = 1.0$, determined in a MC simulation and with density functional theory employing the HNC approximation.

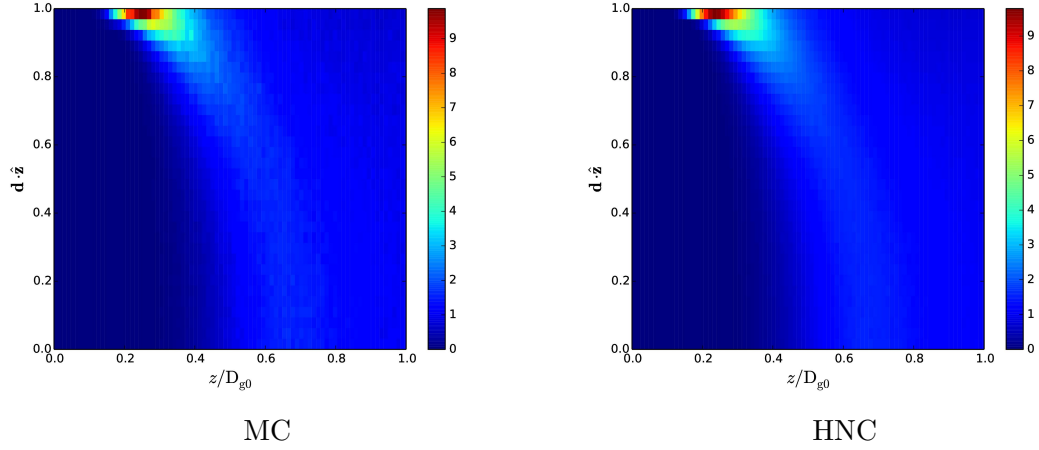


Figure 4.8: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ close to the wall for the effective system with a reduced density of $\rho^* = 3.0$, determined in a MC simulation and with density functional theory employing the HNC approximation.

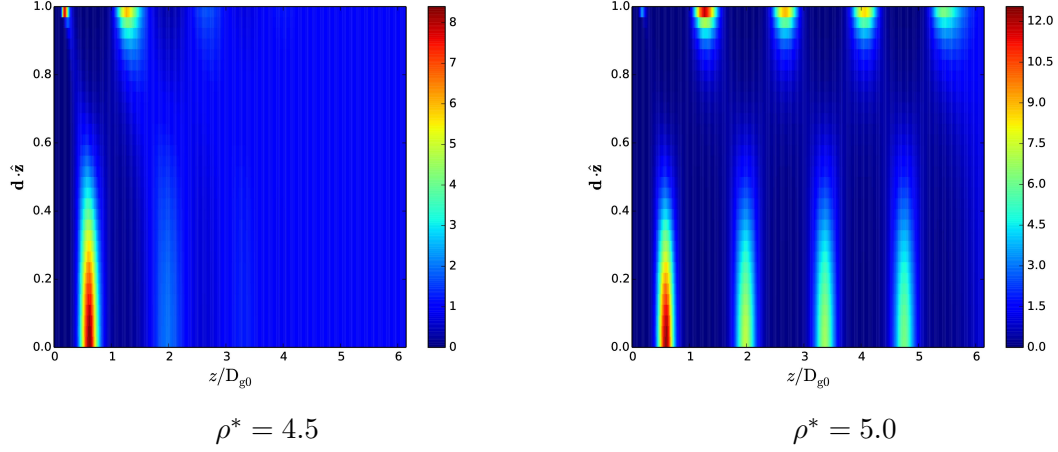


Figure 4.9: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ in the presence of a wall for the effective system determined with density functional theory employing the MFT approximation at densities $\rho^* = 4.5$ and 5.0 .

visualized the results of MFT at densities $\rho^* = 4.5$ and 5.0 , where it predicts a layered structure which starts to develop at density $\rho^* = 4.5$ and is already leading to long range correlations for $\rho^* = 5.0$. Interestingly, close to the wall MFT now predicts a clear maximum for rings orienting with their director parallel to the wall. Even closer to the wall there is a weak peak for rings with a director orthogonal to the wall, but it is much less pronounced and it disappears for $\rho^* = 5.0$. The picture that MFT predicts is therefore reminiscent to a liquid crystal, where we have a crystalline arrangement of rings within the z -direction. Initially, the rings are oriented with their surface orthogonal to the wall, afterwards a layer of rings lying parallel to the wall follows, before we see another layer of orthogonal rings, etc.

While the prediction of MFT is very interesting, it is unfortunately not observed in MC simulations at density $\rho^* = 5.0$, as we can see in figure 4.10. However, we have seen before that MFT typically overestimates the strength of the interaction and we can therefore hope that we might observe similar arrangements of the rings in simulations at higher densities. The HNC approach, on the other hand, is still in qualitative, as well as quantitative agreement with the results of simulations.

As we have mentioned before, we have also carried out the HNC approach for higher densities using the the direct pair-correlation function in the bulk determined at density $\rho^* = 5$. In figure 4.11 we show the result which we have obtained in this way at the density $\rho^* = 7$ and we compare it to the simulation results for $\rho^* = 7$ and 8 . The HNC approach now also overestimates the strength of the interaction between the effective particles and

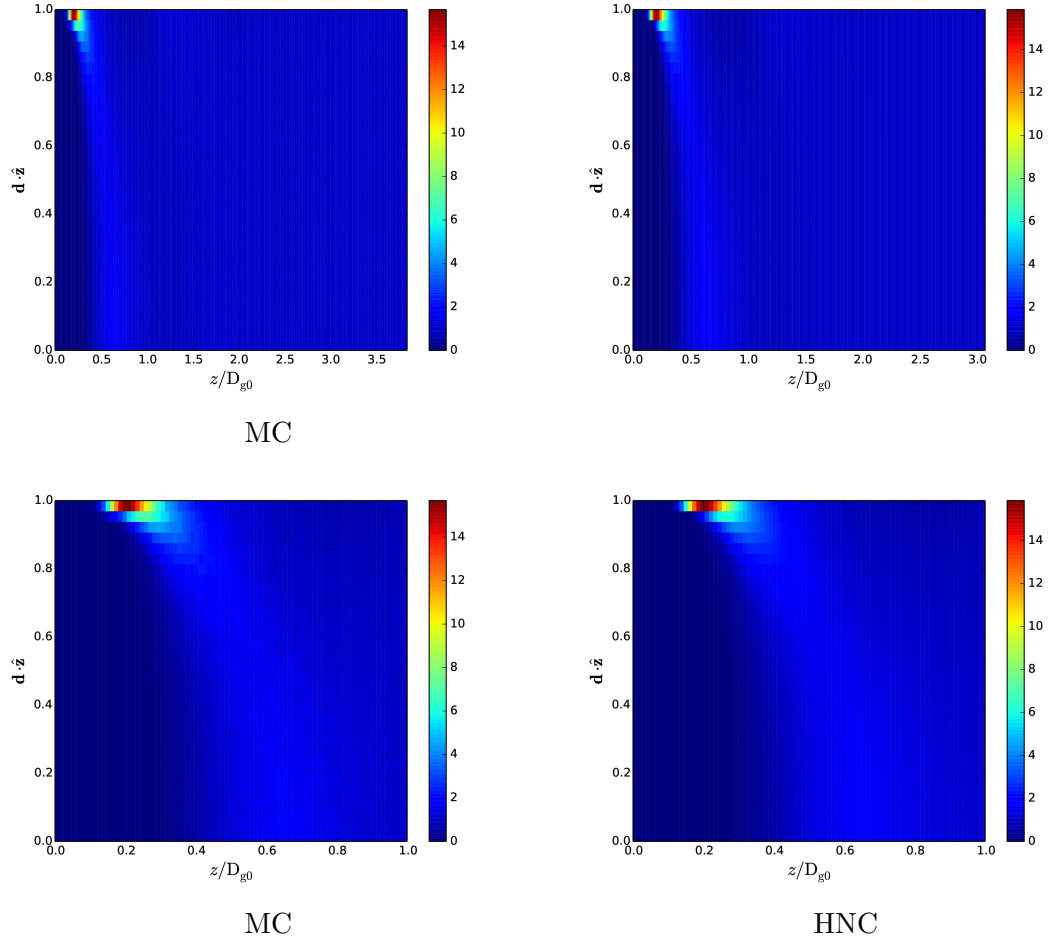


Figure 4.10: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ in the presence of a wall for the effective system with a reduced density of $\rho^* = 5.0$, determined in a MC simulation and with density functional theory employing the HNC approximation. The upper and lower plots show the same distribution but for a different domain of distances z to the wall.

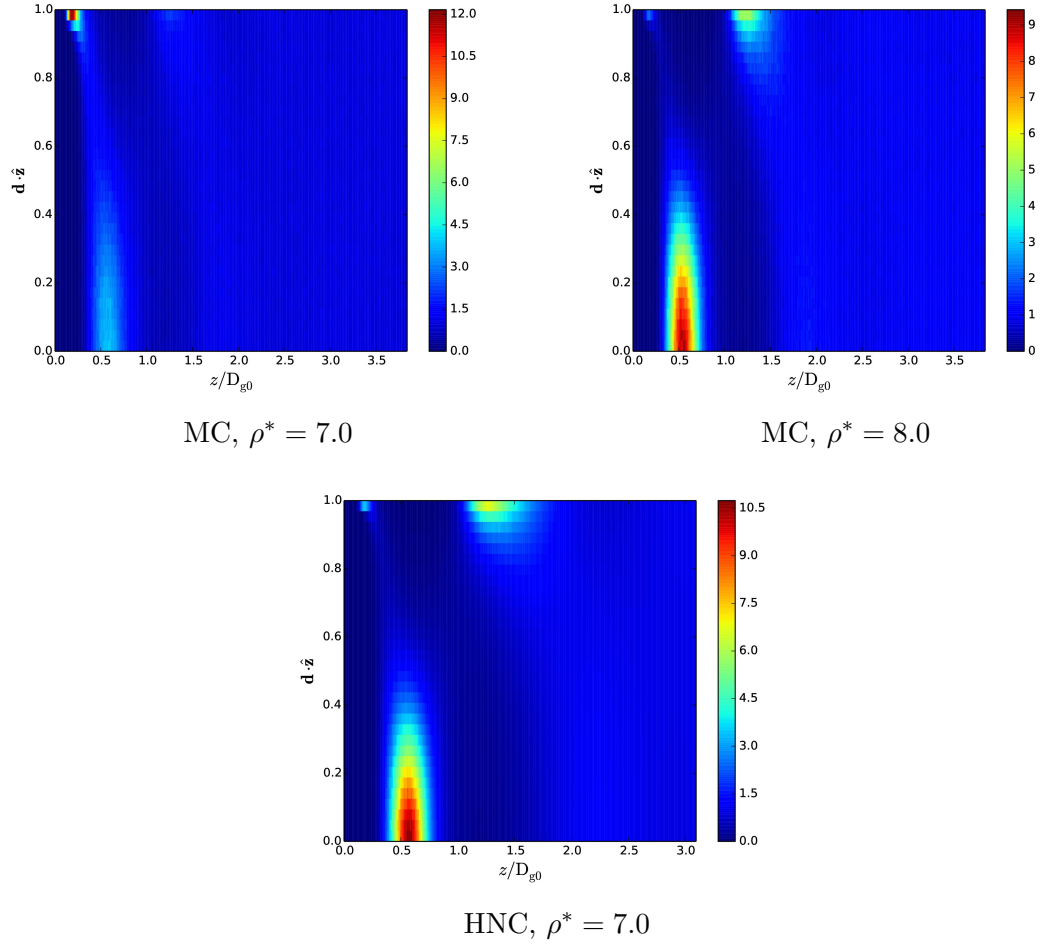


Figure 4.11: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ in the presence of a wall for the effective system determined in a MC simulation for the densities $\rho^* = 7.0, 8.0$ and applying density functional theory employing the HNC approximation for the density $\rho^* = 7.0$.

gives us a distribution function, which is more reminiscent to the MC results at the higher density. Nevertheless, the obtained result is quite interesting. As in the structure predicted by MFT already at lower densities, close to the wall we now observe a clear accumulation of rings oriented such that their surface stands orthogonal to the wall. This result is quite surprising given that the wall itself is purely repulsive.

It is intuitive that the particles are more likely to accumulate close to the wall, since the side of them that faces the wall has no other particles to interact with and the ring will therefore on average interact with fewer other particles. Initially the rings prefer to be parallel to the wall, which is intuitive since in this configuration they will have on average less interaction partners if the rest of the configuration space is filled homogeneously with rings. Now, at even higher densities the rings show the propensity of orienting their director parallel to the wall and their surface orthogonal to it, which might indicate that the wall-ring potential Φ_{wall} allows them to use the configuration space more efficiently and block less space for other rings, if they orient with their surface orthogonal to it. It is interesting to see that the picture predicted by MFT at $\rho^* = 4.5$ is at least to some level qualitatively reproduced at higher densities in simulations, as well as in the HNC approach. We have however not observed long range correlations in z -direction, but a clear layer of rings orthogonal to the wall, followed by another layer parallel to it.

In figure 4.12 we show snapshots of the simulated system at densities $\rho^* = 1, 5$ and 8. One can see that from the density $\rho^* = 1$ to $\rho^* = 5$, the tendency for disks close to a wall, to orient with their surface parallel to the wall increases significantly, before the rings clearly prefer an orientation where their director is parallel to the wall at $\rho^* = 8$.

In order to facilitate the formation of the arrangement of layers predicted by MFT in simulations, we have tried to put the two walls closer together. Judging from the MFT results in the presence of one wall shown in figure 4.9 we would expect that that at least for MFT a distance of $L_z = 3.85D_{g0}$ between the walls should allow for the formation of three layers of disks with their surface oriented orthogonal to the wall. In figure 4.13 we present results from MFT for this wall separation which show precisely this behavior.

We have now also carried out MC simulations and density functional computations employing the HNC approach for $L_z = 3.85D_{g0}$ and have visualized the one particle distribution for densities $\rho^* = 6, 7$ and 8 in figure 4.14. As in the case of one wall, we can see that the HNC approach predicts that the disks orient with their surface orthogonal to the wall at a smaller density than where this behavior is observed in MC simulations. However the density profile predicted by HNC for $\rho^* = 7.0$ is qualitatively very similar to the one observed in MC simulations for $\rho^* = 8.0$, which means that while the HNC gives qualitatively a correct picture of the system it is quantitatively wrong because it

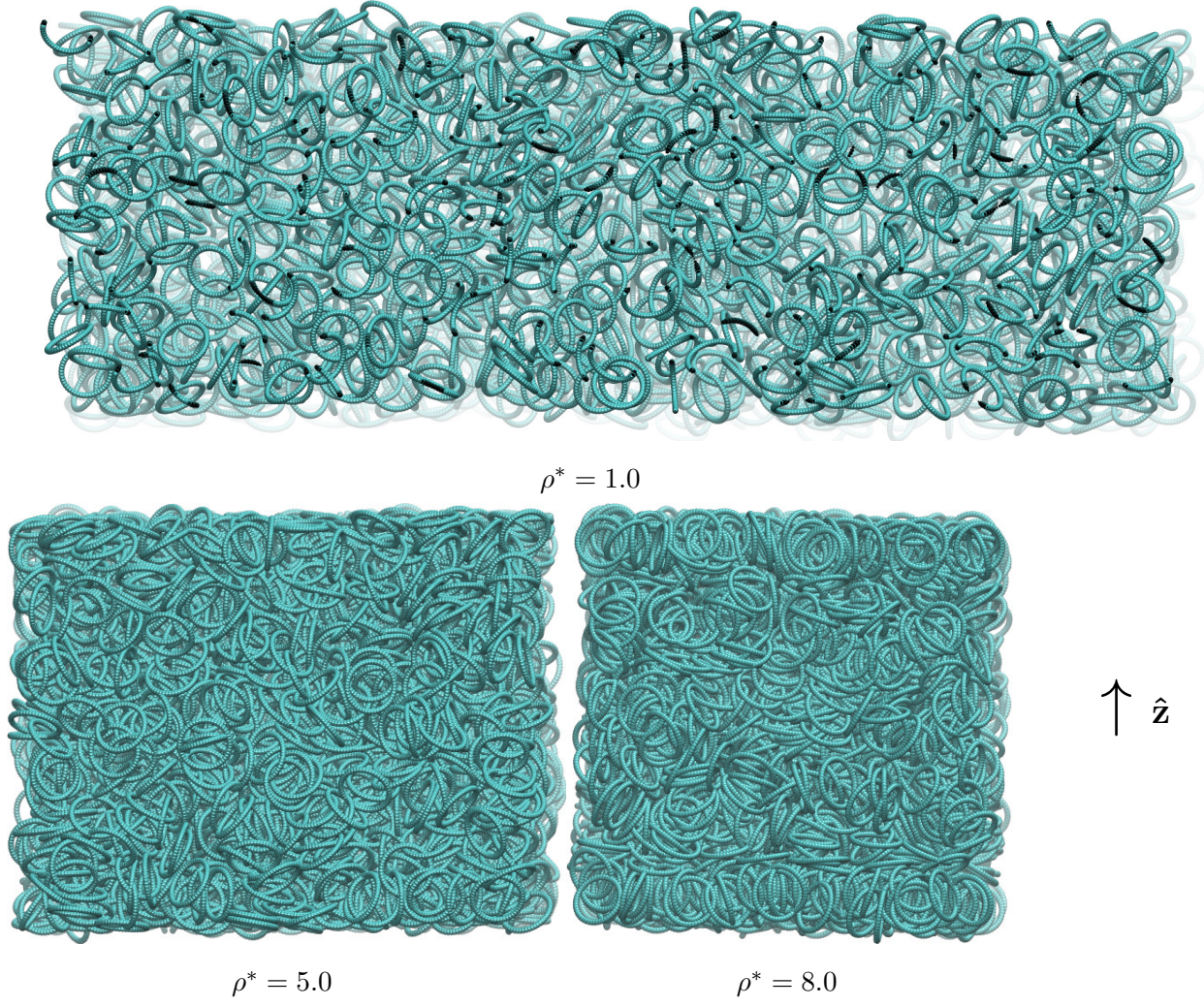


Figure 4.12: Snapshots of a MC simulations of effective disks between two walls separated by a distance $L_z = 7.7D_{g0}$ at three different densities. The unit vector $\hat{z}$, which stands orthogonal to the walls, points upwards.

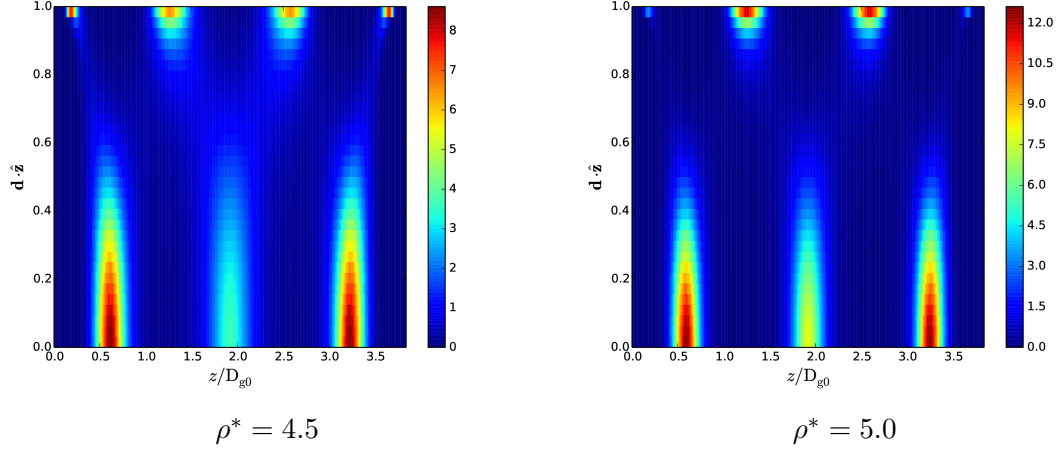


Figure 4.13: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ between two walls separated by the distance $L_z = 3.85D_{g0}$ for the effective system determined with density functional theory employing the MFT approximation at densities $\rho^* = 4.5$ and 5.0 .

overestimates the strength of the interactions between the particles at these high densities. For $\rho^* = 8.0$ we can already see a slight indication of an additional layer of disks with a director parallel to the wall, which we have also seen in the MFT results in figure 4.13.

With the goal of discovering in the MC-simulation the additional layer in the middle of the simulation box at high densities, we have simulated the system for $\rho^* = 14$. The corresponding one particle density is visualized in figure 4.15, where we have used a logarithmic scale and a cutoff for the values of $\rho^{(1)}$ to better resolve fine variations of the density distribution which clearly indicate an accumulation of disks with directors parallel to the wall in the middle of the simulation box. This can also be observed in the snapshot of a system simulated at $\rho^* = 14.0$ in figure 4.16, while it is not visible in the snapshot for $\rho^* = 8.0$. Although the signal is not as clear as predicted by MFT it can at least be said that MFT qualitatively gave us the correct idea of what the structure of the system would look like at high densities, although it highly overestimated the interaction between the effective particles and therefore underestimated the density at which this interesting arrangement of layers can be observed.

Finally, we have tried to observe an additional layer of disks in the simulations by putting the walls farther apart. We have again looked at the MFT results for $\rho^{(1)}$ in the presence of one wall as a guideline to choose an appropriate distance between the walls. In figure 4.9 we can see that in the presence of one wall MFT predicts the formation of 4 layers of rings with directors parallel to the wall, between the wall and the distance $z \approx 5D_{g0}$ away from the wall. If we put an additional wall at $z \approx 5D_{g0}$ we therefore

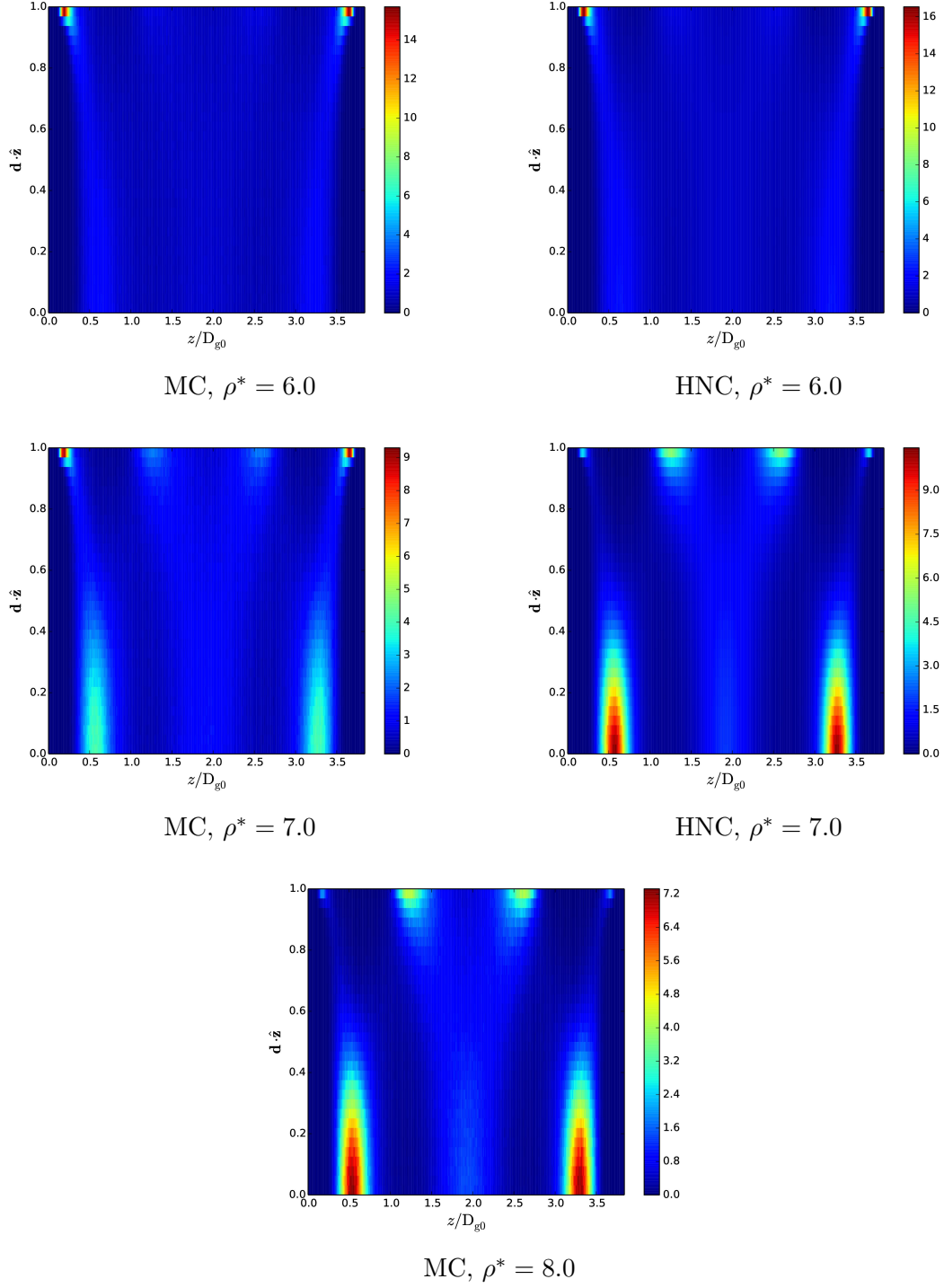


Figure 4.14: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ between two walls separated by the distance $L_z = 3.85D_{g0}$ for the effective system determined in a MC simulation and with density functional theory employing the HNC approximation.

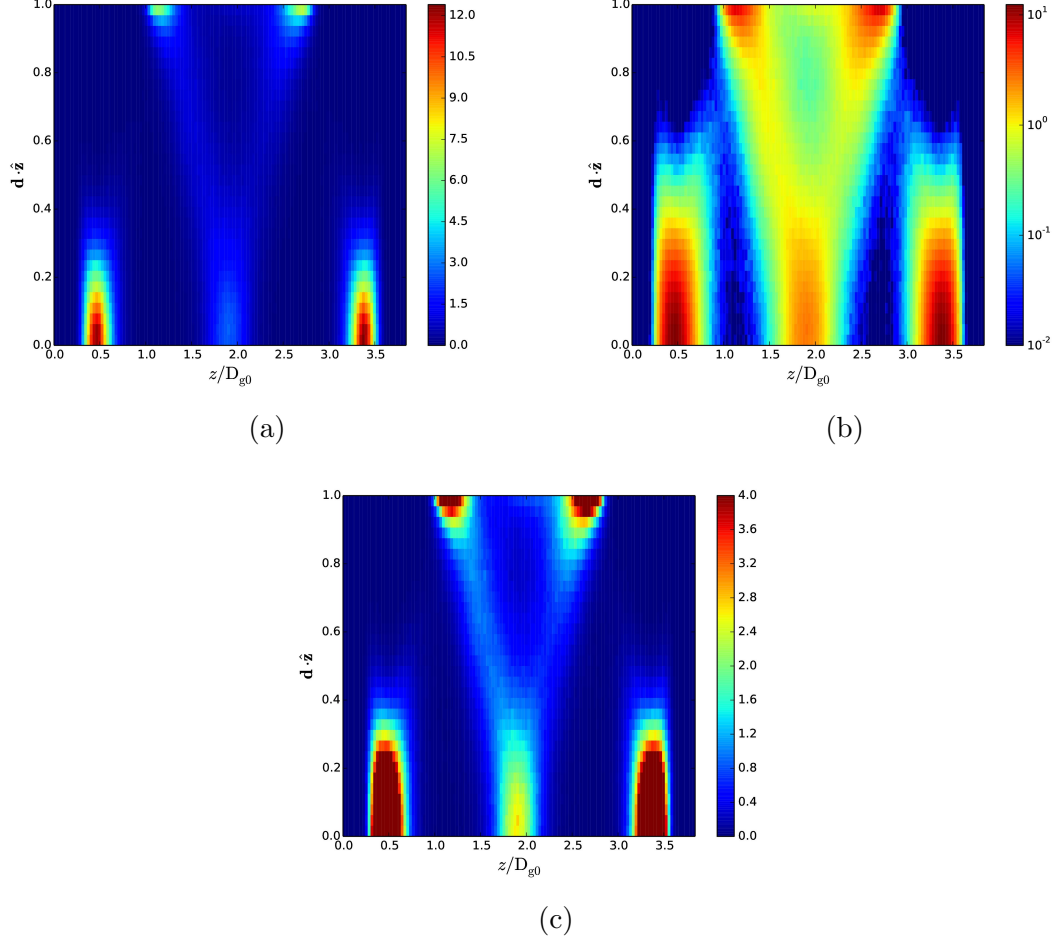
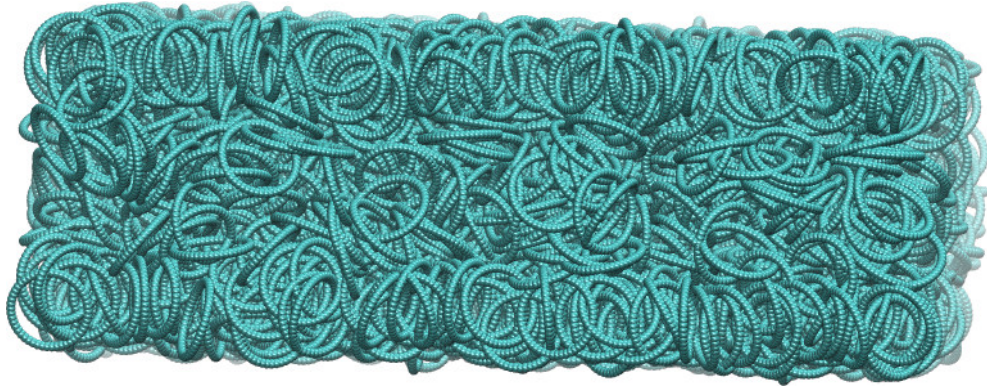


Figure 4.15: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ between two walls separated by the distance $L_z = 3.85D_{g0}$ for the effective system determined in a MC simulation at the density $\rho^* = 14.0$. In snapshot (b) we have used a logarithmic scale, while in snapshot (c) we have cut off the color scale at $\rho^{(1)} = 4$ in order to better resolve the structure of the distribution in the middle of the simulation box.



$$\rho^* = 8.0$$



$$\rho^* = 14.0$$

Figure 4.16: Snapshots of a MC simulations of effective disks between two walls separated by a distance $L_z = 3.85D_{g0}$ at two different densities.

expect MFT to predict the formation of these 4 layers between the two walls. We have thus computed the one-particle density profile $\rho^{(1)}$ between two walls separated by the distance $L_z = 5.38D_{g0}$ in MFT which is visualized in figure 4.17 for the densities $\rho^* = 4.5$ and 5.0. As expected the MFT results exhibits the formation of 4 layers of rings with directors parallel to the wall. However we have not been able to obtain the additional layer in MC simulations of the same system. Thus we have also carried out simulations for a larger distance between the walls, namely $L_z = 6.15D_{g0}$, where the MC results turned out to be more promising. We have presented simulation results for $\rho^* = 14$ in figure 4.18. While the maxima in the density distribution $\rho^{(1)}$ measured in the MC simulation, corresponding to the different layers of disks, are not as sharply peaked as predicted in MFT for $L_z = 5.38D_{g0}$, they clearly indicate an alternating arrangement of layers of disks, which is also visible in a snapshot of the system.

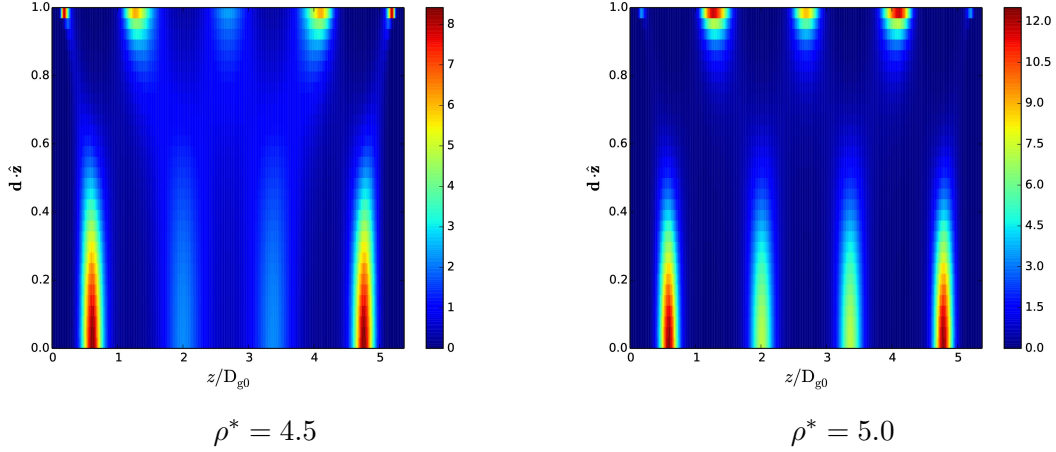


Figure 4.17: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ between two walls separated by the distance $L_z = 5.38D_{g0}$ for the effective system determined with density functional theory employing the MFT approximation at densities $\rho^* = 4.5$ and 5.0.

We have also computed the MFT prediction of $\rho^{(1)}$ for a wall separation of $L_z = 6.15D_{g0}$ and show the resulting density distribution in figure 4.19, where we can see that the MFT result shows one additional layer of rings with respect to the distribution obtained in MC simulations.

4.5 Conclusions

We have shown that density functional theory (DFT) does a very good job in describing the isotropic effective system in the bulk, where the predictions of MFT, as well as the

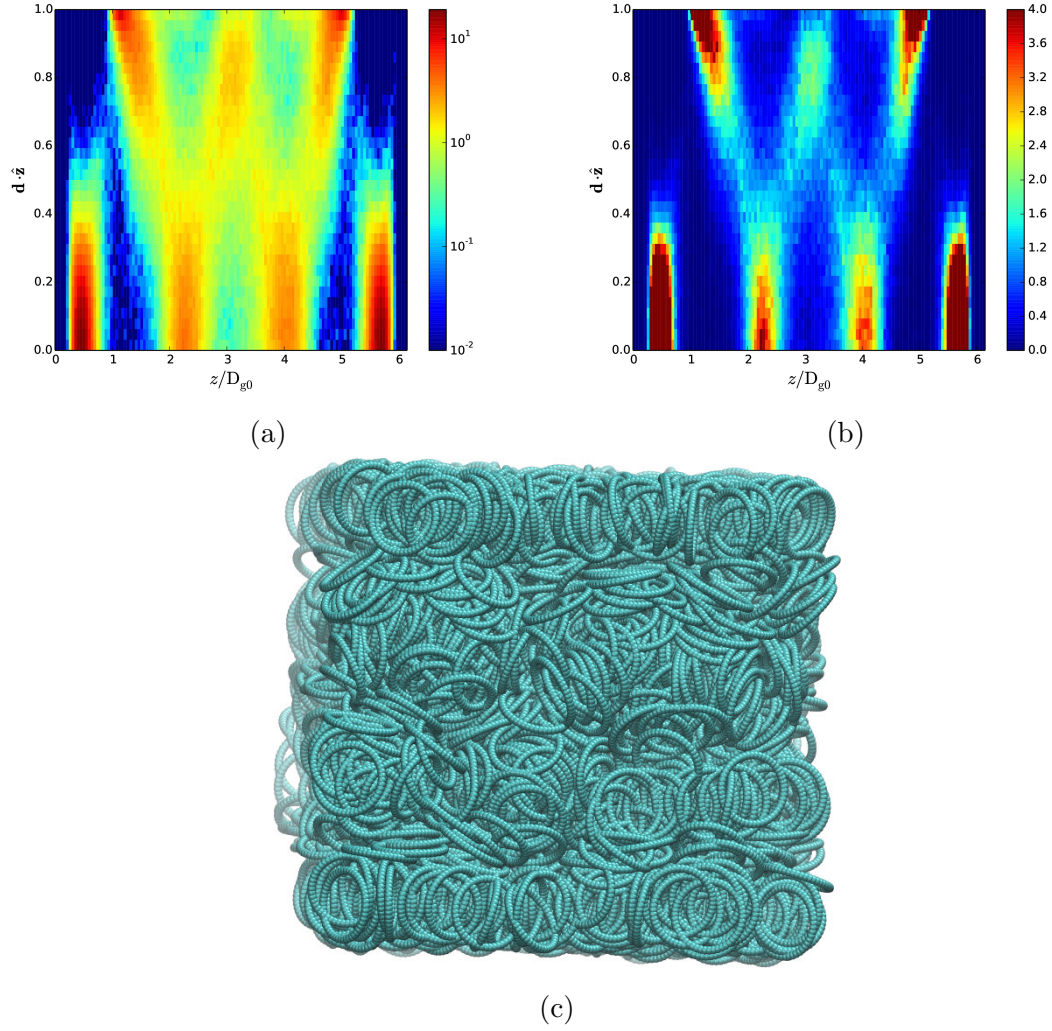


Figure 4.18: MC Simulation results of the effective system between two walls separated by the distance $L_z = 6.15D_{g0}$ at the density $\rho^* = 14.0$. In (a) and (b) we show the one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$, where we have used a logarithmic scale in (a) and cut off the color scale at $\rho^{(1)} = 4$ in (b) to better resolve fine variations in the probability distribution. In (c) a snapshot of the simulated system is presented.

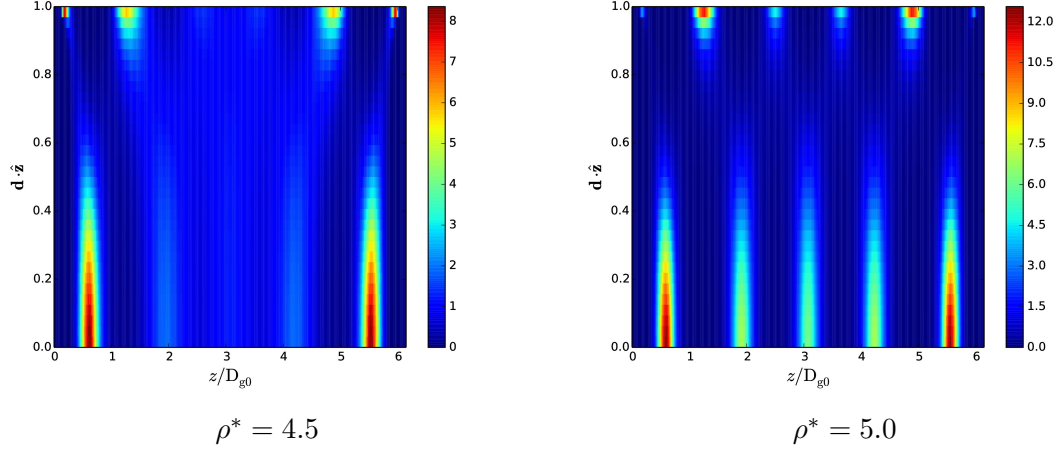


Figure 4.19: The one-particle density $\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$ between two walls separated by the distance $L_z = 6.15D_{g0}$ for the effective system determined with density functional theory employing the MFT approximation at densities $\rho^* = 4.5$ and 5.0 .

ones obtained with the HNC closure are in excellent agreement with simulation results. For the anisotropic system, the evaluation of the DFT predictions becomes computationally more challenging and we have also seen that the MFT approximation strongly overestimates the strength of the interactions. The extension of the HNC closure to anisotropic systems on the other hand offers a description which is in excellent agreement with simulation results in the bulk for all densities investigated. For future work it would be interesting to study the HNC approach at even higher densities and also to carry out the numerical integrations on a finer grid, which should be feasible by exploiting the fact that the computationally heavy part of the numerical integrations is the evaluation of $3N_{\cos\theta_2}N_{\cos\theta}N_\varphi N_r^2$ discrete Fourier transformations of arrays with N_r elements, which we have up to now all carried out on a single processing unit. It would be straightforward to parallelize these computations, even to the level of individual discrete Fourier transformations, for instance by the use of existing algorithmic packages that implement the FFT algorithm on graphics cards. To go further into this direction, it was however important to first establish that the solutions of the equations derived in the anisotropic density functional theory are an improvement with respect to results from the isotropic theory, which at least for the HNC approach is clearly the case. The HNC approach in the bulk gives us a prediction for the full anisotropic pair-correlation function $g(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$, as well as for the direct-pair correlation function $c^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$. The latter is useful to apply DFT to predict the one-particle density of rings in the vicinity of a wall or between two walls, where we have also obtained results that are in quantitative agreement with

simulations up to densities $\rho^* = 5.0$ applying an HNC-like approach. We have found that at high densities the effective disks close to the wall(s) orient with their surface standing orthogonal to it. This interesting behavior is reproduced in the density functional theory approaches as well as in simulations. In experiments it was shown that disk-like coronene molecules orient in a similar fashion close to germanium surfaces, although the attraction between coronene molecules plays an important role in this ordering and thus the underlying mechanism is different to our case[102]. The MFT approach also predicts an interesting alternating layering of the disks and although this structure is not as clearly reproduced in simulations, we can see the formation of alternating layers in systems simulated between two walls. We think that this structure is interesting by itself and it also shows us that while the MFT approach strongly overestimates the strength of the interactions between the effective particles it still captures some important features of the system and can serve as a guideline for the discovery of interesting behavior in the simulations.

5 Influence of Rigidity and Knot Complexity on the Knotting of Confined Polymers

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We employ computer simulations and thermodynamic integration to analyse the effects of bending rigidity and slit confinement on the free energy cost of tying knots, $\Delta F_{\text{knotting}}$, on polymer chains under tension. A tension-dependent, non-zero optimal stiffness κ_{min} exists, for which $\Delta F_{\text{knotting}}$ is minimal. For a polymer chain with several stiffness domains, each containing a large amount of monomers, the domain with stiffness κ_{min} will be preferred by the knot. A local analysis of the bending in the interior of the knot reveals that local stretching of chains at the braid region is responsible for the fact that the tension-dependent optimal stiffness has a non-zero value. The reduction in $\Delta F_{\text{knotting}}$ for a chain with optimal stiffness relative to the flexible chain can be enhanced by tuning the slit width of the 2D confinement and increasing the knot complexity. The optimal stiffness itself is independent of the knot types we considered, while confinement shifts it towards lower values.

5.1 Introduction

Whilst in the macroscopic world it is clear that the effort needed to tie a knot in wire or string will always increase if it is made more rigid, for equivalent microscopic objects, polymers, the same does not hold. Instead, it is found that the free energy cost of knotting a polymer, $\Delta F_{\text{knotting}}$, has a minimum at a non-zero stiffness [25]. This finding is particularly interesting in the context of biological macromolecules, such as DNA or RNA, where on the one hand knotting is known to occur [32, 103] and have significant effects on key processes [14, 15, 16], whilst on the other rigidity may depend sensitively on the base sequence [18, 19, 20], leading to varying flexibility along the polymer. Furthermore, there is evidence of correlations between DNA stiffness and sites preferred by type II topoisomerases [25], enzymes that regulate knotting [17].

It is expected that the rigidity dependence of $\Delta F_{\text{knotting}}$ will affect the behaviour of knots in DNA with non-uniform flexibility, for example by localising them in regions with favourable stiffness. However, previous work [25] neglected a key qualitative feature of biological DNA, namely that it is typically highly confined [104, 105, 106]. Confinement of a knotted polymer in a good solvent may significantly affect its properties. For example, in contrast to three dimensions where they are weakly localised, knots in polymers adsorbed on a surface are strongly localised [107, 108]. Considering the properties of polymers confined in a slit, simulations of DNA found a non-monotonic dependence of the knotting probability on the slit width [109] and for flexible polymers evidence was found that the particular topology is important [110]. Whilst previous work on knotting in confinement has focussed on polymers that have one specific stiffness, here we apply a simple model for a polymer chain under tension, to investigate the dependence of $\Delta F_{\text{knotting}}$ on rigidity for various widths of the geometrical confinement. We find that a local stretching of the chains at the braiding region of the knots is responsible for the fact that the optimal bending rigidity for knot formation, κ_{min} , differs from zero. Geometric confinement, however, pushes this optimal rigidity towards smaller values. The effect of confinement on κ_{min} , as well as the amount by which $\Delta F_{\text{knotting}}$ is reduced for the optimal rigidity κ_{min} depends sensitively on the tension applied to the polymer chain.

The rest of the paper is organized as follows: We first present our model and details about the simulation in Section 5.2. In Section 5.3 we define and explain the observables that have been measured in our simulations. In particular, we define our notion of *bending* of the polymer chain and establish its connection to $\Delta F_{\text{knotting}}$. Section 5.4 introduces the analysis of the *local bending* in the interior of the knot, which is carried out to investigate which part of the knot is responsible for the reduction of $\Delta F_{\text{knotting}}$ for polymers with non-zero bending stiffness κ_{min} relative to a fully flexible chain. We present our results

in Section 5.5, whereas in Section 5.6 we summarize and draw our conclusions.

5.2 Model and simulation details

For the polymer chain (linear or knotted), we employ a standard, self-avoiding bead-spring model with rigidity κ , confined parallel to the (x, z) -plane and under tension τ . The interaction part of the Hamiltonian thus reads as:

$$\begin{aligned}
V(\{\mathbf{r}_i\}) = & \kappa \sum_i (1 - \hat{\mathbf{r}}_{i-1,i} \cdot \hat{\mathbf{r}}_{i,i+1}) - \frac{kR_0^2}{2} \sum_i \ln \left[1 - \left(\frac{\mathbf{r}_{i,i+1}}{R_0} \right)^2 \right] \\
& + 4\epsilon \sum_{j>i} \sum_i \left[\left(\frac{\sigma}{r_{i,j}} \right)^{12} - \left(\frac{\sigma}{r_{i,j}} \right)^6 + \frac{1}{4} \right] \Theta(2^{1/6}\sigma - r_{i,j}) \\
& + k_B T \sum_i \left(\frac{y_i}{d} \right)^2 - \tau L_z.
\end{aligned} \tag{5.1}$$

In Eq. (5.1), $\mathbf{r}_{i,j} = \mathbf{r}_j - \mathbf{r}_i$ is the vector from bead i to bead j , located at position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, with the unit vector $\hat{\mathbf{r}}_{i,j} = \mathbf{r}_{i,j}/|\mathbf{r}_{i,j}|$. The first term represents the bending energy of the chain, where κ is the bending rigidity. The second and third terms are the connectivity and steric terms, respectively, whereas $\Theta(\omega)$ is the Heaviside step function of ω , which renders the Lennard-Jones potential purely repulsive. We choose $\epsilon = k_B T$, $k = 30k_B T/\sigma^2$, and $R_0 = 1.5\sigma$, preventing the chain from crossing itself and thus conserving its topology. The chain is confined in a slit parallel to the (x, z) plane, which is realized via a harmonic external potential acting on the y -component of the coordinate of each monomer, expressed by the fourth term in Eq. (5.1). The last term applies a tension τ on the chain along the z -direction of the setup, with L_z denoting the extension of the chain along this direction.

We used the LAMMPS simulation package [73] to carry out constant- $N\tau T$ Molecular Dynamics (MD) simulations. The polymers consist of $N = 256$ monomers for the chains simulated at tensions $\tau = 0.8 k_B T/\sigma$ and $\tau = 0.4 k_B T/\sigma$, and of $N = 512$ monomers for the simulations at tensions $\tau = 0.2 k_B T/\sigma$ and $\tau = 0.1 k_B T/\sigma$. The longer polymer chains at the two smaller tensions are necessary due to the larger knot size for these tension values. The chains are placed in a simulation box with volume $V = 100\sigma \times 150\sigma \times L_z$ at the two higher tensions and $V = 200\sigma \times 300\sigma \times L_z$ for the lower tensions. The tension τ is realized via a barostat coupled to the fluctuating z -length of the simulation box, whilst the box lengths in the x - and y -directions are fixed to 100σ and 150σ for the higher tensions 200σ and 300σ for the lower tensions respectively. The polymer is connected across the periodic boundary conditions in the z -direction to guarantee that the knot is preserved. We also use periodic boundary conditions in the x -direction, while for the y -direction

confinement prevents the polymer chain from getting outside the simulation-box. For both the thermostat and the barostat, we used a Nose-Hoover chain with 3 degrees of freedom [111]. With m denoting the monomer mass and $\beta = (k_B T)^{-1}$, $t_0 = \sqrt{m\sigma^2\beta}$ sets the unit of time. We integrated the equations of motion with a timestep $\Delta t = 10^{-3}t_0$. The equilibration time was 2×10^7 timesteps, and data were collected during a total of 3×10^8 timesteps.

5.3 Definition and interpretation of Observables

Definition and physical interpretation of $\Delta F_{\text{knotting}}(\kappa)$: Let $F_{\text{lin,knot}}(\kappa)$ be the free energies of an unknotted and a knotted chain, respectively, for given κ , τ and chain length. We define $\Delta F_{\text{knotting}}(\kappa) \equiv F_{\text{knot}}(\kappa) - F_{\text{lin}}(\kappa)$, a quantity that gives a measure for the effort to tie a knot into the chain of N monomers. In our simulations, we do not calculate the absolute value for $\Delta F_{\text{knotting}}(\kappa)$ but its value relative to $\Delta F_{\text{knotting}}(\kappa = 0)$ of a flexible chain, a procedure that removes the N -dependence for a linear and a knotted chain of the same degree of polymerization N . Thus, we calculate $\Psi(\kappa) \equiv \Delta F_{\text{knotting}}(\kappa) - \Delta F_{\text{knotting}}(0)$, which has a direct physical interpretation: Let us consider a long polymer chain with various domains, which differ by their respective bending stiffness κ_i and the number of monomers they contain N_i . Then, the quantity $\Psi(\kappa)$ allows us to predict the probability for the knot to be found in the i -th domain relative to the probability for it being in the j -th domain as:

$$\frac{P_i}{P_j} = \frac{N_i}{N_j} \exp[-\beta(\Psi(\kappa_i) - \Psi(\kappa_j))]. \quad (5.2)$$

An implicit assumption entering Eq. (5.2) is that the length of the chain segments, N_i , is much longer than the knot size N_K , so that for most configurations the part of the polymer chain that is affected by the knot is localized in only one of the domains. Due to the applied tension τ the knotted part of the chain will always remain finite. In Ref.[25], it was shown that at fixed κ the size of the knot does not scale with N , the number of monomers on the chain, but rather as $N_K \sim (k_B T/\tau)^\alpha$ with some exponent α . The reason for this, is that the stretched polymer forms a series of tension blobs,[5] whose size scales with the tension τ but not with N . The knot can only be in one of those blobs, therefore N_K will be finite for any non-zero tension τ . Therefore, for sufficiently large N_i , Eq. (5.2) indeed provides a good prediction for P_i . In Ref. [25] the prediction of Eq. (5.2) was tested for a simulation of a polymer chain with two stiffness domains.

Definition and interpretation of the chain's bending $\hat{B}$: With $\hat{\mathbf{r}}_{j,j+1}$ denoting the unit vector between monomers j and $j+1$, we define the quantity

$$\hat{B} \equiv \sum_i (1 - \hat{\mathbf{r}}_{i-1,i} \cdot \hat{\mathbf{r}}_{i,i+1}) \quad (5.3)$$

for any configuration of its monomers and call it the *bending* of the chain; evidently it holds that $\hat{B} \geq 0$. One can check that this definition of the bending is sensible for various special cases. For instance, for a configuration with a straight polymer chain this definition gives the minimum value for $\hat{B}$, namely $\hat{B} = 0$. The contribution to $V(\{\mathbf{r}_i\})$ defined in (5.1) due to the bending stiffness is $\kappa\hat{B}$. Moreover $B_T(\kappa) \equiv \langle \hat{B} \rangle$ is the thermodynamic expectation value of the same for a chain of topology $T \in \{\text{knot}, \text{linear}\}$.

With $F_T(\kappa)$ denoting the free energy of the polymer, it holds that $\partial F_T(\kappa)/\partial\kappa = B_T(\kappa)$. This allows us to calculate how the cost of knotting changes with bending stiffness κ : Introducing $\Delta B(\kappa) \equiv B_{\text{knot}}(\kappa) - B_{\text{linear}}(\kappa)$, it follows that $\partial\Delta F_{\text{knotting}}(\kappa)/\partial\kappa = \Delta B(\kappa)$. The free energy cost of knotting is therefore:

$$\Delta F_{\text{knotting}}(\kappa) = \Delta F_{\text{knotting}}(0) + \int_0^\kappa \Delta B(\kappa') d\kappa',$$

and thus

$$\Psi(\kappa) = \int_0^\kappa \Delta B(\kappa') d\kappa'. \quad (5.4)$$

The existence of a minimum of $\Psi(\kappa)$ for $\kappa \neq 0$ will depend on the sign of the slope of $\Psi(\kappa)$ at $\kappa = 0$, $\Delta B(0)$. If $\Delta B(0) < 0$, we expect an optimal knotting rigidity $\kappa_{\min} \neq 0$, whereas we anticipate a monotonically increasing function $\Psi(\kappa)$ in the opposite case, $\Delta B(0) \geq 0$. This is a reasonable expectation, since we will always obtain $\Delta B(\kappa) > 0$ for sufficiently stiff chains. Indeed, for $\beta\kappa \gg 1$, a linear polymer will adopt an almost straight configuration with $\hat{B} \approx 0$, as configurations with non-zero $\hat{B}$ are penalized by a high bending energy. $\hat{B} = 0$ is unique for the straight configuration, which is of course not knotted. Therefore $\Delta B(\kappa) > 0$ will hold for all knots in the $\beta\kappa \gg 1$ regime.

To illustrate this further, let us for example consider a stiff polymer chain with a trefoil knot. Its minimal energy is obtained for a straight polymer chain with an approximately circular domain at the location of the knot. The circle is tangent to the braid point and contains $N_K(\kappa) \cong \sqrt{2\pi^2\kappa/(\tau\ell)}$ monomers, where $\ell \cong \sigma$ is the bond length [112]. Accordingly, $\Delta B(\kappa) \cong \sqrt{2\pi^2\tau\ell/\kappa} > 0$ in this limit.

5.4 Analysis of the local bending in the knotted domain

Having in mind the goal of localizing which part of the polymer in the vicinity of the knot is contributing to an increased or decreased average bending and therefore to a non vanishing $\Delta B(\kappa)$, we need to determine the knotted domain on the polymer chain. We define the knotted state of open subsections by introducing a topologically neutral closure scheme, which transforms an open string into a ring polymer that has a mathematically

well defined topological state [23, 113, 114]. We used a scheme where the end points of the open polymer are connected to a sphere at infinity in the direction of the vector from the centroid to the respective end point. The knotted part of the polymer chain is then the smallest domain for which the closure yields a ring polymer that has the correct Alexander polynomial.

Once the ends of the knot have been identified, we introduce a new enumeration scheme for the monomers, denoted by the Greek integer index α , which can have positive as well as negative values. The two monomers in the *interior* of the knot that lie n bonds away from the endpoints obtain the index $\alpha = -n$, whereas the two monomers to be found n bonds away at the *exterior* of the knot are assigned the index $\alpha = n$; accordingly, $\alpha = 0$ for the two endpoints of the knot. There exist, thus, for every value of α two position vectors $\mathbf{r}_\alpha^j$, $j = L, R$, where L/R denotes whether the monomer is at separation α from the left/right endpoint of the knot. Accordingly, we define the local bending contribution from the two monomers carrying the index α as:

$$\hat{b}_\alpha \equiv \sum_{j=L,R} (1 - \hat{\mathbf{r}}_{\alpha-1,\alpha}^j \cdot \hat{\mathbf{r}}_{\alpha,\alpha+1}^j). \quad (5.5)$$

For $\alpha < 0$, $\hat{b}_\alpha$ measures the *local* bending of angles *in the interior* of the knot, while for $\alpha > 0$, $\hat{b}_\alpha$ measures the *local* bending *outside* of the domain that was identified as knotted. The domain limits for $\alpha \in [\alpha_{\min}, \alpha_{\max}]$ depend on the instantaneous configuration, as the number of monomers on the knot N_K determines how negative α can become. The range of α is constant, $\alpha_{\max} - \alpha_{\min} + 1 = N/2$.

We introduce a characteristic function $\hat{\chi}_\alpha = 1$ or 0 depending on whether the index α occurs for a given conformation or not and define the *local* bending difference between a knotted and a linear chain as

$$\Delta b_\alpha(\kappa) \equiv \left\langle \hat{\chi}_\alpha \left(\hat{b}_\alpha - b_{\text{linear}}(\kappa) \right) \right\rangle. \quad (5.6)$$

In Eq. (5.6) above, $b_{\text{linear}}(\kappa) \equiv 2B_{\text{linear}}(\kappa)/N$ is the thermodynamic average of the bending of two angles on a linear chain. It follows that

$$\Delta B(\kappa) = \sum_{\alpha=-M}^M \Delta b_\alpha(\kappa), \quad (5.7)$$

where $M = N/2$ is the smallest value guaranteeing $[\alpha_{\min}, \alpha_{\max}] \subset [-M, M]$ for all polymer configurations.

5.5 Results

Results for the local bending of unconfined polymers are shown in Figs. 5.1(a) and 5.1(b) for two different values of the applied tension. As can be seen, the quantity $\Delta b_\alpha(\kappa)$

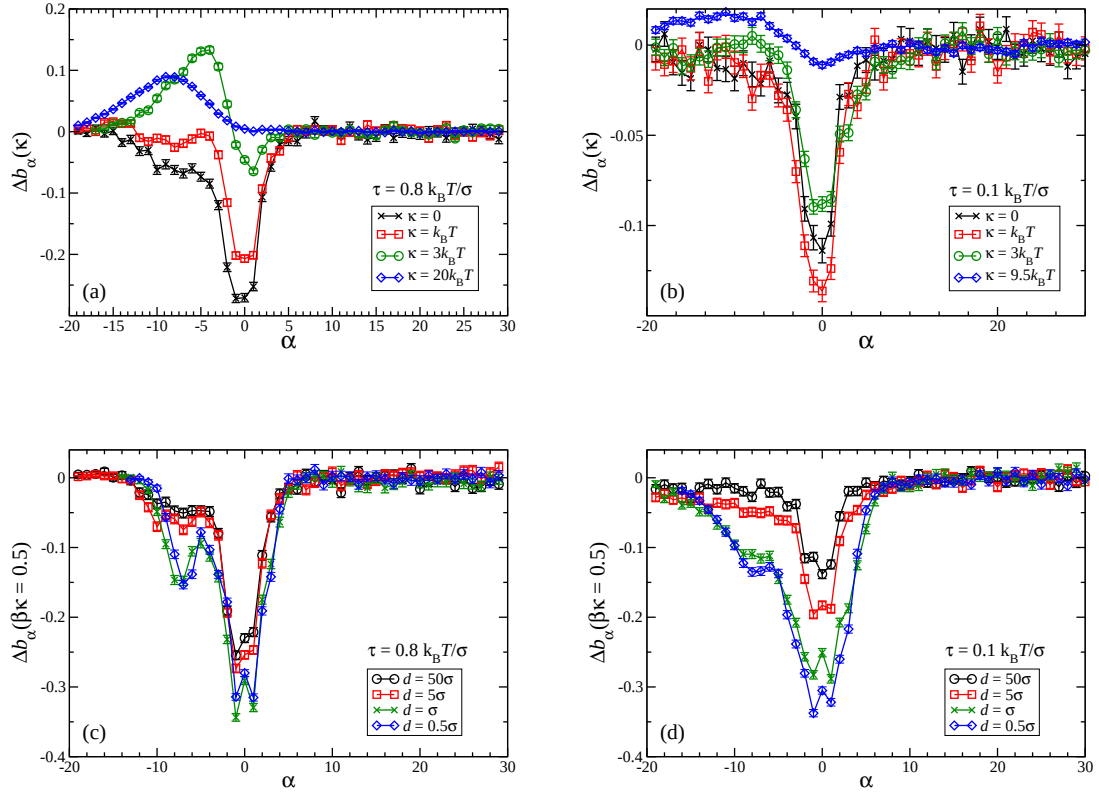


Figure 5.1: (a), (b): The average local bending difference $\Delta b_\alpha(\kappa)$ (see text) between knotted and linear unconfined polymers of different rigidities, as indicated in the legend. (c), (d): The same quantity at fixed bending rigidity $\kappa = 0.5 k_B T$ for different degrees of slit confinement, as indicated in the legend. In panels (a) and (c) data for the tension $\tau = 0.8 k_B T/\sigma$ are shown, while in panels (b) and (d) for $\tau = 0.1 k_B T/\sigma$.

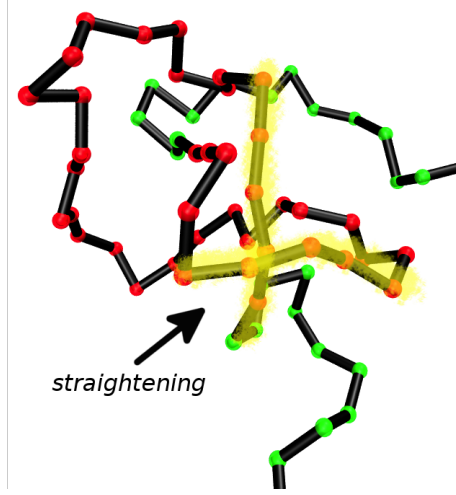


Figure 5.2: Simulation snapshot of the knotted domain of an unconfined, fully flexible polymer chain with a trefoil knot under the tension $\tau = 0.8 k_B T / \sigma$. The straightened-out segments in the vicinity of the strand crossings are highlighted.

vanishes within less than 10 beads outside the knot; outside this region, a knotted chain hardly differs in its bending from an unknotted one. According to Eqs. (5.4) and (5.7), the area under the curves in Figs. 5.1(a) and 5.1(b) determines the slope or $\Psi(\kappa)$ at any κ -value. The major negative contribution to $\Delta B(\kappa)$ for $\kappa = 0$ comes from a small number of monomers close to the knot ends, i.e., in the braiding-region of the knot, in which monomers start getting into the knotted domain. The bending suppression is therefore related to the interaction of the different strands at the crossings, which effectively confines the strands and hence reduces their random bending. Thus, the negative slope of $\Delta F_{\text{knottting}}(\kappa)$ at $\kappa = 0$ arises from this *additional* straightening of the knotted chain with respect to its flexible, unknotted counterpart. As $\Delta B(\kappa = 0)$, which is equal to the area under the respective curves in Figs. 5.1(a) and 5.1(b), is negative, a flexible knotted chain is, on average, *less bent* than its unknotted counterpart, contrary to the intuitive expectation that knotting inevitably *increases* the total bending of a polymer. In Fig. 5.2 we show a simulation snapshot of the knotted domain of a flexible chain, in which the parts of the molecule that get ‘straightened out’ due to the knot are highlighted. As κ grows, we eventually reach the intuitively expected regime in which knotting increases bending, see, e.g., the curve for $\kappa = 20 k_B T$ in Fig. 5.1(a), for which $\Delta B(\kappa) > 0$.

Comparing the curves of Fig. 5.1(a) and (b), one sees that $\Delta B(\kappa)$ for $\kappa = 0$ is more negative for $\tau = 0.8 k_B T / \sigma$ than for $\tau = 0.1 k_B T / \sigma$. This is due to the fact that at smaller τ the braid region is looser and the bending suppression due to the different strands at

the crossings is reduced. On the contrary, if we increase κ , we arrive at a regime where $\Delta B(\kappa)$ is more negative for smaller tensions τ . At $\beta\kappa = 3.0$, ΔB is already positive for $\tau = 0.8 k_B T/\sigma$, due to the positive contribution of $\Delta b_\alpha(\kappa)$ in the interior of the knot, which arises as the knot enforces the polymer to form a loop. The bending throughout a loop is larger if the loop is smaller. For $\tau = 0.1 k_B T/\sigma$ the knot size is increased, which is the reason why the positive $\Delta b_\alpha(\kappa)$ contribution in the interior of the knot is significantly smaller than for $\tau = 0.8 k_B T/\sigma$. Accordingly, for lower tensions the negative net result for $\partial\Psi(\kappa)/\partial\kappa$ persists for higher κ -values than for higher tensions. As can be seen in Fig. 5.1(b), we see a reversal of $\partial\Psi(\kappa)/\partial\kappa$ from negative to positive values only at a rigidity as high as $\beta\kappa \cong 9$.

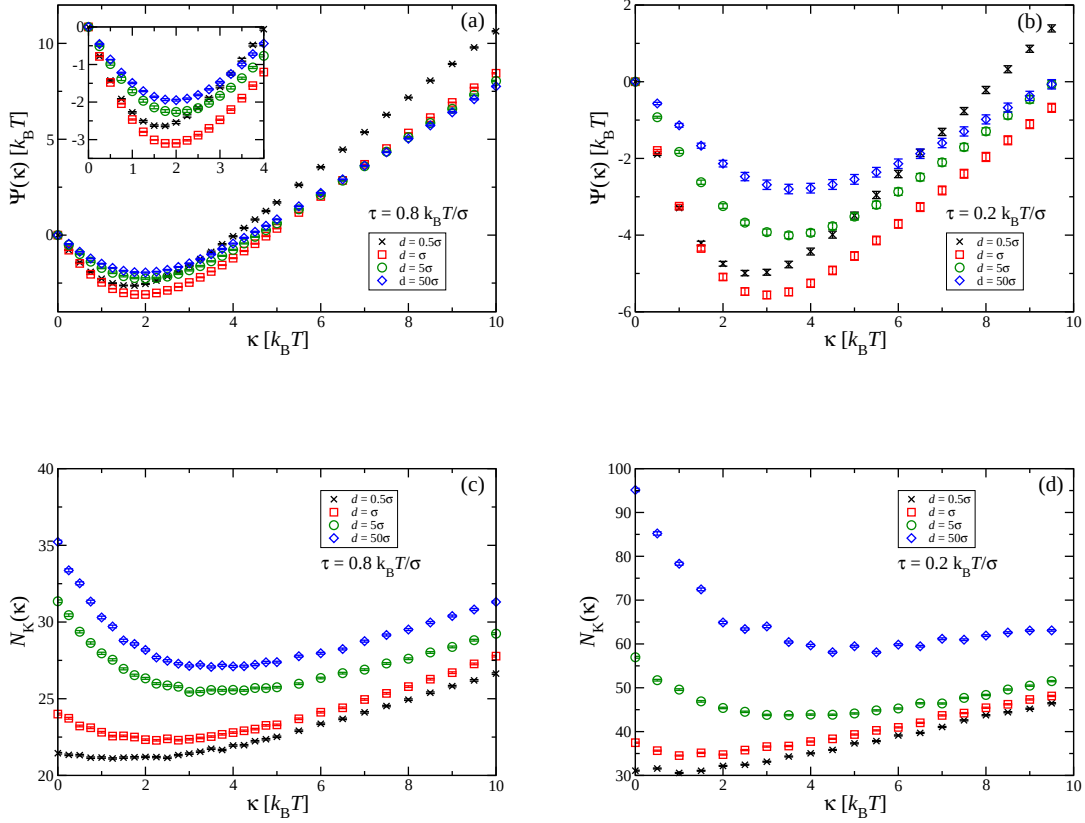


Figure 5.3: (a), (b): The quantity $\Psi(\kappa)$ for different confinements, as indicated in the legend. The inset in (a) shows a zoom of the main panel in the region of the minimum of $\Psi(\kappa)$. (c), (d) The dependence of the number of monomers in the knot, $N_K(\kappa)$, on chain rigidity. In panels (a) and (c) results for the tension $\tau = 0.8 k_B T/\sigma$ are shown, whereas in panels (b) and (d) the tension is $\tau = 0.2 k_B T/\sigma$.

We now turn our attention to the confined case. It turns out that the effects of con-

finement are most transparent at a small, but non-zero value of the bending rigidity, thus we show in Figs. 5.1(c) and 5.1(d) results for $\Delta b_\alpha(\kappa)$ for $\beta\kappa = 0.5$, which is characteristic for all values of $\kappa \leq \kappa_{\min}$, the latter being the value of the rigidity for which $\Psi(\kappa)$ attains its minimum value $\Psi_{\min}$. Here, striking differences between the tensions $\tau = 0.8 k_B T/\sigma$ and $\tau = 0.1 k_B T/\sigma$ show up. While for $\tau = 0.8 k_B T/\sigma$ there is hardly any difference between the confined and unconfined polymers for slit widths as small as $d = 5\sigma$, for $\tau = 0.1 k_B T/\sigma$, confinement enhances Δb_α at the beginning of the knot by almost a factor two. For both tensions, the suppression of bending through knotting becomes *even stronger* as a result of the geometric constraints and thus $\Delta B(\kappa)$ is more negative for the polymer in the slit than it is for the free polymer. This is consistent with the interpretation given above for the case of the unconfined polymer, since the slit confinement forces the strands at the braid region to come closer which further reduces the random bending in the braid region. This effect, however, is more pronounced for smaller tensions, where the braiding region without confinement is looser than for polymer chains under higher tensions.

There exists a correlation between the slopes of $\Psi(\kappa)$ and $N_K(\kappa)$ shown in Fig. 5.3. In the high- κ domain, $\Psi(\kappa) \sim N_K(\kappa) \sim \sqrt{\kappa}$, as is evident from the discussion following Eq. (5.4). For $\kappa = 0$, the knot is swollen due to the presence of steric interactions, maximizing in this way its entropy. However, for non-zero $\kappa \sim k_B T$, the fluctuations of the monomers are restricted in the first place, enabling thus a tighter braided region and a concomitant reduction of knot size. Thus also for small κ the slopes of $\Psi(\kappa)$ and $N_K(\kappa)$ are expected to have the same sign. Note, however, that the value $\tilde{\kappa}$ that minimizes $N_K(\kappa)$ does not coincide with $\kappa_{\min}$, e.g., for very strong confinements $\kappa_{\min} \neq 0$, whereas $\tilde{\kappa}$ is, within simulation resolution, vanishingly small.

The dependence of the rigidity $\kappa_{\min}$ for which $\Psi(\kappa)$ has its minimum on the degree of confinement for different applied tensions is summarized in Fig. 5.4(a). We find that for a tension of $\tau\sigma = 0.8 k_B T$, $\kappa_{\min}$ is only affected by confinement for slit-widths lying at the monomer scale. In this regime of ultra-strong confinement, the energy cost that chain segments would have to pay to go one above the other in a gradual fashion at the braiding regions are too high. This is caused by the external potential, which assigns an increasingly high energetic cost for every monomer that deviates strongly from the $y = 0$ -plane. Accordingly, it is preferable for the system to form localized ‘kinks’ of one or two monomers in the braiding region, which expose a minimal number of monomers to the regions of high external potential, while at the same time creating strong bending there.

The situation is quite different, however, for lower tensions. In this case, also a

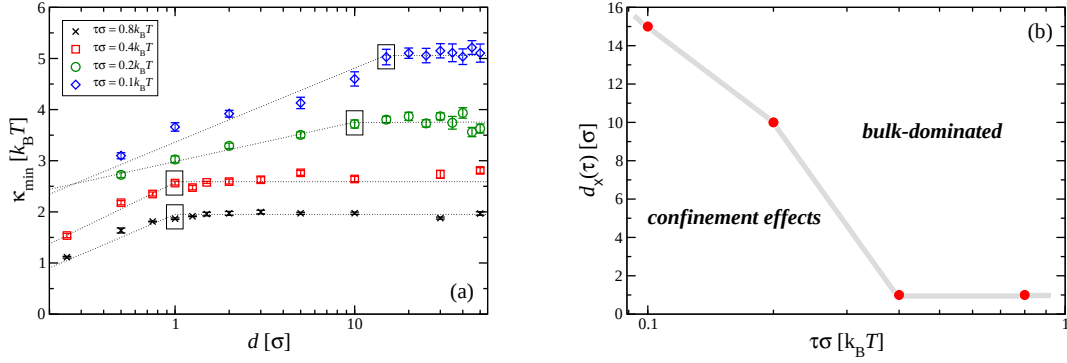


Figure 5.4: (a): The dependence of the optimal value for the rigidity, $\kappa_{\min}$, on confinement for several applied tensions. The dotted lines are guides to the eye, delineating the two regimes where $\kappa_{\min}$ is influenced by confinement, where $\kappa_{\min}$ is d -dependent, and the bulk-dominated regime, where it is not. The crossover data points $d_x(\tau)$ between the two regimes are marked with boxes. (b) The dependence of $d_x(\tau)$ on the applied tension τ . The data points (red circles) are connected with thick gray segments, separating the bulk-dominated regime above the line by the confinement-affected regime below it.

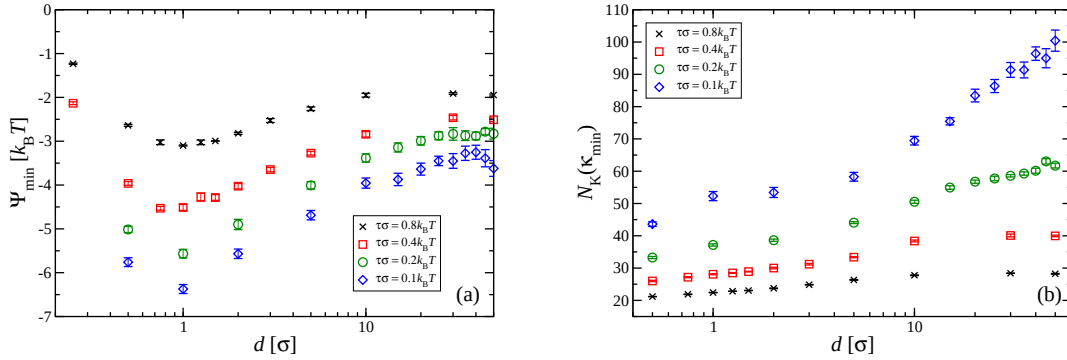


Figure 5.5: (a): The dependence of $\Psi_{\min}$, the value of $\Psi(\kappa)$ at the optimal rigidity $\kappa_{\min}$, on d , the slit-width of the confinement. (b): The knot size at the optimal rigidity as a function of d . Applied tensions as indicated in the legends.

moderate confinement of the order of 10 bond lengths, can significantly affect the value of $\kappa_{\min}$. To better quantify the effects of confinement, we employ a simple, rough-and-ready separation of the data points shown in Fig. 5.4(a) into two groups: for high values of d , the points form plateaus at the bulk values of $\kappa_{\min}$, which we connect by horizontal lines. Through the other groups of points straight lines are drawn by hand, which intersect the horizontal ones at tension-dependent crossover confinement widths $d_{\times}(\tau)$. These values denote, by construction, the crossover of the behaviour of $\kappa_{\min}$ from bulk-dominated, for $d > d_{\times}(\tau)$, to confinement-affected, for $d < d_{\times}(\tau)$. The results are summarized in Fig. 5.4(b), where it can be seen that $d_{\times}(\tau)$ is significantly increased for lower tensions. As we discuss below, the reason the situation is strikingly different for lower tensions seems to be related to the fact that the knot size is then significantly increased with respect to higher tensions.

The increased effects of confinement as τ decreases are also manifested on the value of $\Psi_{\min}$ as well as on the knot size $N_K(\kappa_{\min})$. The former quantity is shown in Fig. 5.5(a) and the latter in Fig. 5.5(b). As can be seen in Fig. 5.5(a), and in contrast to the values $\kappa_{\min}$ itself, even in the case of higher tension the corresponding depth of the minimum $\Psi_{\min}$ is influenced by a confining slit width of the order of 10 bond lengths. However, for lower tensions, the effect on $\Psi_{\min}$ is felt at even larger slit widths. Furthermore, the difference between the value $\Psi_{\min}$ in the bulk ($d/\sigma \gg 1$) and the one for the optimal slit width is enhanced. The fact that the effect of the confinement on the knot size is more pronounced for smaller tensions, as shown in Fig. 5.5(b), correlates well with the finding that confinement shifts $\kappa_{\min}$ to lower values for sufficiently small tensions. As we have seen in Figs. 5.1(a) and 5.1(b) one of the contributions that eventually render $\partial\Psi(\kappa)/\partial\kappa$ positive, is the bending in the interior of the knot, which arises as the knot enforces the polymer to form a loop. This contribution is larger for smaller knot sizes, and it is therefore consistent that $\kappa_{\min}$ will be shifted by confinement if the latter is able to significantly reduce the knot size.

Up to now, all results have been derived for the simplest, trefoil knot; real polymers can, however, display a large variety of increasingly complex knots [115, 116]. Considering other knots allows us on the one hand to put the general character of our results to the test, and also to corroborate our assertion that the crossings at the braiding region are responsible for the reduction of $\Psi(\kappa)$ at finite κ -values. Indeed, more complex knots have more crossing points, where the strands of the polymer chain interact with each other. Thus, according to our analysis above, one should expect that a more complex knot will lead to lower values of $\Delta B(\kappa)$ and $\Psi_{\min}$ for small but finite κ . Our findings for different knot topologies (denoted in the Alexander-Briggs notation [117]) are summarized in Figs.

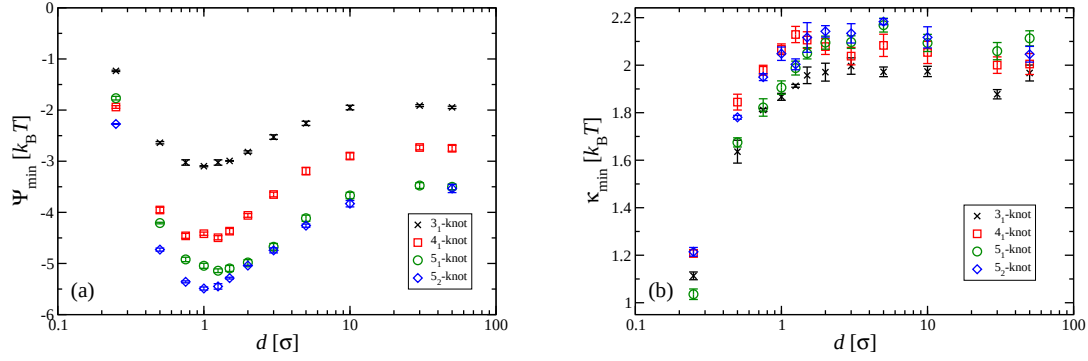


Figure 5.6: (a) The dependence of $\Psi_{\min}$ on confinement for tension $\tau = 0.8 k_B T / \sigma$ and different knot types, as indicated in the legend. (b) The corresponding optimal value of the rigidity $\kappa_{\min}$ for different slit widths and knot types.

5.6(a) and 5.6(b). The data in Fig. 5.6(a) confirm that the main effect of the increased knot complexity is the addition of crossing points which all result in a similar bending suppression as the crossing points of the trefoil knot. Accordingly, for the knot topologies investigated, $\Psi_{\min}$ is approximately proportional to the number of minimal crossings of the respective knot diagram, at least for confinements with $d \geq \sigma$. It is also striking that for the unconfined case, $\Psi_{\min}$ is, within error bars, identical for the 5₁ and 5₂ topologies. A test of whether $\Psi_{\min}$ is in good approximation proportional to the minimal number of crossings of arbitrarily complex knots is beyond the scope of this work. However, the number of strand-crossings will increase with knot complexity. Accordingly, the free energy penalty for putting a knot on a stiff polymer ($\kappa \neq 0$) can be much lower than the one for putting it on a fully flexible polymer ($\kappa = 0$), by amounts that grow with the knot complexity. Whereas $\Psi_{\min}$ is sensitive to the knot type, $\kappa_{\min}$ is not, as can be ascertained from the results shown in Fig. 5.6(b). All data fall within a narrow band of width $\Delta\kappa_{\min} \cong 0.2k_B T$ irrespective of the knot topology.

The tensions considered in our work are of the order of $k_B T / \sigma$. At room temperature and a monomer length scale of 1 nm this corresponds to the pN-scale. These tensions result in values of $\kappa_{\min} \approx 5 k_B T$. As it was found in previous work [25], without confinement $\kappa_{\min}$ scales approximately as $\sim \tau^{-1/2}$. A reduction of the tension down to the fN-scale, which is typical of double-stranded DNA molecules [118], will bring $\kappa_{\min}$ at the order of $100 k_B T$. Our results imply that at these lower tensions the effect of confinement on $\kappa_{\min}$ can be expected to be even more pronounced.

5.6 Conclusions

In summary, we have demonstrated that the local stretching at the braiding region and close to the crossing points is the physical mechanism responsible for the minimization of the free energy penalty of knotting of a linear polymer for non-vanishing values of the bending rigidity. Confinement can affect the location of the optimal rigidity for sufficiently low tensions, when it is at the same time significantly affecting the knot size. We therefore expect the geometrical reduction of dimensionality to become relevant for the location of the knots of chains with variable rigidity if the latter are under sufficiently small tensions. For tensions at the fN-scale, which are typical of double-stranded DNA molecules[118], we therefore expect that confinement to strongly influence the value of the optimal rigidity. On the other hand, the amount of reduction of the knotting of free energy by rigidity strongly depends on the topology of the knot and it increases with the knot complexity, scaling roughly with the number of minimal crossings of the knot. Accordingly, we anticipate that more complex knots will localize more strongly in the optimal regions of a chain than simpler ones. Recent advances in tying knots on polymers by optical tweezers [119, 120] and adsorbing them on mica surfaces [108] should allow for experimental testing of our predictions.

6 Conclusions and Outlook

In this work we have introduced a coarse grained model for the description of semiflexible ring polymers, where the macromolecules are represented as soft disks which interact via an anisotropic effective potential. The interactions in the effective description were chosen such that the correct correlation functions are reproduced at infinite dilution. By carrying out simulations of systems of effective particles and comparing them with the results obtained in monomer-resolved computations, we have demonstrated that the effective model is capable to capture the essential Physics over a wide range of densities for rings with a contour to persistence length ratio of $N/s_p \lesssim 10$. In particular, the anisotropic effective model is a dramatic improvement over an isotropic description, where the ring polymers are represented by their center of mass. Our work therefore provides an efficient scheme for the coarse-graining of semiflexible ring polymers and also introduces a realistic class of systems for which anisotropic, ultrasoft and penetrable interactions are physically meaningful.

A particularly interesting phenomenon observed for semiflexible ring polymers is the formation of stacks, which we have analyzed by employing an algorithm for the identification of tube-like structures. We show that the effective as well as the monomer resolved model predict the formation of large columns with more than 100 members at high densities. We have also extended our effective description to study bidisperse mixtures of ring polymers. At high densities stacks also formed in the investigated bidisperse mixtures, but instead of columns of oblate rings interpenetrated by prolate ones, the stacks were formed by large rings interpenetrated by small ones. The mechanism of the stack formation of mixtures was thus quite different to the one observed in monodisperse systems. For future work it would be interesting to extend this analysis to more general polydisperse mixtures and to investigate the formation of stacks in these systems, as well as the possibility of ordered structures.

The simplifications achieved in the effective description of the semiflexible ring polymers also allowed us to analyze them by means of density functional theory (DFT). We have computed pair correlation functions in the isotropic and anisotropic effective model by employing mean field theory (MFT) and the hypernetted chain approximation (HNC). For the isotropic system the predictions obtained by both MFT and HNC were in excellent agreement with simulation results, however at higher densities the isotropic model itself misses important features by neglecting the anisotropic nature of the interactions. In the case of the anisotropic effective model MFT consistently predicted results which were similar to simulation results at a higher density. The HNC approximation, on the

other hand, performed very well at all densities investigated. We have also employed DFT to predict the one-particle density of rings in the vicinity of a wall and between walls. To this end we have again employed MFT and a HNC-like approach where a first order expansion of the one-particle density around the homogeneous fluid was used to derive a self-consistent equation for the one-particle density. For the anisotropic direct pair-correlation function in the bulk, which is required for the latter approach, we have used the result obtained employing the HNC approximation. We have compared the results of both approaches with Monte Carlo simulations and found that by increasing the density one can flip the rings close to the wall. Moreover MFT predicts the formation of an alternating arrangement of layers at high densities. While this interesting structure is not observed in simulations with one single wall, it is to some extent reproduced in simulations between two walls. While the MFT results were quantitatively not predictive, the results of the HNC-like approach were in quantitative agreement with simulations over a wide range of densities. Since the behavior of effective rings in the vicinity of wall(s) turned out to be quite unexpected, it would be interesting to carry out corresponding large-scale simulations of monomer-resolved rings for future work. Furthermore, the algorithms, which we employ to solve the self-consistent equations from the DFT of the anisotropic effective model, could be sped up significantly by parallelization, which would make them more useful for practical applications in the future, in particular to apply the HNC approach at higher densities.

By carrying out simulations of knotted polymer chains we have investigated the phenomenon that on a polymer chain with varying stiffness the knots do not always prefer the domain with the smallest rigidity. We have demonstrated that the local stretching at the braiding region is the physical mechanism responsible for the non-vanishing value of the bending rigidity that is preferred by a knot in equilibrium. We have also shown that confinement can affect the value of this optimal rigidity for sufficiently low tensions, when it is at the same time significantly affecting the knot size. Moreover, for the different knot topologies, which we have investigated, the value of the optimal rigidity remained unchanged, while the extent by which the knot preferred the optimal domain was strongly affected. For future work it would be interesting to see whether this behavior continues for more complex knot topologies. Tying knots on polymers by optical tweezers should allow for experimental testing of our predictions.

A Calculation of the Anisotropic Effective Potential

As discussed in section 2.2, we wish to sample $P(r, \cos \theta_1, \cos \theta_2, \varphi)$ for a system of two ring polymers, in order to obtain a numerical expression for the anisotropic effective potential between them. We know that for large values of r , when the polymers can not interact with each other, P will correspond to the ideal case, P_{id} . Therefore the interesting configurations for us are those values of r that result in overlaps between the ellipsoids of gyration. We use a biasing potential between the centers of mass of the two rings to restrict r to certain *umbrella windows*:

$$V_{\text{bias}}^{(j)}(r) = \frac{k_j}{2} (r - r_j)^2. \quad (\text{A.1})$$

With r_j , k_j we can tune respectively the location and width of the window for r in which configurations are sampled. We carry out simulations for a range of different r_j and k_j values and calculate histograms $P_{\text{bias}}^{(j)}(Q)$ in the effective coordinates. Here, Q stands for $(r, \cos \theta_1, \cos \theta_2, \varphi)$ as a collective variable and thus denotes a bin in the effective coordinates, whereas j is the index of the respective biased simulation and thus determines k_j and r_j . The binning in the 4D space is identical for all biased simulations. We use the *Self-Consistent Histogram Method* by Ferrenberg and Swendsen[75, 76] to combine the different $P_{\text{bias}}^{(j)}(Q)$, which results in an estimate $P_{\text{est},j}(Q)$ for the histogram $P(Q)$ of the unbiased system. The starting point of this method is that every simulation does in principle give an estimate for the histogram $P(Q)$ of the unbiased simulation:

$$P_{\text{est},j}(Q) = N^{(j)} \exp\left(\beta V_{\text{bias}}^{(j)}(Q)\right) P_{\text{bias}}^{(j)}(Q). \quad (\text{A.2})$$

Here, $V_{\text{bias}}^{(j)}$ denotes the bias potential in the j -th simulation, given by (A.1) and $N^{(j)}$ is a normalization factor, which can be expressed as

$$N^{(j)} = \sum_Q P(Q) \exp\left(-\beta V_{\text{bias}}^{(j)}(Q)\right), \quad (\text{A.3})$$

assuming that both $P(Q)$ and $P_{\text{bias}}^{(j)}(Q)$ are normalized. However, this estimate for $P(Q)$ will only be useful for Q bins that have good statistics in the j -th simulation, which in our case means that the bins are at an r coordinate that is close to the r_j value of the respective bias. Another problem with this expression is that in order to calculate $N^{(j)}$ we already need to know the sought-for quantity $P(Q)$. To deal with the first problem, we combine the individual estimates obtained from each j -th simulation, to form an improved estimate:

$$P_{\text{est}}(Q) = \sum_j c^{(j)}(Q) P_{\text{est},j}(Q). \quad (\text{A.4})$$

With $c^{(j)}(Q)$ we can tune the weight of $P_{\text{est},j}(Q)$ in the $P(Q)$ estimate. We require $\sum_j c^{(j)}(Q) = 1$. In bins where the j -th simulation has bad statistics we will choose $c^{(j)}(Q)$ close to 0, such that the $P_{\text{est},j}(Q)$ estimate contributes only in bins where it is useful. The error of $P_{\text{est}}(Q)$ can be estimated via the Poisson distribution and it can be minimized via the following choice for the $c^{(j)}(Q)$:

$$c^{(j)}(Q) = \frac{\exp\left(-\beta V_{\text{bias}}^{(j)}(Q)\right) M^{(j)} N^{(j)}}{\sum_k \exp\left(-\beta V_{\text{bias}}^{(k)}(Q)\right) M^{(k)} N^{(k)}}. \quad (\text{A.5})$$

Here $M^{(j)}$ is the number of uncorrelated configurations sampled in the j -th simulation. With Eqs. A.2-A.5 we now arrive at an expression for an estimate of $P(Q)$. However, as $N^{(j)}$ depends on $P(Q)$ the expression (A.3) can only be evaluated if $P(Q)$ is known in the first place. We can deal with this problem by using $P_{\text{est}}(Q)$ for $P(Q)$ in the formula for $N^{(j)}$ (A.3) to obtain a self-consistency problem for $P_{\text{est}}(Q)$, which can be solved iteratively. As a starting point for this iterative procedure an initial guess for $P_{\text{est}}(Q)$ has to be provided. However, after many iterations the procedure is expected to converge to the same distribution, independent of the given initial condition. We started the iterative algorithm with a uniform distribution for $P_{\text{est}}(Q)$.

B Expansion of the anisotropic pair-correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$

As the anisotropic effective potential $V_{\text{eff}}(r, \cos \theta_1, \cos \theta_2, \varphi)$ and the corresponding pair-correlation function $g(r, \cos \theta_1, \cos \theta_2, \varphi)$ depend on 4 variables, it is hard to visualize them. Nevertheless we can obtain a quantitative measure of the anisotropy in g and V_{eff} by carrying out an expansion of g :

$$g(r, \cos \theta_1, \cos \theta_2, \varphi) = \sum_n c_n(r) f_n(\cos \theta_1, \cos \theta_2, \varphi). \quad (\text{B.1})$$

Here, f_n are modes that depend on the angular degrees of freedom only and they form a complete basis for the angular dependence of g .

To obtain a suitable set of basis functions f_n for the dependence of g on the directors $\mathbf{d}^{(1,2)}$ for a given vector $\mathbf{r}$ between the rings, we started with an expansion to a sum of products of spherical harmonics:

$$\gamma(\mathbf{d}^{(1)}, \mathbf{d}^{(2)}) = \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} c_{l_1, m_1, l_2, m_2} Y_{l_1}^{m_1}(\cos \theta_1, \varphi_1) Y_{l_2}^{m_2}(\cos \theta_2, \varphi_2). \quad (\text{B.2})$$

Here γ denotes g at a given $\mathbf{r}$. By $\cos \theta_i$ and φ_i the director $\mathbf{d}^{(i)}$ is represented in spherical coordinates. We use a reference frame where the connection vector $\mathbf{r}$ between the two rings points to the north-pole and therefore φ_i denotes the azimuthal angle around $\mathbf{r}$. With Y_l^m we denote the spherical harmonics[121]. They fulfil the orthonormality relation $\int d\Omega \bar{Y}_l^m(\cos \theta, \varphi) Y_{l'}^{m'}(\cos \theta, \varphi) = \delta_{l,l'} \delta_{m,m'}$ with $d\Omega = d\cos \theta d\varphi$, where $\bar{z}$ denotes the complex conjugation of a complex number z . This allows us to compute the expansion coefficients via integration:

$$c_{l_1, m_1, l_2, m_2} = \int d\Omega_1 d\Omega_2 \bar{Y}_{l_1}^{m_1}(\cos \theta_1, \varphi_1) \bar{Y}_{l_2}^{m_2}(\cos \theta_2, \varphi_2) \gamma(\cos \theta_1, \varphi_1, \cos \theta_2, \varphi_2). \quad (\text{B.3})$$

Due to the symmetries of γ , we will now be able to compute or relate many of the coefficients and thus arrive at a reduced set of basis functions $\{f_{l_1, l_2, m}\}$ with which we can still represent γ exactly. We first use the continuous symmetry under rotations around the connection vector $\mathbf{r}$:

$$\gamma(\cos \theta_1, \varphi_1, \cos \theta_2, \varphi_2) = \gamma(\cos \theta_1, \varphi_1 - \varphi_2, \cos \theta_2, 0). \quad (\text{B.4})$$

Using (B.3) and $Y_l^m(\cos \theta, \varphi) \propto \exp(im\varphi)$ one can show that c_{l_1, m_1, l_2, m_2} vanishes for $m_1 \neq -m_2$ due to this symmetry. In the following, we enumerate the expansion modes with $m \equiv m_1 = -m_2$. Next we use that $\mathbf{d}^{(i)}$ is equivalent to $-\mathbf{d}^{(i)}$ and therefore γ

fulfils the symmetry $\gamma(\mathbf{d}^{(1)}, \mathbf{d}^{(2)}) = \gamma(-\mathbf{d}^{(1)}, \mathbf{d}^{(2)}) = \gamma(\mathbf{d}^{(1)}, -\mathbf{d}^{(2)})$. Since $Y_l^m(\mathbf{d}) = (-1)^l Y_l^m(-\mathbf{d})$, c_{l_1, m_1, l_2, m_2} are zero if either l_1 or l_2 are odd.

The monomer-resolved model is symmetric under a mirror transformation, which is therefore also a symmetry of the effective model. If we consider a state with $\varphi_2 = 0$ and mirror it by a plane spanned by $\mathbf{r}$ and $\mathbf{d}^{(2)}$ we obtain a state with identical $\mathbf{r}$, $\mathbf{d}^{(2)}$ and $\cos \theta_1$, while φ_1 changes sign. Hence we obtain:

$$\begin{aligned} \gamma(\cos \theta_1, \varphi_1, \cos \theta_2, \varphi_2) &= \gamma(\cos \theta_1, \varphi_1 - \varphi_2, \cos \theta_2, 0) = \\ \gamma(\cos \theta_1, \varphi_2 - \varphi_1, \cos \theta_2, 0) &= \gamma(\cos \theta_1, \varphi_2, \cos \theta_2, \varphi_1). \end{aligned} \quad (\text{B.5})$$

For the first and the last step we used (B.4). Therefore γ is invariant under exchanging φ_1 and φ_2 . We therefore have $c_{l_1, m, l_2, -m} = c_{l_1, -m, l_2, m}$.

Everything discussed so far also holds if we calculate the effective interaction between different rings, e.g. for rings with a different number of monomers. The final symmetry, which we will exploit now, only holds if we have identical rings. In this case we obtain an equivalent state if we swap the orientations of the two ring polymers:

$$\gamma(\cos \theta_1, \varphi_1, \cos \theta_2, \varphi_2) = \gamma(\cos \theta_2, \varphi_2, \cos \theta_1, \varphi_1) = \gamma(\cos \theta_2, \varphi_1, \cos \theta_1, \varphi_2) \quad (\text{B.6})$$

For the last transformation we used (B.5). Hence for identical rings γ is also invariant under an exchange of θ_1 and θ_2 and we therefore know that $c_{l_1, m, l_2, -m} = c_{l_2, m, l_1, -m}$.

We now group basis functions if we a priori know that γ has identical coefficients $c_{l_1, m, l_2, -m}$ with respect to them. We sum the modes in each group and divide by $\sqrt{\#}$, where $\#$ is the number of modes in the group. For identical rings $\#$ is at most 4, but can also be smaller if $l_1 = l_2$ or $m = 0$. For different rings $\# = 2$ if $m \neq 0$ and 1 otherwise. In this way we obtain a new set of basis functions $f_{l_1, l_2, m}$. The indices of $f_{l_1, l_2, m}$ refer to the indices of one of the modes in the group from which $f_{l_1, l_2, m}$ was constructed, with the additional constraint that $m \geq 0$ and $l_2 \geq l_1$ in the case of identical rings. As an example we can consider $f_{2, 4, 1}$, which is set to $(Y_2^1 Y_4^{-1} + Y_2^{-1} Y_4^1 + Y_4^1 Y_2^{-1} + Y_4^{-1} Y_2^1) / \sqrt{4}$ in the case of identical and $(Y_2^1 Y_4^{-1} + Y_2^{-1} Y_4^1) / \sqrt{2}$ in the case of different rings. The new basis functions $f_{l_1, l_2, m}$ only depend on $\varphi \equiv |\varphi_1 - \varphi_2|$ and not on φ_1, φ_2 separately. Thus $|\varphi_1 - \varphi_2|$ is precisely the φ coordinate defined in (2.6), on which g depends. Expanding the angular dependence of g with our new basis functions, we obtain

$$g(r, \cos \theta_1, \cos \theta_2, \varphi) = \sum_{l_1=\{0, 2, 4, \dots\}} \sum_{l_2=\{l_1, l_1+2, l_1+4, \dots\}} \sum_{m=0}^{\min(l_1, l_2)} c_{l_1, l_2, m}(r) f_{l_1, l_2, m}(\cos \theta_1, \cos \theta_2, \varphi). \quad (\text{B.7})$$

In the case of different rings, the sum over l_2 does not start at l_1 but at 0. Like $\{Y_{l_1}^m Y_{l_2}^{-m}\}$,

also $\{f_{l_1, l_2, m}\}$ fulfil the orthonormality relation

$$\int d\Omega_1 d\Omega_2 f_{l_1, l_2, m}(\cos \theta_1, \cos \theta_2, \varphi) f_{l'_1, l'_2, m'}(\cos \theta_1, \cos \theta_2, \varphi) = \delta_{l, l'} \delta_{m, m'}. \quad (\text{B.8})$$

Note that complex conjugation is not necessary as $f_{l_1, l_2, m}$ are real functions in contrast to $Y_{l_1}^m Y_{l_2}^{-m}$. Hence, we can obtain the coefficients $c_{l_1, l_2, m}(r)$ via an integration analogous to (B.3):

$$c_{l_1, l_2, m}(r) = \int d\Omega_1 d\Omega_2 f_{l_1, l_2, m}(\cos \theta_1, \cos \theta_2, \varphi) g(r, \cos \theta_1, \cos \theta_2, \varphi). \quad (\text{B.9})$$

To calculate $c_{l_1, l_2, m}(r)$ we could do a numerical integration of $g(r, \cos \theta_1, \cos \theta_2, \varphi)$. A different approach for the calculation of $c_{l_1, l_2, m}(r)$ is to express the integral in (B.9) as an average over configurations of a system of 2 ring polymers for fixed r . We sample these configurations from the simulations with the bias potential $V_{\text{bias}}(r)$ given in (A.1), which we carried out for calculating g on a 4D grid using *umbrella sampling*. As $V_{\text{bias}}(r)$ does not change the relative weight of configurations with identical r values, we can use the configurations that fall in a small window of r values to estimate averages over the angular degrees of freedom at some fixed r value. The average of the expansion modes $f_{l_1, l_2, m}$ over the configurations of the rings is related to $c_{l_1, l_2, m}(r)$ as follows:

$$\begin{aligned} \langle f_{l_1, l_2, m} \rangle_r &= \frac{\int d\Omega_1 d\Omega_2 g(r, \cos \theta_1, \cos \theta_2, \varphi) f_{l_1, l_2, m}(\cos \theta_1, \cos \theta_2, \varphi)}{\int d\Omega_1 d\Omega_2 g(r, \cos \theta_1, \cos \theta_2, \varphi)} = \\ &= \frac{c_{l_1, l_2, m}(r)}{(4\pi)^2 g^{\text{iso}}(r)}. \end{aligned} \quad (\text{B.10})$$

Here we used (2.9) and (B.9) for the final step. g^{iso} is easy to calculate numerically once we know g . The advantage of this approach with respect to a numerical evaluation of (B.9) is that we do not need to introduce a grid in the angular degrees of freedom. In particular if we want to calculate $c_{l_1, l_2, m}(r)$ coefficients for high l_1, l_2 values the correctness of the result in the first approach depends sensitively on the number of grid points and also on the numerical method for carrying out the integration. Calculating averages on the other hand is straight-forward and we can easily estimate the statistical error using the standard deviation of block-averages. For these reasons we calculate the expansion coefficients $c_{l_1, l_2, m}(r)$ and estimate their errors following the latter approach.

The larger l_i , the faster the $f_{l_1, l_2, m}$ functions can change when the director $\mathbf{d}^{(i)}$ is varied. $f_{0,0,0} = (4\pi)^{-1}$ is constant and therefore gives the isotropic contribution. By comparing $c_{0,0,0}(r)$ with the size of the coefficients for $(l_1, l_2, m) \neq (0, 0, 0)$ we can quantify the importance of anisotropy in the effective interaction.

We find that with the 14 coefficients $c_{l_1, l_2, m}(r)$ for which $l_1, l_2 \leq 4$ we already get a reasonable approximation of g . This is true, even for the smallest rings investigated

($N = 20$), where the anisotropy is most important. This fact allows us to store the essential information in the anisotropic potential with only a few functions of one variable, $c_{l_1, l_2, m}(r)$, instead of a 4D grid with a very large number of grid points. Using only the coefficient $c_{0,0,0}(r)$ we recover $g^{\text{iso}}(r)$ of the isotropic effective model.

C Density Functional Theory Framework For Isotropic and Anisotropic Models

C.1 Self consistent equations for the pair correlation function in a system of identical particles

In the case of the isotropic effective model, we consider a fluid of identical particles interacting via a pair potential $v(r)$. We use density functional theory to obtain schemes to approximately determine the pair-correlation function $g(r)$. This gives us the information of how the density varies in the vicinity of a reference particle, which is sufficient to derive the thermodynamics of the system [101]. In the framework of density functional theory it is possible to derive approximate equations, so-called closure relations, involving the full and the less-intuitive direct pair-correlation function. In addition, there is always an exact relation between the direct and the full pair-correlation, namely the celebrated Ornstein-Zernike equation. This equation in combination with a closure results in a system of self-consistent integral equations, which in principle allows for the computation of the pair-correlation function, at least in a numerical fashion. Since all the closure relations involve approximations, their success depends on the particular system investigated. It is therefore useful to consider several closure relations and investigate their performance for different applications. With the approximate result for the pair-correlation function there are at least three different ways to obtain the equation of state, but unlike for the exact pair-correlation function, the resulting equation of states are different. This problem is known as *thermodynamic inconsistency*.

In this appendix we will first introduce the most important concepts of density-functional theory on which we will rely in the following. In particular we will give a definition of the direct pair-correlation function, which will later pop up in approximations of the full pair-correlation function. Then we present a derivation and some physical interpretation of the Ornstein-Zernike relation, which relates the direct and the full pair-correlation function. Applying the so-called Percus idea, we then derive the *hypernetted-chain* and the *Percus-Yevick* closures. We will also show how to use the same trick in combination with mean field theory to arrive at an additional self-consistent equation that does not require the use of the Ornstein-Zernike equation. Finally we briefly discuss the problem of thermodynamic inconsistency and how to solve the resulting self-consistent equations numerically.

C.1.1 Prerequisites from Density Functional Theory

We consider a system of identical particles, which can interact via some general multi particle interaction potential $V_N(\mathbf{r}^N)^*$. In the presence of an external potential $\Phi(\mathbf{r})$ the interaction part of the Hamiltonian reads

$$V_N(\mathbf{r}^N) + \sum_{i=1}^N \Phi(\mathbf{r}_i). \quad (\text{C.1})$$

We consider this system in the grand canonical ensemble, where the chemical potential μ , the volume V and the temperature T are fixed. Such a system can be realized by bringing it in contact with a reservoir with which both heat and matter can be exchanged. The grand partition sum is defined as

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \exp[-\beta V_N(\mathbf{r}^N)] \left(\prod_{i=1}^N \frac{1}{\Lambda^3} \exp[\beta(\mu - \Phi(\mathbf{r}_i))] \right) d\mathbf{r}^N, \quad (\text{C.2})$$

where $\beta = 1/k_B T$ denotes the reduced temperature, and $\Lambda = \left(\frac{2\pi\beta\hbar^2}{m} \right)^{1/2}$ the de Broglie thermal wavelength. The grand potential Ω is defined as

$$\Omega = -\frac{\log(\Xi)}{\beta}. \quad (\text{C.3})$$

The n -particle density is given as

$$\rho^{(n)}(\mathbf{r}^n) = \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{1}{(N-n)!} \int \exp[-\beta V_N(\mathbf{r}^N)] \left(\prod_{i=1}^N \frac{1}{\Lambda^3} \exp[\beta(\mu - \Phi(\mathbf{r}_i))] \right) d\mathbf{r}^{(N-n)}. \quad (\text{C.4})$$

The grand potential Ω is a functional of the function $\psi(\mathbf{r}) = \mu - \Phi(\mathbf{r})$, which is called the *intrinsic chemical potential*. We can fix the volume V of the system by setting $\psi(\mathbf{r}) = -\infty$ for $\mathbf{r}$ outside the system. The equilibrium state of the grand canonical ensemble is thus fixed by T and $\psi(\mathbf{r})$. The grand canonical potential is related to the internal energy U and the free energy F by Legendre transformations in (S, T) and (N, μ)

$$\Omega = F - N\mu = U - TS - N\mu. \quad (\text{C.5})$$

We can also describe an equilibrium state via $(S, \Phi(\mathbf{r}), N)$ and then an infinitesimal change in the state variables results in:

$$\delta U = T\delta S + \int \rho^{(1)}(\mathbf{r})\delta\Phi(\mathbf{r})d\mathbf{r} + \mu\delta N. \quad (\text{C.6})$$

*We do not immediately restrict ourselves to particles that only interact via a pair potential $v(r)$, since it is initially not difficult to discuss the more general case.

Therefore we obtain

$$\begin{aligned}
\delta\Omega &= \delta U - \delta(TS) - \delta(N\mu) \\
&= -S\delta T - N\delta\mu + \int \rho^{(1)}(\mathbf{r})\delta\Phi(\mathbf{r})d\mathbf{r} \\
&= -S\delta T - \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r}.
\end{aligned} \tag{C.7}$$

In the last equation we used $N = \int \rho^{(1)}(\mathbf{r})d\mathbf{r}$. Using the theory of functional derivatives, we can thus recover $\rho^{(1)}(\mathbf{r})$ from $\Omega(T, \psi(\mathbf{r}))$ via

$$\rho^{(1)}(\mathbf{r}) = -\frac{\delta\Omega}{\delta\psi(\mathbf{r})}. \tag{C.8}$$

In addition (C.7) implies $S = -\frac{\partial\Omega}{\partial T}$. Alternatively Eq. (C.8) can be shown by differentiating the expression for $\Xi(T, \psi(\mathbf{r}))$ given in Eq. (C.2) with respect to $\psi(\mathbf{r})$. It is straightforward, although a bit tedious, to evaluate second order derivatives of $\Omega(T, \psi(\mathbf{r}))$ in this manner

$$\frac{\delta^2\Omega}{\delta\psi(\mathbf{r})\delta\psi(\mathbf{r}')} = -\beta [\rho^{(2)}(\mathbf{r}, \mathbf{r}') + \rho^{(1)}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') - \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')] . \tag{C.9}$$

Evaluating even higher derivatives one obtains a hierarchy of physically meaningful functions, namely the n -fold density correlation functions

$$\frac{\delta^n\Omega}{\delta\psi(\mathbf{r}_1)\dots\delta\psi(\mathbf{r}_n)} = -\beta^n H^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \quad n \geq 2. \tag{C.10}$$

With the $\{\rho^{(1)}, H^{(n)}\}$ functions one can recover the n -particle probability densities $\{\rho^{(n)}\}$. However, we will only deal with functional derivatives of up to degree two.

An important theorem, which is at the heart of density functional theory, is that for a given one particle density distribution $\rho^{(1)}(\mathbf{r})$ it is possible to find exactly one choice for $\psi(\mathbf{r})$ for which the system assumes the imposed $\rho^{(1)}(\mathbf{r})$. This statement is proved in Appendix B of Ref. [101]. Due to this fact it is possible to describe the state of the system with $(T, \rho^{(1)}(\mathbf{r}))$ instead of $(T, \psi(\mathbf{r}))$. In Eq. (C.7) we see that $\psi(\mathbf{r})$ and $\rho^{(1)}(\mathbf{r})$ are conjugated variables (i.e. $\frac{\delta\Omega}{\delta\psi(\mathbf{r})} = -\rho^{(1)}(\mathbf{r})$) and therefore the thermodynamic potential for the variables $(T, \rho^{(1)}(\mathbf{r}))$ is the Legendre transformation of $\Omega(T, \psi(\mathbf{r}))$ with respect to $\psi(\mathbf{r})$:

$$\mathcal{F}(T, \rho^{(1)}(\mathbf{r})) = \Omega + \int \rho^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}. \tag{C.11}$$

$\mathcal{F}$ is called the *intrinsic free energy* and has the following differential

$$\delta\mathcal{F} = -S\delta T + \int \delta\rho^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}. \tag{C.12}$$

Using Eq. (C.5) one obtains

$$\mathcal{F} = F - \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r}, \quad (\text{C.13})$$

a relation which helps us to appreciate the name *intrinsic free energy* for $\mathcal{F}$, which is the total free energy minus the energy in the external field $\phi(\mathbf{x})$. $\mathcal{F}$ is a functional of the one particle density $\rho^{(1)}(\mathbf{r})$ and hence theories building on the functional $\mathcal{F}$ are called *density functional theories*. For the ideal gas, where $V_N(\mathbf{r}^N) = 0$, the integrals (C.2) and (C.4) for Ξ and $\rho^{(1)}(\mathbf{r})$ can be evaluated explicitly:

$$\begin{aligned} \rho^{(1)}(\mathbf{r}) &= \frac{\exp(\beta\psi(\mathbf{r}))}{\Lambda^3}, \\ \beta\mathcal{F}^{\text{id}} &= \int \rho^{(1)}(\mathbf{r}) (\log [\Lambda^3 \rho^{(1)}(\mathbf{r})] - 1) d\mathbf{r}. \end{aligned} \quad (\text{C.14})$$

$\mathcal{F}^{\text{id}}$ can also be carried over for $V_N(\mathbf{r}^N) \neq 0$ and we then define the excess part of the intrinsic free energy $\mathcal{F}$ as

$$\mathcal{F}^{\text{ex}} = \mathcal{F} - \mathcal{F}^{\text{id}}. \quad (\text{C.15})$$

Functional derivatives of $\mathcal{F}^{\text{ex}}$ are called direct correlation functions:

$$c^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = -\beta \frac{\delta^n \mathcal{F}^{\text{ex}}}{\delta \rho^{(1)}(\mathbf{r}_1) \dots \delta \rho^{(1)}(\mathbf{r}_n)}. \quad (\text{C.16})$$

There always exists an exact relation between $c^{(2)}(\mathbf{r}, \mathbf{r}')$ and the two particle probability density $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$, namely the celebrated Ornstein-Zernike equation (OZE). Since we neither know $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ nor $c^{(2)}(\mathbf{r}, \mathbf{r}')$ the OZE alone is not sufficient to determine $\rho^{(2)}$ and we need an additional relation between $c^{(2)}$ and $\rho^{(2)}$, which is called a *closure*. To achieve this one is usually forced to stick to approximations. The OZE in connection with a closure allows for the determination of $\rho^{(2)}$, provided one can solve the resulting self-consistent integral equations, which is usually only possible in a numerical fashion.

C.1.2 The Ornstein-Zernike Equation

To obtain the OZE, we first relate $\rho^{(1)}$ and $c^{(1)}$. From Eq. (C.12) we know that $\psi(\mathbf{r})$ can be determined as the functional derivative of $\mathcal{F}$ by $\rho^{(1)}(\mathbf{r})$:

$$\psi(\mathbf{r}) = \frac{\delta \mathcal{F}}{\delta \rho^{(1)}(\mathbf{r})} = \frac{\delta \mathcal{F}^{\text{ex}}}{\delta \rho^{(1)}(\mathbf{r})} + \frac{\delta \mathcal{F}^{\text{id}}}{\delta \rho^{(1)}(\mathbf{r})} = -\frac{c^{(1)}(\mathbf{r})}{\beta} + \frac{\delta \mathcal{F}^{\text{id}}}{\delta \rho^{(1)}(\mathbf{r})}. \quad (\text{C.17})$$

Using the expression for $\mathcal{F}^{\text{id}}$ given in Eq. (C.14) we obtain the desired relation between $\rho^{(1)}$ and $c^{(1)}$

$$\beta\psi(\mathbf{r}) = -c^{(1)}(\mathbf{r}) + \log [\Lambda^3 \rho^{(1)}(\mathbf{r})], \quad (\text{C.18})$$

which is equivalent to

$$\rho^{(1)}(\mathbf{r}) = \frac{\exp [\beta\psi(\mathbf{r}) + c^{(1)}(\mathbf{r})]}{\Lambda^3}. \quad (\text{C.19})$$

By differentiating the expression for $\psi(\mathbf{r})$ in Eq. (C.18) we get

$$\beta \frac{\delta\psi(\mathbf{r})}{\delta\rho^{(1)}(\mathbf{r}'')} = -c^{(2)}(\mathbf{r}, \mathbf{r}'') + \frac{\delta(\mathbf{r} - \mathbf{r}'')}{\rho^{(1)}(\mathbf{r})}. \quad (\text{C.20})$$

The chain rule of functional differentiation tells us that

$$\int \beta \frac{\delta\psi(\mathbf{r})}{\delta\rho^{(1)}(\mathbf{r}'')} \frac{\delta\rho^{(1)}(\mathbf{r}'')}{\delta\psi(\mathbf{r}')} d\mathbf{r}'' = \beta\delta(\mathbf{r} - \mathbf{r}'). \quad (\text{C.21})$$

Due to Eq. (C.8) $\delta\rho^{(1)}(\mathbf{r}'')/\delta\psi(\mathbf{r}')$ corresponds to a second order functional derivative of Ω with respect to ψ , for which an expression is given in (C.9). Therefore a convolution of Eq. (C.20) with $\delta\rho^{(1)}(\mathbf{r}'')/\delta\psi(\mathbf{r}')$ yields the relation

$$\begin{aligned} \beta\delta(\mathbf{r} - \mathbf{r}') = & \quad (\text{C.22}) \\ - \int \left[-c^{(2)}(\mathbf{r}, \mathbf{r}'') + \frac{\delta(\mathbf{r} - \mathbf{r}'')}{\rho^{(1)}(\mathbf{r})} \right] & \beta [\rho^{(2)}(\mathbf{r}'', \mathbf{r}') + \rho^{(1)}(\mathbf{r}'')\delta(\mathbf{r}'' - \mathbf{r}') - \rho^{(1)}(\mathbf{r}'')\rho^{(1)}(\mathbf{r}')] d\mathbf{r}'', \end{aligned}$$

which is precisely the sought for Ornstein-Zernike equation that gives an exact relation between $\rho^{(2)}$ and $c^{(2)}$. Integrating out the δ -functions and making use of the pair correlation function

$$h^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{\rho^{(2)}(\mathbf{r}, \mathbf{r}') - \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')}{\rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')}, \quad (\text{C.23})$$

we obtain the following simplified expression for the OZE:

$$h^{(2)}(\mathbf{r}, \mathbf{r}') = c^{(2)}(\mathbf{r}, \mathbf{r}') + \int c^{(2)}(\mathbf{r}, \mathbf{r}'')\rho^{(1)}(\mathbf{r}'')h^{(2)}(\mathbf{r}'', \mathbf{r}')d\mathbf{r}''. \quad (\text{C.24})$$

As mentioned before one needs an additional relation between $c^{(2)}$ and $h^{(2)}$, a so-called closure, in order to calculate $h^{(2)}$ with the help of the OZE. That the OZE alone does not allow us to compute any observables of the model should not surprise us, since it is completely independent of the potential $V_N(\mathbf{r}^N)$ between the particles and holds for the ideal gas, as well as for a system of strongly interacting particles. Often the OZE is not derived but stated as a definition for the direct correlation function $c^{(2)}$ (because given $h^{(2)}$ there exists exactly one function $c^{(2)}$ for which the OZE is fulfilled). However, if one introduces the OZE as a definition for another unknown function $c^{(2)}$ it is difficult to come up with an additional connection between $h^{(2)}$ and this newly defined function. In the following the definition of $c^{(2)}$ as a second order derivative of $\mathcal{F}^{\text{ex}}$ will be important for deriving closures for the OZE.

Before we do so however, we discuss a possible physical interpretation of the OZE: The total correlation of particles at $\mathbf{r}$ and $\mathbf{r}'$ is represented by $h^{(2)}(\mathbf{r}, \mathbf{r}')$, which has

contributions due to direct correlations, described by $c^{(2)}(\mathbf{r}, \mathbf{r}')$, and indirect correlations. The indirect correlations arise due to direct correlations with other particles that in turn correlate with a particle at position $\mathbf{r}'$. Since the other particles again correlate directly and indirectly with a particle at position $\mathbf{r}'$ one needs to compute an infinite series of integrals over the direct correlation functions in order to compute the indirect correlations between particles at $\mathbf{r}$ and $\mathbf{r}'$. This can be seen explicitly by recursively solving the OZE:

$$\begin{aligned} h^{(2)}(\mathbf{r}, \mathbf{r}') &= c^{(2)}(\mathbf{r}, \mathbf{r}') + \int c^{(2)}(\mathbf{r}, \mathbf{r}'') \rho^{(1)}(\mathbf{r}'') c^{(2)}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \\ &+ \int \int c^{(2)}(\mathbf{r}, \mathbf{r}'') \rho^{(1)}(\mathbf{r}'') c^{(2)}(\mathbf{r}'', \mathbf{r}''') \rho^{(1)}(\mathbf{r}''') c^{(2)}(\mathbf{r}''', \mathbf{r}') d\mathbf{r}'' d\mathbf{r}''' \\ &+ \dots \end{aligned} \quad (\text{C.25})$$

Therefore it is physically plausible that short ranged direct correlations can result in long ranged indirect correlations.

C.1.3 The Percus Idea

In the following we will restrict ourselves to models, where we have identical particles, which all interact with the same pair potential, i.e.

$$V_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N v(\mathbf{r}_i - \mathbf{r}_j). \quad (\text{C.26})$$

One elegant starting point for deriving approximate closure relations for the OZE is an idea by Percus [122]. If we apply the external field $\Phi(\mathbf{r}) = v(\mathbf{r})$ the probability density $\rho^{(1)}(\mathbf{r}, \Phi = v)$ for finding a particle at position $\mathbf{r}$ in this external field, should be identical to the probability for finding a particle at position $\mathbf{r}$ given that one particle is located at the origin. Therefore one should be able to express the pair correlation function $h(\mathbf{0}, \mathbf{r})$ in the system without an external field by $\rho^{(1)}(\mathbf{r}, \Phi = v)$. Henceforth approximations of $\rho^{(1)}(\mathbf{r}, \Phi = v)$, which usually involve expressions of the direct correlation function $c^{(2)}$, yield approximate closure relations for the OZE.

The one particle density $\rho^{(1)}(\mathbf{r})$ in the absence of an external field is a constant in space*:

$$\rho^{(1)}(\mathbf{r}, \Phi = 0) = \rho. \quad (\text{C.27})$$

The expression for $\Xi(\Phi)$ and $\rho^{(1)}(\mathbf{r}, \Phi)$ given in Eqs. (C.2) and (C.4) allow us to rigorously derive the following intuitive result, which is the concise mathematical equation describing

*Strictly speaking this is only true if one uses periodic boundary conditions or ignores boundary effects by only considering $\mathbf{r}$ values inside the very large volume V of the system.

the idea of Percus:

$$\rho^{(1)}(\mathbf{r}, \Phi = v) = \frac{\rho^{(2)}(\mathbf{0}, \mathbf{r}, \Phi = 0)}{\rho}. \quad (\text{C.28})$$

For the pair correlation function of the system without an external potential, i.e. $\Phi(\mathbf{r}) = 0$, we thus obtain:

$$h^{(2)}(\mathbf{r}, \mathbf{r}') = h^{(2)}(\mathbf{r} - \mathbf{r}') = \frac{\rho^{(1)}(\mathbf{r} - \mathbf{r}', \Phi = v)}{\rho} - 1. \quad (\text{C.29})$$

Equation (C.19) allows us to express $\rho^{(1)}(\mathbf{r}, \Phi = v)$ with $c^{(1)}(\mathbf{r}, \Phi = v)$:

$$\begin{aligned} h^{(2)}(\mathbf{r}) &= \frac{\exp(\beta(\mu - v(\mathbf{r})) + c^{(1)}(\mathbf{r}, \Phi = v))}{\Lambda^3 \rho} - 1 \\ &= \exp[-\beta v(\mathbf{r}) + c^{(1)}(\mathbf{r}, \Phi = v) - c^{(1)}(\mathbf{r}, \Phi = 0)] - 1 \\ &= \exp[-\beta v(\mathbf{r}) + \Delta c^{(1)}(\mathbf{r})] - 1. \end{aligned} \quad (\text{C.30})$$

C.1.4 The Hypernetted-Chain and the Percus-Yevick closures

Our strategy now is to approximate $\exp[\Delta c^{(1)}(\mathbf{r})]$ in Eq. (C.30), which will yield different closure relations, depending on the applied approximations. According to Eq. (C.29) the change in $\rho^{(1)}(\mathbf{r})$ due to the applied external field $\Phi = v$ is given by

$$\Delta \rho^{(1)}(\mathbf{r}) = \rho h^{(2)}(\mathbf{r}). \quad (\text{C.31})$$

We obtain a closure by expanding $\Delta c^{(1)}(\mathbf{r})$ up to first order in $\Delta \rho^{(1)}$:

$$\begin{aligned} \Delta c^{(1)}(\mathbf{r}) &\approx \int \Delta \rho^{(1)}(\mathbf{r}') \left. \frac{\delta c^{(1)}(\mathbf{r})}{\delta \rho^{(1)}(\mathbf{r}')} \right|_{\Phi=0} d\mathbf{r}' \\ &= \int \Delta \rho^{(1)}(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}', \end{aligned} \quad (\text{C.32})$$

where $c^{(2)}(\mathbf{r}, \mathbf{r}') = c^{(2)}(\mathbf{r} - \mathbf{r}')$ denotes the direct pair correlation function for $\Phi = 0$. Plugging this result into Eq. (C.30) we obtain a closure relation, which is commonly known as the *hypernetted-chain* (HNC) approximation*:

$$\begin{aligned} h^{(2)}(\mathbf{r}) &= \exp[-\beta v(\mathbf{r})] \exp \left[\int \rho h^{(2)}(\mathbf{r}') c^{(2)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \right] - 1 \\ &= \exp[-\beta v(\mathbf{r})] \exp[h^{(2)}(\mathbf{r}) - c^{(2)}(\mathbf{r})] - 1, \end{aligned} \quad (\text{C.33})$$

*One might wonder why this closure relation is named *hypernetted-chain* approximation. The reason for this is that one can also derive this closure relation by a diagrammatic expansion of the pair-correlation function. The class of diagrams, which one effectively sums up if one uses this closure, is called *hypernetted-chain* diagrams [123], due to their graphical appearance, and they lend their name to the closure.

we have used the OZE in the final step. The HNC closure was first introduced in Ref. [123]. Instead of $\Delta c^{(1)}(\mathbf{r})$ one can also expand $\exp [\Delta c^{(1)}(\mathbf{r})]$ up to first order in $\Delta \rho^{(1)}$:

$$\begin{aligned}\exp [\Delta c^{(1)}(\mathbf{r})] &\approx 1 + \Delta c^{(1)}(\mathbf{r}) \\ &\approx 1 + \int \Delta \rho^{(1)}(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'.\end{aligned}\quad (\text{C.34})$$

Using this approximation in (C.30) yields the so-called Percus-Yevick (PY) closure:

$$\begin{aligned}h^{(2)}(\mathbf{r}) &= \exp [-\beta v(\mathbf{r})] \left(1 + \int \rho h^{(2)}(\mathbf{r}') c^{(2)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \right) - 1 \\ &= \exp [-\beta v(\mathbf{r})] (1 + h^{(2)}(\mathbf{r}) - c^{(2)}(\mathbf{r})) - 1,\end{aligned}\quad (\text{C.35})$$

we have again used the OZE in the final step. The PY closure was independently proposed in Refs. [124] and [125]. By linearizing the HNC closure in $(h^{(2)}(\mathbf{r}) - c^{(2)}(\mathbf{r}))$ one obtains the PY closure.

The integral equations obtained with the HNC and PY closures in connection with the OZE are the classical integral equations of liquid-state theory. Since the expansion in density fluctuations converges very well for $\rho \rightarrow 0$, both closures correctly predict $h^{(2)}(\mathbf{r}) = \exp [-\beta v(\mathbf{r})] - 1$ in this limit. Both closures are in agreement with the density expansion of $h^{(2)}(\mathbf{r})$ up to order ρ and as a consequence they give the correct second and third virial coefficients in the expansion of the equation of state. However, terms in $h^{(2)}(r)$ of order ρ^2 and beyond are not predicted correctly and therefore the approximations will eventually break down at high densities.

Both closures can also be obtained as a diagrammatic expansion of the pair correlation function, where they correspond to the sum of certain classes of diagrams. In fact the HNC closure contains a larger class of diagrams, which however does not imply that it is always more successful than the PY closure, since both approximations do not agree with the density expansion of $h^{(2)}(r)$ beyond order ρ . If the PY integral equations are more successful than the use of the HNC closure, which is often the case for short ranged potentials, this has to be due to a cancellation of errors. For bounded interaction potentials $v(r)$ which are long ranged the HNC is usually more successful than the PY closure. In this work we have not applied the PY but only the HNC closure.

C.1.5 Self Consistent Equation from Mean Field Theory

In the mean field theory (MFT) approximation the energy required to place a particle at position $\mathbf{r}$ is approximated by the average energy that would be required, if all the other particles were independently distributed by the one particle distribution function $\rho^{(1)}(\mathbf{r})$:

$$E_{\text{MFT}}(\mathbf{r}, \Phi) = \int d\mathbf{r}' \rho^{(1)}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') + \Phi(\mathbf{r}). \quad (\text{C.36})$$

Loosely speaking one says that in this approximation the interaction energy of every particle is computed in the *mean field* of all the others. In this approximation we can easily arrive at an expression for the one particle distribution function $\rho^{(1)}(\mathbf{r})$: If $E_{\text{MFT}}(\mathbf{r})$ is the energy required to place a particle at position $\mathbf{r}$, $\rho^{(1)}(\mathbf{r})$ is proportional to the Boltzmann factor of this energy:

$$\rho^{(1)}(\mathbf{r}, \Phi) \sim \exp[-\beta E_{\text{MFT}}(\mathbf{r}, \Phi)]. \quad (\text{C.37})$$

Using the Percus idea we arrived at Eq. (C.29)

$$h^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{\rho^{(1)}(\mathbf{r} - \mathbf{r}', \Phi = v)}{\rho} - 1, \quad (\text{C.38})$$

which we can now use to obtain a self-consistent equation for the pair correlation function in the MFT approximation. To achieve this we only have to fix the normalization constant C in

$$\rho^{(1)}(\mathbf{r}, \Phi = v) = C \exp \left[-\beta \int d\mathbf{r}' \rho^{(1)}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') - \beta v(\mathbf{r}) \right]. \quad (\text{C.39})$$

To this end we can use that $\rho^{(1)}(\mathbf{r} \rightarrow \infty, \Phi = v) = \rho$, where ρ is the bulk density. Since $v(\mathbf{r} \rightarrow \infty) = 0$ this brings us to the identity

$$\rho = C \exp \left[-\beta \int d\mathbf{r}' \rho v(\mathbf{r} - \mathbf{r}') \right], \quad (\text{C.40})$$

and we thus obtain

$$\rho^{(1)}(\mathbf{r}, \Phi = v) = \rho \exp \left[-\beta \int d\mathbf{r}' [\rho^{(1)}(\mathbf{r}') - \rho] v(\mathbf{r} - \mathbf{r}') - \beta v(\mathbf{r}) \right]. \quad (\text{C.41})$$

Together with Eq. (C.37) we thus arrive at the following self-consistent equation for the pair correlation function:

$$h^{(2)}(\mathbf{r}) = \exp \left[-\beta \rho \int d\mathbf{r}' h^{(2)}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') - \beta v(\mathbf{r}) \right] - 1. \quad (\text{C.42})$$

Interestingly we have obtained an expression, which is almost identical to the one in Eq. (C.33), with the only difference that the interaction potential v is used in place of the direct pair-correlation function $c^{(2)}$.

C.1.6 Thermodynamic Inconsistency

By using the HNC or PY closure in combination with the OZE we can now determine the density correlation function $h^{(2)}(r)$ by solving the obtained integral equations numerically. We then wish to predict the thermodynamics of the system with this information. One

can express the pressure P , the compressibility χ_T and the internal energy U of the system with $h^{(2)}(r)$:

$$P = \rho k_B T - \frac{2\pi\rho^2}{3} \int_0^\infty r^3 \frac{dv(r)}{dr} (h^{(2)}(r) + 1) dr, \quad (\text{C.43})$$

$$\chi_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = 1 + 2\pi\rho \int r^2 h^{(2)}(r) dr, \quad (\text{C.44})$$

$$\frac{U}{N} = \frac{3k_B T}{2} + 2\pi\rho \int_0^\infty r^2 v(r) (h^{(2)}(r) + 1) dr. \quad (\text{C.45})$$

The relation (C.43) directly gives us the equation of state for the system. However one can also determine P with the formula for the compressibility (C.44) and the internal energy (C.45). To obtain P from Eq. (C.44) we can integrate χ_T^{-1}/ρ , which corresponds to $(\partial P/\partial \rho)_T$, by the density ρ starting from $\rho = 0$, where the pressure P vanishes. In order to use Eq. (C.45) to determine the equation of state we need to remember that U is related to the derivative of the free energy F with respect to β :

$$U = \left(\frac{\partial(\beta F)}{\partial \beta} \right)_{V,N}. \quad (\text{C.46})$$

For $\beta \rightarrow 0$, we have $T \rightarrow \infty$ and are therefore in the limit of the ideal gas, where we can calculate the free energy analytically. Thus, we can compute the free energy F by integrating U with respect to β and one can then compute P by differentiating F by the volume.

Obtaining P using Eqs. (C.43), (C.44) and (C.45) is commonly referred to as the *virial*, *compressibility* and *energy route* to the equation of state. If we used the exact $h^{(2)}(r)$ all expressions for P would be identical but because we had to stick to approximations they usually yield different results. This is known as the problem of *thermodynamic inconsistency*.

The HNC closure is a special case, because one can also derive it by approximating the full free energy functional with a simpler one for which the HNC closure is not an approximation but exact [101]. The $h^{(2)}(r)$ obtained by the use of the HNC closure is therefore the exact pair density correlation function of a well defined free energy functional. It is possible to show, that the derivative of that free energy with respect to the volume gives the same result as the *virial route* to the equation of state [126]. Therefore for the HNC the *virial* and *energy route* to the equation of state are equivalent.

C.1.7 Numerical solution of the self consistent equations

The self consistency equations, which we need to solve are of the form

$$h^{(2)}(\mathbf{r}) = F[h^{(2)}](\mathbf{r}), \quad (\text{C.47})$$

where F is some functional of $h^{(2)}$. We solve these equations numerically via an iterative scheme that starts with some initial *guess* function f_0 and where successive iterations are computed as

$$f_{n+1} = f_n + \Delta s (F[f_n] - f_n). \quad (\text{C.48})$$

The constant Δs is usually set to a value smaller than 1. When applying this iterative scheme, we hope that f_n converges to a function that solves equation (C.47). Whether or not the iteration scheme converges also depends on the size of Δs . If one chooses Δs too large the scheme might not converge, however if Δs is very small one progresses in very small steps and will therefore need to carry out many iterations. For all the applications in this work we have obtained convergence with the choice $\Delta s = 0.1$. For the initial *guess* function f_0 we have chosen a flat profile.

In order to apply the functional F on some function f , we need to carry out convolutions in 3 dimensions, which are of the form

$$f \star h(\mathbf{r}) \equiv \int d\mathbf{r}' f(\mathbf{r} - \mathbf{r}') h(\mathbf{r}'). \quad (\text{C.49})$$

However, the isotropic interaction potential in the effective model only depends on $|\mathbf{r}|$, i.e. we have that $v(\mathbf{r}) = v(|\mathbf{r}|)$. Due to this fact the functions that appear in the convolutions in the self-consistency equations are also spherically symmetric. We compute convolutions with the help of the convolution-theorem

$$\widehat{f \star h}(\mathbf{k}) = \widetilde{f}(\mathbf{k}) \widetilde{h}(\mathbf{k}), \quad (\text{C.50})$$

where $\widetilde{f}$ denotes the Fourier transformation of the function f , which is defined as

$$\widetilde{f}(\mathbf{k}) \equiv \int d\mathbf{r} f(\mathbf{r}) \exp[-i\mathbf{k} \cdot \mathbf{r}]. \quad (\text{C.51})$$

For a spherically symmetric function we can carry out the angular integrations:

$$\begin{aligned} \widetilde{f}(k) &= \frac{4\pi}{k} \int_0^\infty dr r f(r) \sin(kr) \\ &= i \frac{2\pi}{k} \int_{-\infty}^\infty dr r f(r) \exp[-ikr] \\ &= i \frac{2\pi}{k} \widehat{rf}(k), \end{aligned} \quad (\text{C.52})$$

where $f(r)$ is extended to negative values of r by setting $f(-r) \equiv f(r)$. Henceforth we can express the three dimensional Fourier transformation of a spherically symmetric function f by the one dimensional Fourier transformation of the function $rf(r)$, which we denote by $\widehat{rf}(k)$. Using this relation to simplify the Fourier transforms within the convolution-theorem (C.50) we arrive at the equation

$$\widehat{rf \star h}(k) = i \frac{2\pi}{k} \widehat{rf}(k) \widehat{rh}(k). \quad (\text{C.53})$$

This allows us to efficiently compute the Fourier series coefficients of the one dimensional function $rf \star h$ defined on a finite interval, i.e. $r \in [-L/2, L/2]$. Strictly speaking the relation can only be applied for $L \rightarrow \infty$, but we can choose L large enough, such that $rf \star h$, rf , as well as rh are very close to zero for $|r| > L/2$ and the Fourier series coefficients computed for the interval $[-L/2, L/2]$ are practically identical to the Fourier transformed functions at the respective k values.

The Fourier series coefficients of a function $f(r)$ defined on the interval $r \in [-L/2, L/2]$ are given as

$$\widehat{f}_n \equiv \int_{-L/2}^{L/2} dr f(r) \exp \left[-i \frac{2\pi}{L} nr \right], \quad (\text{C.54})$$

and the inverse transformation reads

$$f(r) = \frac{1}{L} \sum_{n=-\infty}^{\infty} \widehat{f}_n \exp \left[i \frac{2\pi}{L} nr \right]. \quad (\text{C.55})$$

Thus for large enough L Eq. (C.53) implies

$$\widehat{rf \star h}_n = i \frac{2L}{n} \widehat{rf}_n \widehat{rh}_n. \quad (\text{C.56})$$

Therefore the Fourier series coefficients of rf and rh allow the computation of $\widehat{rf \star h}_n$, except for the special case $n = 0$, where the equation is not usable. However, f as well as h and therefore also $f \star h$ are even functions in r , which means that $rf \star h$ is odd in r and its $n = 0$ Fourier series coefficient therefore vanishes.

Finally we have to think about how to compute the Fourier series coefficients (C.54) and the inverse transformation (C.55) efficiently. Let us assume that we have tabulated f on N equidistant grid points $r_j = -L/2 + (j + \frac{1}{2}) \Delta r$, where $\Delta r = L/N$. If we assume that the Fourier spectrum of the function $f(r)$ is limited such that Fourier series coefficients that correspond to modes with a wavelength $\lambda \leq \Delta r/2$ vanish, it is possible to compute the Fourier series coefficients $\{\widetilde{f}_{-N/2+1}, \dots, \widetilde{f}_{N/2-1}\}^*$ via a discrete Fourier transformation:

$$\widehat{f}_n = \sum_{j=0}^{N-1} f(r_j) \exp \left[-i \frac{2\pi}{N} r_j \right]. \quad (\text{C.57})$$

If the Fourier spectrum of $f(r)$ includes modes with wavelengths smaller or equal to $\Delta r/2$ this formula is not correct anymore, because if one tries to compute the Fourier series coefficient for the wavenumber $2\pi/\lambda$ with the discrete Fourier transformation, one obtains the sum of the coefficients for the wavenumbers $2\pi/\lambda + j\pi/\Delta r$, with $j \in \mathbb{Z}$. This mistake is known as *aliasing* and one therefore only obtains the correct result if the

*For simplicity we assume that N is even.

Fourier series coefficients of $f(r)$ for all the wavenumbers at $j \neq 0$ vanish*. This means we have to choose the number of grid points N large enough, such that the function $f(r)$ does not change significantly between two grid points and the Fourier series coefficients for wavelengths $\lambda \leq \Delta r/2$ are therefore very small. It is then simple to carry out the back transformation using Eq. (C.55):

$$f(r_j) = \frac{1}{L} \sum_{n=-N/2+1}^{N/2-1} \widehat{f}_n \exp \left[i \frac{2\pi}{L} n r_j \right]. \quad (\text{C.58})$$

To compute the integral given in (C.49) for two spherically symmetric functions f and h , we have therefore first computed the Fourier series coefficients $\widehat{r f}_n$ and $\widehat{r h}_n$ using Eq. (C.57). We can then determine the coefficients $\widehat{r f \star h}_n$ with the relation (C.56), from which we can finally compute $f \star h$ using Eq. (C.58). Applying the *fast Fourier transformation* algorithm to carry out the three discrete Fourier series transformations required for this computation the total computational complexity of this algorithm is of $\mathcal{O}(N \log N)$, where N is the number of grid points for which we have tabulated the functions $f(r)$ and $g(r)$.

C.2 Self consistent equations for the pair correlation function in the anisotropic system

In the case of the anisotropic effective model the particles are disks, which are represented by their center of mass $\mathbf{r}$ and their director $\mathbf{d}$. The interaction energy between two disks $(\mathbf{r}_1, \mathbf{d}_1)$ and $(\mathbf{r}_2, \mathbf{d}_2)$ is given by $v(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{d}_1, \mathbf{d}_2)$. The interaction potential v is anisotropic and thus also depends on the directors of the interacting particles. In this appendix we will first generalize the density functional theory for a system of identical particles to a system containing multiple types of particles. We will see that important relations like the Ornstein-Zernike equation, as well as the closure relations have natural extensions in this more general framework. Afterwards we will interpret the system of particles interacting via an anisotropic interaction potential as a special case of a system containing different particle types. This allows us to efficiently obtain the self-consistent equations for the anisotropic case without the need to re-derive them explicitly.

**Aliasing* is an important concept in the field of digital signal processing. A central theorem in this field is the Nyquist-Shannon sampling theorem, which states that if one samples a signal $f(t)$ at times $j\Delta t$, one can exactly reproduce the Fourier series coefficients by a discrete Fourier transformation if the frequency spectrum of $f(t)$ contains no modes with an angular frequency larger than or equal to the so-called Nyquist frequency of the sampling process, which is $\pi/\Delta t$. If there are higher frequency modes present in $f(t)$ they also distort the results that the discrete Fourier transformation obtains for the low frequency modes due to *aliasing*. In our case the situation is of course completely analogous.

C.2.1 A system with multiple types of particles

Let us first consider a system with N particles of type 1 and M particles of type 2, which interact via two body interaction potentials, i.e.

$$V_{N,M}(\mathbf{x}^N, \mathbf{y}^M) = \sum_{i=1}^N \sum_{j=i+1}^N v_{1,1}(\mathbf{x}_i - \mathbf{x}_j) + \sum_{i=1}^M \sum_{j=i+1}^M v_{2,2}(\mathbf{y}_i - \mathbf{y}_j) + \sum_{i=1}^N \sum_{j=1}^M v_{1,2}(\mathbf{x}_i - \mathbf{y}_j), \quad (\text{C.59})$$

here $v_{i,j}$ denotes the interaction potential between particles of type i and j . A more elegant way to write the interaction energy is to introduce the symbol τ_i , which denotes the type of the particle with the index i . Then the interaction energy of N particles is given by

$$V_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N v_{\tau_i, \tau_j}(\mathbf{r}_i - \mathbf{r}_j). \quad (\text{C.60})$$

This expression is simpler and in addition it has the advantage that it remains valid if more than two particle types are present. To extend the formalism for identical particles to the case of multiple ones, it is useful to introduce distinct external potentials for different particle types. The interaction energy is then given as

$$V_N(\mathbf{r}^N) + \sum_{i=1}^N \Phi_{\tau_i}(\mathbf{r}_i). \quad (\text{C.61})$$

The formalism of density functional theory discussed in the previous appendix seamlessly generalizes to the case of multiple particles, although one has to be a bit more careful concerning the notation. For instance the n -particle probability density of Eq. (C.4) is now given by

$$\rho_{\tau_1, \dots, \tau_n}^{(n)}(\mathbf{r}^n) = \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{1}{(N-n)!} \int \exp[-\beta V_N(\mathbf{r}^N)] \left(\prod_{i=1}^N \frac{1}{\Lambda^3} \exp[\beta(\mu_{\tau_i} - \Phi_{\tau_i}(\mathbf{r}_i))] \right) d\mathbf{r}^{(N-n)}. \quad (\text{C.62})$$

As one can see the generalized n -particle density has n additional indices, which denote the different particle types to which the n -particle density relates to. Likewise the chemical potential μ_{τ} , the external potential Φ_{τ} , the pair correlation function $h_{\tau_1, \tau_2}^{(2)}$, the two body direct correlation function $c_{\tau_1, \tau_2}^{(2)}$, the *intrinsic chemical potential* ψ_{τ} and many other quantities obtain additional indices, since it is necessary to denote the particle types to which these quantities refer to. But apart from this additional index cluttering the underlying ideas of the framework remain mostly unchanged and one can usually *guess* the generalized relations. For instance the Ornstein-Zernike equation becomes

$$h_{\tau_1, \tau_2}^{(2)}(\mathbf{r}, \mathbf{r}') = c_{\tau_1, \tau_2}^{(2)}(\mathbf{r}, \mathbf{r}') + \sum_{\tau} \int c_{\tau_1, \tau}^{(2)}(\mathbf{r}, \mathbf{r}'') \rho_{\tau}^{(1)}(\mathbf{r}'') h_{\tau, \tau_2}^{(2)}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''. \quad (\text{C.63})$$

While this equation can of course be derived rigorously, the corresponding proof would be completely analogous to the one for the OZE for identical particles (C.24), which was presented in the preceding appendix. Analogously one can generalize the HNC closure (C.33)

$$h_{\tau_1, \tau_2}^{(2)}(\mathbf{r}) = \exp[-\beta v_{\tau_1, \tau_2}(\mathbf{r})] \exp[h_{\tau_1, \tau_2}^{(2)}(\mathbf{r}) - c_{\tau_1, \tau_2}^{(2)}(\mathbf{r})] - 1, \quad (\text{C.64})$$

the PY approximation (C.35)

$$h_{\tau_1, \tau_2}^{(2)}(\mathbf{r}) = \exp[-\beta v_{\tau_1, \tau_2}(\mathbf{r})] (1 + h_{\tau_1, \tau_2}^{(2)}(\mathbf{r}) - c_{\tau_1, \tau_2}^{(2)}(\mathbf{r})) - 1, \quad (\text{C.65})$$

as well as the self consistent equation we obtained by using MFT in combination with the Percus idea (C.42)

$$h_{\tau_1, \tau_2}^{(2)}(\mathbf{r}) = \exp \left[-\beta v_{\tau_1, \tau_2}(\mathbf{r}) - \beta \sum_{\tau} \rho_{\tau} \int d\mathbf{r}' h_{\tau_1, \tau}^{(2)}(\mathbf{r}') v_{\tau, \tau_2}(\mathbf{r} - \mathbf{r}') \right] - 1, \quad (\text{C.66})$$

for multiple particle types. The resulting systems of self-consistent equations can be solved with the same numerical iteration schemes applied for the self-consistent equations for identical particles, with the only difference that several convolutions have to be carried out numerically at each iteration step.

For the *real* $h_{\tau_1, \tau_2}^{(2)}$ we do of course have that $h_{\tau_1, \tau_2}^{(2)} = h_{\tau_2, \tau_1}^{(2)}$. This is also the case for the solution of the self consistent equations obtained as the combination of the OZE and the HNC, as well as the PY closure. But it is not necessarily true for the solution of the self-consistent equation from MFT. Although the symmetry of the real system is broken, this does not necessarily imply that MFT is a bad approximation. To illustrate this we have numerically solved (C.66) as well as (C.64) for a simple system of two types of particles that interact via different Gaussian potentials:

$$v_{\tau_1, \tau_2}(r) \equiv \epsilon_{\tau_1, \tau_2} \exp[-r^2/R_{\tau_1, \tau_2}], \quad (\text{C.67})$$

with $\epsilon_{1,1} = 11.6$, $\epsilon_{2,2} = 3.45$, $\epsilon_{1,2} = 6.4$, $R_{1,1} = \sqrt{34}$, $R_{2,2} = \sqrt{31}$ and $R_{1,2} = \sqrt{33}$. We consider the system at the density $\rho_1 = \rho_2 = 1.49/R_{1,1}^3$. We show the results for the HNC and the MFT approximations in figure C.1. One can see that while the results are very similar in both approximations, there is a small difference between $h_{1,2}^{(2)}$ and $h_{2,1}^{(2)}$ in the results obtained via the MFT approximation. This does not render the results of MFT insensible, but shows that the theory slightly breaks a symmetry of the underlying model.

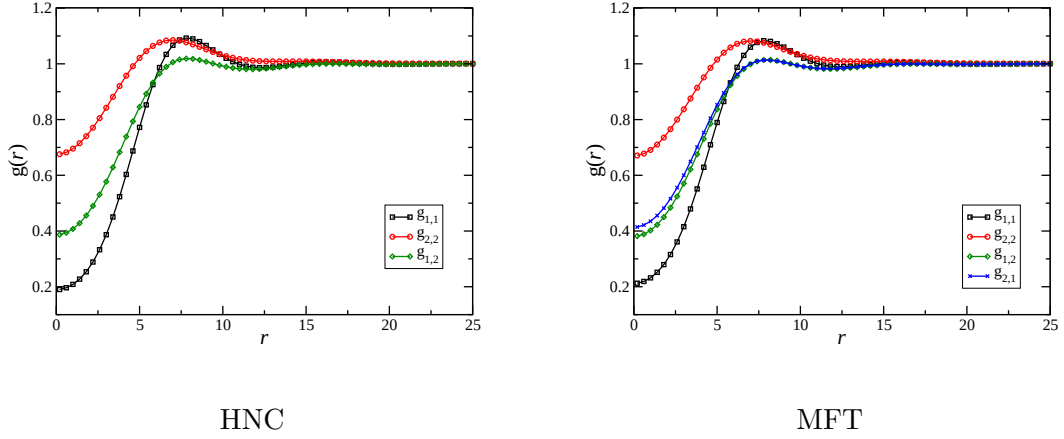


Figure C.1: Pair correlation function $g(r) = h^{(2)}(r) + 1$ for a system of particles interacting via Gaussian potentials. The results in the left plot are obtained using the HNC closure, while the results in the right are the solution of the self consistent equation from MFT. In the left the $g_{2,1}$ function does not appear separately since we correctly obtain $g_{1,2} = g_{2,1}$ in the HNC approximation.

C.2.2 A system with an anisotropic interaction potential

In the case of the anisotropic effective system, the particles are soft disks, which are represented by their center of mass $\mathbf{r}$ and a director $\mathbf{d}$. While the particles are identical they interact via anisotropic pair potentials. The interaction energy reads

$$V_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j=i+1}^N v(\mathbf{r}_i - \mathbf{r}_j, \mathbf{d}_i, \mathbf{d}_j). \quad (\text{C.68})$$

If we compare this expression to Eq. (C.60) we see that this system of identical particles interacting via an anisotropic interaction potential is equivalent to a system of multiple particle types, where the particle type is denoted by the director. This means that we can use the density functional theory for multiple particle types, which we have already discussed, to arrive at self-consistent equations for the anisotropic pair correlation function. The only difference is that the director assumes the role of a continuous type index and thus sums over the particle type index τ become integrations over the director $\mathbf{d}$. Furthermore the bulk density for particle type τ , which is denoted by ρ_τ , becomes $\frac{\rho}{4\pi}$, since the different directors are uniformly distributed in the bulk. For the OZE equation we therefore obtain

$$h^{(2)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{d}_1, \mathbf{d}_2) = c^{(2)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{d}_1, \mathbf{d}_2) + \int d\Omega \frac{\rho}{4\pi} \int d\mathbf{r} c^{(2)}(\mathbf{r}_1 - \mathbf{r}, \mathbf{d}_1, \mathbf{d}) h^{(2)}(\mathbf{r} - \mathbf{r}_2, \mathbf{d}, \mathbf{d}_2), \quad (\text{C.69})$$

where $d\Omega$ denotes the integration over the director $\mathbf{d}$. The HNC approximation becomes

$$h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = \exp[-\beta v(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)] \exp[h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) - c^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)] - 1, \quad (\text{C.70})$$

the PY closure reads

$$h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = \exp[-\beta v(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)] (1 + h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) - c^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)) - 1, \quad (\text{C.71})$$

and the MFT in combination with the Percus idea results in

$$h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = \exp \left[-\beta v(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) - \beta \int d\Omega \frac{\rho}{4\pi} \int d\mathbf{r}' h^{(2)}(\mathbf{r}', \mathbf{d}_1, \mathbf{d}) v(\mathbf{r} - \mathbf{r}', \mathbf{d}, \mathbf{d}_2) \right] - 1. \quad (\text{C.72})$$

Analogously to the case for the two types of particles interacting via different Gaussian potentials for which we presented results in figure C.1, the MFT does not necessarily respect the $h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = h^{(2)}(\mathbf{r}, \mathbf{d}_2, \mathbf{d}_1)$ symmetry.

C.2.3 Numerical solution of the self consistent equations for the system with anisotropic interactions

The self consistency equations, which we need to solve in the anisotropic case are of the form

$$h^{(2)}(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = F[h^{(2)}](\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2), \quad (\text{C.73})$$

where F is a functional of $h^{(2)}$. We solve this problem iteratively following essentially the same approach as described in appendix C.1.7. The only difference is that we now do not just use a flat profile as an initial condition, but rather increase the density in small steps of $\Delta\rho$ and use the solution for $\rho - \Delta\rho$ as the initial condition for the iterative scheme at density ρ . The integrals which have to be carried out for the evaluation of the functional F are now also more difficult:

$$f \star h(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) \equiv \int d\mathbf{r}' d\Omega f(\mathbf{r}, \mathbf{d}_1, \mathbf{d}) h(\mathbf{r} - \mathbf{r}', \mathbf{d}, \mathbf{d}_2), \quad (\text{C.74})$$

where $\int d\Omega$ denotes the integration over the director $\mathbf{d}$. We will refer to this expression as an *anisotropic convolution*. The functions f and h both exhibit a rotational symmetry, i.e.:

$$f(R\mathbf{r}, R\mathbf{d}_1, R\mathbf{d}_2) = f(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2), \quad (\text{C.75})$$

where R is an arbitrary rotation matrix. The anisotropic convolution $f \star h$ is therefore also rotationally symmetric and it is sufficient to compute $f \star h$ for $\mathbf{d}_1 = \hat{\mathbf{z}}$ and $\mathbf{d}_2 = \sin\theta_2\hat{\mathbf{x}} + \cos\theta_2\hat{\mathbf{z}}$, since it is always possible to find a choice for R , $\mathbf{x}$ and $\cos\theta_2$ such that

$$(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2) = (R\mathbf{x}, R\hat{\mathbf{z}}, \sin\theta_2 R\hat{\mathbf{x}} + \cos\theta_2 R\hat{\mathbf{z}}). \quad (\text{C.76})$$

The knowledge of $f \star h(\mathbf{r}, \hat{\mathbf{z}}, \sin \theta_2 \hat{\mathbf{x}} + \cos \theta_2 \hat{\mathbf{z}})$ therefore allows for the reconstruction of the entire function $f \star h$ and we are left with the computation of

$$\begin{aligned} f \star h(\mathbf{r}, \cos \theta_2) &\equiv f \star h(\mathbf{r}, \hat{\mathbf{z}}, \sin \theta_2 \hat{\mathbf{x}} + \cos \theta_2 \hat{\mathbf{z}}) \\ &= \int d \cos \theta d \varphi \int d \mathbf{r}' f(\mathbf{r}, \hat{\mathbf{z}}, \mathbf{d}) h(\mathbf{r} - \mathbf{r}', \mathbf{d}, \sin \theta_2 \hat{\mathbf{x}} + \cos \theta_2 \hat{\mathbf{z}}). \end{aligned} \quad (\text{C.77})$$

The integration over the spherical coordinates of $\mathbf{d}$ is denoted by $\int d \cos \theta d \varphi$. The inner integration corresponds to a three dimensional convolution over two functions that do not exhibit spherical symmetry. Using the convolution theorem in Eq. (C.50) we can thus carry out the inner integral with computational complexity of $\mathcal{O}(N_r^3 \log N_r)$, where N_r is the number of grid points in which we have discretized the three dimensions of $\mathbf{r}$. To this end we approximate the Fourier transformations in the convolution theorem by Fourier series coefficients, which we can compute using Eq. (C.57), as long as the convoluted functions are slowly changing between grid points, which means that the tabulated function values are a good representation of the continuous functions. The functions which are to be convoluted depend on $\mathbf{d}$ and $\cos \theta_2$. When we carry out the integration over $d \cos \theta d \varphi$ we discretize $\cos \theta$ and φ within $N_{\cos \theta}$ and N_φ intervals, while $\cos \theta_2$ is discretized within $N_{\cos \theta_2}$ bins. In total we thus need to carry out a number of $\mathcal{O}(N_{\cos \theta_2} N_{\cos \theta} N_\varphi N_r^3 \log N_r)$ computations to evaluate the anisotropic convolution $f \star h$. Because all the functions remain invariant if we flip an individual director, it is sufficient to compute two times the integration over $\cos \theta \in [0, 1]$ for $\cos \theta_2 \in [0, 1]$.

Due to rotational symmetry the functions f , h and $f \star h$ are only 4 instead of 7 dimensional. We have originally tabulated these functions with the effective variables $(r, \cos \theta_1, \cos \theta_2, \varphi)$ defined in Eq. (2.6). If one knows f and g at these effective coordinates, one can in principle evaluate them for all values of $(\mathbf{r}, \mathbf{d}_1, \mathbf{d}_2)$ due to rotational symmetry. However we only know the function values on a rectangular grid in the effective coordinates and if we for instance need to evaluate $f(\mathbf{r}, \hat{\mathbf{z}}, \sin \theta_2 \hat{\mathbf{x}} + \cos \theta_2 \hat{\mathbf{z}})$ at a grid point in $(\mathbf{r}, \cos \theta_2)$ space, the corresponding point in the effective coordinates $(r, \cos \theta_1, \cos \theta_2, \varphi)$ will in general not lie directly on the grid. We have used linear interpolation to approximate the function on a grid point in the $(\mathbf{r}, \cos \theta_2)$ variables with the tabulated function values on the grid in $(r, \cos \theta_1, \cos \theta_2, \varphi)$ space. In general we use linear interpolation in this way to transform the functions between different coordinate spaces.

C.3 Self consistent equations for the density distribution function in the presence of one or between two walls

We introduce one or two walls by applying an external potential to the disk-like particles. If the walls are orthogonal to the z -direction the potential depends only on the z -coordinate of the center of mass, as well as on the angle of the director $\mathbf{d}$ of a disk with respect to the z -axis. We will denote this external potential as the function $\Phi_{\text{wall}}(z, \mathbf{d} \cdot \hat{\mathbf{z}})$. Without the presence of an external potential the one-particle density is independent of the particles location or orientation but due to the external potential it will become dependent on z and $\mathbf{d} \cdot \hat{\mathbf{z}}$. When we have implemented the Percus idea in appendix C.1.3 we had to compute the one-particle density when the pair potential v was applied as an external potential and we have therefore already tackled a very similar problem before. We can formally express the one-particle density function as

$$\rho^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) = \frac{\rho}{4\pi} \exp \left[-\beta \Phi_{\text{wall}}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) + \Delta c^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) \right], \quad (\text{C.78})$$

where ρ is the bulk density and $\Delta c^{(1)}$ denotes the change in the one-particle direct correlation function due to the presence of the wall. The normalization of $\rho^{(1)}$ is chosen such that $\rho^{(1)} d\Omega d\mathbf{r}$ gives the average number of particles that have a director $\mathbf{d}$ within the solid angle $d\Omega$ and are found within the volume element $d\mathbf{r}$. When we derived the HNC and the PY closures for the bulk system, we have expanded $\Delta c^{(1)}$ up to first order in the density and we will once again follow this strategy:

$$\begin{aligned} \Delta c^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) &\approx \int d\Omega' d\mathbf{r}' \Delta \rho^{(1)}(z', \mathbf{d}' \cdot \hat{\mathbf{z}}) \left. \frac{\delta c^{(1)}(\mathbf{r}, \mathbf{d})}{\delta \rho^{(1)}(\mathbf{r}', \mathbf{d}')} \right|_{\Phi=0} \\ &= \int d\Omega' d\mathbf{r}' [\rho^{(1)}(z', \mathbf{d}' \cdot \hat{\mathbf{z}}) - \rho] c^{(2)}(\mathbf{r} - \mathbf{r}', \mathbf{d}, \mathbf{d}'). \end{aligned} \quad (\text{C.79})$$

Here $c^{(2)}$ denotes the direct pair correlation function for $\Phi = 0$, i.e. the bulk system, for the bulk density ρ . Since $\rho^{(1)} - \rho$ only depends on z and $\mathbf{d} \cdot \hat{\mathbf{z}}$ it is possible to factor them out of some of the integrations. To do this we write the director $\mathbf{d}'$ in terms of spherical coordinates and thus represent it by $\cos \theta'$ and φ' . We obtain

$$\Delta c^{(1)}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) \approx \int d\cos \theta' dz' [\rho^{(1)}(z', \cos \theta') - \rho] \int dx' dy' d\varphi' c^{(2)}((x', y', z - z'), \mathbf{d}, \mathbf{d}'). \quad (\text{C.80})$$

To simplify the notation we introduce the function $\bar{c}(z, \cos \theta, \cos \theta')$ as

$$\bar{c}(z, \cos \theta, \cos \theta') \equiv \int dx' dy' d\varphi' c^{(2)}((x', y', z), \mathbf{d}, \mathbf{d}'), \quad (\text{C.81})$$

where $\cos \theta$ and $\cos \theta'$ are the angles of $\mathbf{d}$ and $\mathbf{d}'$ with respect to the z -axis. The self-consistent equation obtained by inserting the approximation (C.80) into equation (C.78)

thus becomes

$$\rho^{(1)}(z, \cos \theta) = \frac{\rho}{4\pi} \exp \left[-\beta \Phi_{\text{wall}}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) + \int d \cos \theta' dz' [\rho^{(1)}(z', \cos \theta') - \rho] \bar{c}(z - z', \cos \theta, \cos \theta') \right]. \quad (\text{C.82})$$

The function $\bar{c}$ is purely a property of the bulk system, which is however density dependent. There are various ways to determine the function $\bar{c}$. One could for instance measure the anisotropic pair-correlation function in a simulation of the bulk system and use the OZE given in Eq. (C.69) to determine the corresponding direct pair correlation function. In this work we have used Eq. (C.70), namely the HNC closure for the anisotropic system, to determine the direct pair correlation function from the anisotropic pair-correlation function. For the computation of the anisotropic pair-correlation function we have iteratively solved the system of self-consistent equation given by the OZE in combination with the HNC closure.

We have derived an additional self-consistent equation for this system, which makes use of the MFT approximation which was already applied in appendix C.1.5 to obtain a self-consistent equation for the pair correlation function in the bulk system. To this end the energy $E(z, \cos \theta, \Phi_{\text{wall}})$ required to place a ring at a distance z away from a wall and orient its director at an angle θ with respect to the z -axis, is estimated by the average energy that would be required if all the other particles were independently distributed by the one particle distribution function $\rho^{(1)}(z, \cos \theta)$:

$$E(z, \cos \theta, \Phi_{\text{wall}}) \approx \int d\Omega' d\mathbf{r}' \rho^{(1)}(z', \cos \theta') v(\mathbf{r} - \mathbf{r}', \mathbf{d}, \mathbf{d}') + \Phi_{\text{wall}}(z, \cos \theta). \quad (\text{C.83})$$

The one particle distribution function is then proportional to the Boltzmann factor of this energy. Fixing the normalization of $\rho^{(1)}$ we obtain the following relation

$$\begin{aligned} \bar{v}(z, \cos \theta, \cos \theta') &\equiv \int dx' dy' d\varphi' v((x', y', z), \mathbf{d}, \mathbf{d}'), \\ \rho^{(1)}(z, \cos \theta) &= \frac{\rho}{4\pi} \exp \left[-\beta \Phi_{\text{wall}}(z, \mathbf{d} \cdot \hat{\mathbf{z}}) \right. \\ &\quad \left. + \int d \cos \theta' dz' [\rho^{(1)}(z', \cos \theta') - \rho] \bar{v}(z - z', \cos \theta, \cos \theta') \right], \end{aligned} \quad (\text{C.84})$$

where ρ corresponds to the overall density in the system. This self-consistent equation is almost identical to Eq. (C.82) with the only difference that the direct pair-correlation function $c^{(2)}$ is replaced by the interaction potential v .

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