

Self-assembly of nanorods on quasicrystalline substrates

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Abstract

Quasicrystals possess long-range positional order with a non-crystallographic rotational symmetry. Quasicrystalline order leads to interesting surface properties. Adsorbates on quasicrystalline surfaces can form new self-assembled structures. In this work we study by computer simulations the phase behavior and mobility of hard rods in a quasicrystalline substrate potential. The quasicrystalline substrate is derived from the interference pattern of five laser beams and possesses a decagonal rotational symmetry. We take two different particle models into account namely the hard needles and the hard spherocylinders. Hard needles are the simplest form of elongated particles which form liquid crystalline phases. They do not exhibit an excluded volume. To take excluded volume effects into account, we also studied the hard spherocylinder model. In two dimensions the hard rods are known to undergo a density driven phase transition from an isotropic phase to a quasi-nematic phase. When the substrate potential is present, we find different phase behavior for two rod lengths. Short rods can connect only two minima of the substrate potential. Long rods are able to connect many potential minima.

Under the influence of the substrate, the short needles form disconnected clusters located between two potential minima. The orientations of the clusters are aligned with the symmetry directions of the potential. Through the formation of clusters the quasi-nematic order gets destroyed. At high densities and high potential strengths a nematic order can be frozen in. Long needles also form clusters under the influence of the substrate potential. In contrast to the short needles the clusters are not disconnected but are able to share a few minima. The clusters form lines which are oriented along the symmetry directions of the potential. In this way, a nematic phase can be stabilized. The distances between the lines follow two interwoven Fibonacci sequences. At low densities the needles form small regions of clusters oriented along different symmetry directions of the substrate. This non-nematic decagonal phase can also be frozen in at high densities and high potential strengths.

Similar to the short needles the short spherocylinders form disconnected clusters under the influence of the potential at low densities. Due to their finite width the system becomes crowded with increasing density. The directional order decreases

significantly and finally the preferred directions of the clusters shift against the symmetry directions of the potential at high densities. At sufficiently high potential strengths the long spherocylinders order themselves onto lines. The positional order is very weak and gets lost at high densities. The long spherocylinders remain in a decagonal directional order even for high densities. We also investigate the mobility of the spherocylinders with kinetic Monte Carlo simulations. With increasing potential strength the short spherocylinders get trapped at their minimum positions. In more dense systems the mobility of the short rods rises. In contrast to short spherocylinders the long spherocylinders can slide along the lines connecting the potential minima. This results in a high mobility of the long rods even at high potential strengths.

Zusammenfassung

Quasikristalle besitzen eine langreichweitige Positionsordnung mit einer nicht kristallografischen Rotationssymmetrie. Die quasikristalline Ordnung führt zu interessanten Eigenschaften ihrer Oberflächen. In dieser Arbeit untersuchen wir das Phasenverhalten und die Mobilität von harten Stäbchen auf einem quasicrystallinen Substrat mittels Computersimulationen. Das quasicrystalline Substrat wird durch die Interferenz von fünf Laser Strahlen erzeugt und besitzt eine dekadonale Rotationssymmetrie. Wir untersuchen zwei verschiedene Teilchenmodelle, das der harten Nadeln und das der harten Spherozylinder. Die harten Nadeln sind das simpelste Teilchenmodell welches flüssigkristalline Phasen aufweist. Sie besitzen aber kein Volumen. den Einfluss eines Teilchenvolumens untersuchen wir im Modell der harten Spherozylinder. In einem zweidimensionalen System findet unter Erhöhung der Dichte der Stäbchen ein Phasenübergang von der isotropen in eine quasi-nematische Phase statt. Auf dem Substrat zeigen Stäbchen zweier verschiedener Längenskalen unterschiedliches Phasenverhalten. Die kurzen Stäbchen können nur zwei Minima des Substrates verbinden. Die langen Stäbchen können mehrere Minima verbinden.

Unter dem Einfluss des Substrates finden sich die kurzen Nadeln zwischen den Minima des Potentials zu Clustern zusammen, die jeweils von einander getrennt liegen. Die Cluster sind nach den Symmetrierichtungen des Substrates ausgerichtet. Durch diesen Prozess wird die quasi-nematische Phase zerstört. Für hohe Dichten und Potentialstärken kann eine nematische Phase eingefroren werden. Auch die langen Nadeln bilden auf dem Substrat Cluster. Im Gegensatz zu den kurzen Nadeln sind diese Cluster miteinander verbunden und können sich Minimapositionen teilen. Mehrere Cluster können sich zu Linien zusammen setzen, die in Richtung der Symmetrieachsen des Substrates liegen. Auf diese Weise kann die quasi-nematische Phase stabilisiert werden. Die Abstände zwischen den Linien folgen zwei verflochtenen Fibonacci Sequenzen. Bei niedrigen Dichten formieren sich die Cluster in unterschiedlich nach den Symmetrieachsen des Potentials ausgerichtete Regionen. Eine solche nicht nematische dekadonal ausgerichtete Phase kann auch bei hohen Dichten und Potentialstärken eingefroren werden.

Ähnlich den kurzen Nadeln bilden die kurzen Spherozylinder unter Einfluss

des Substrats getrennte nach den Symmetrieachsen des Potentials ausgerichtete Cluster. Aufgrund ihres Volumens füllt sich die Fläche bei einer Erhöhung der Dichte. Dabei schwächt sich die dekadonale Ausrichtung deutlich ab und bei sehr hohen Dichten verschieben sich die bevorzugten Richtungen der Stäbchen relativ zu den Symmetrieachsen des Potentials. Die langen Spherozylinder ordnen sich auf dem Substrat entlang von Linien. Die räumliche Ordnung der Stäbchen ist sehr schwach und wird letztendlich durch sehr hohe Dichten völlig zerstört. Die dekadonale Ausrichtung hingegen bleibt selbst bei hohen Dichten erhalten. Zusätzlich haben wir die Mobilität der Stäbchen bestimmt. Unter Erhöhung der Potentialstärke werden die kurzen Stäbchen zwischen den Minimapositionen gefangen. Die Mobilität steigt wieder, wenn die Dichte erhöht wird. Die langen Spherozylinder können entlang der Symmetrielinien des Potentials entlang gleiten. Dadurch bleiben sie selbst bei hohen Potentialstärken mobil.

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1 Introduction

Quasicrystals are solids which exhibit a long range positional order. The order is aperiodic and it can possess rotational symmetries which are forbidden for crystalline structures. Quasicrystals can possess symmetry axes with non-crystallographic eight-, ten- and twelve-fold rotational symmetry. In many quasicrystals physical properties are found to be different from usual crystals but also different from unordered amorphous materials[94, 196]. It is not surprising that since the publication of their first discovery[177], quasicrystals attracted a lot of scientific interest.

The surface properties of quasicrystals are of particular interest. Quasicrystalline surfaces show a low adherence[57, 146, 147] which can be useful for non-sticky coatings but is also an obstacle for epitaxial applications. A detailed understanding of the interfacial films between crystalline and quasicrystalline structures is important for the usage of quasicrystals, e.g. to enhance the adhesion between quasicrystals and simple metal substrates [52]. Monolayers of adatoms can adopt the quasicrystalline structures or arrange themselves in new fascinating structures. In experiments with quasicrystalline alloys adatoms formed new self-assembled structures[56, 60, 62, 132, 183]. The investigations are also directed towards the understanding of the growth of quasicrystalline structures from quasicrystalline templates.

Colloidal systems provide a model system for atomic order. They exist in different size and shapes and their interactions are easy to control in experiments[164, 165, 216]. The length scales and time scales of the dynamic of colloidal particles allow to study the phase behavior of colloidal systems on the level of single particle trajectories. Colloidal particles can be controlled by external fields like intense laser beams[73, 96]. The patterns of interfering laser beams can create two dimensional crystalline and quasicrystalline structures[171]. These patterns serve as

substrates which mimic the structural properties of quasicrystalline surfaces. One can investigate new structures and phase transitions on quasicrystalline surfaces with colloidal particles confined to such two dimensional laser substrates[170]. Experimental and theoretical studies with spherical particles on a decagonal substrate found new interesting phase behavior[71, 137, 138, 139, 169].

We extend the well studied setup of colloids on a quasicrystalline substrate from spherical colloids to rodlike particles. Hard rodlike particles exhibit a long and a short axis. In two dimensions this anisotropic shape introduces an additional orientational degree of freedom[70]. At sufficiently high densities rodlike particles align their orientations along a common director and form a nematic phase. In a nematic phase, a long-ranged order of the orientations of the rods is established while the center of mass positions of the particles stay liquid like disordered. The nematic phase is therefore the simplest example of a liquid crystal. In two dimensions the nematic order is called quasi-long-ranged because orientational correlations decay algebraically and the nematic director can only be defined locally in a finite radius around each particle[65].

Hard rods can also effectively model organic molecules on quasicrystalline surfaces like alkenes or aromatic hydrocarbons. The most common application of rodlike particles are liquid crystal displays[91]. In such devices the liquid-crystalline particles are placed into confined geometries. The interactions of particles with the interfaces play an important role for their phase ordering in the bulk and the possibility of switching between different states[116].

We identify new phases of hard rods under the influence of a quasicrystalline decagonal substrate potential. The orientational degree of freedom of hard rods leads to interesting directional order along the decagonal symmetry directions of the substrate potential in combination with pronounced cluster formation. At high densities this ordering competes with the quasi-nematic phase. The interaction of the rods with the potential is strongly dependent on the length of the rods with respect to the typical length scale of the substrate potential. The nematic order can be enhanced as well as destroyed by the substrate potential. In this work, we investigate this interesting phase behavior and the mobility of hard rods on a quasicrystalline substrate with computer simulations.

The outline of the work is as follows. In chapter 2 we present the properties of quasicrystals and quasicrystalline surfaces. The chapter also introduces our decagonal substrate created from the interference pattern of five laser beams. In the following chapter 3, we introduce the properties of nematic liquids in general and our particle models in particular. We briefly summarize the phase transitions of the hard rod models we analyzed in two dimensions. Furthermore, we explain the quantities to investigate the phase transitions and the phase regions in detail. At the end of chapter 3 we present the interaction of the hard rods with the substrate potential and its structural characteristics. In chapter 4, we give the details of the simulation techniques used in this work. In chapter 5 we present the results of our study of the hard-needle model. We display the phase diagram for short and long needles and give a detailed account of the new phases and structures. In chapter 6 we summarize the results of our investigations of the hard-spherocylinder model. The phase behavior of spherocylinders significantly differs from those of the needles. In addition, we have also investigated the dynamics of the spherocylinders with kinetic Monte Carlo simulations. We conclude our findings in chapter 7 and give an outlook of future topics which may arise from the results of this work.

Parts of this work have been published in [A] and in [B].

2 Quasicrystals

In this chapter we introduce first the quasicrystals in general. Thereafter we present the properties of atomic quasicrystalline surfaces. Afterwards we give an introduction to colloidal systems in general and two dimensional systems under the influence of laser fields in particular. An explanation of the experimental setup of colloids on a quasicrystalline substrate follows and we present our quasicrystalline decagonal substrate potential. In the last part of the chapter we explain the mathematical concepts of quasicrystals and the Penrose tilings in particular.

2.1 Introduction to quasicrystals

Before the discovery of the quasicrystalline matter only two types of ordered solid matter has been known. On the one hand unordered structures like amorphous materials. On the other hand crystalline materials with a periodic long-range spatial order. The different species of crystals are classified by their rotational and translational symmetry. The possible point groups to build a crystal in two or three dimensions are well known. A lattice belonging to a crystalline point group possesses n -fold rotational symmetry if it is invariant under a rotation of an angle of $2\pi/n$ with respect to a well defined rotational axis. The only possible values for n for a periodic lattice are $n = 1, 2, 3, 4, 6$. The distinct properties of crystalline matter arises from this well ordered structure. Until the discovery of quasicrystals the crystalline periodic structures believed to be the only possibilities of long-ranged ordered matter. Quasicrystals possess at least one non-crystallographic rotational symmetry. They were discovered first in 1982 by D. Shechtman when he was investigating alloys of Al and Mn . This first quasicrystal has an icosahedral symmetry consisting of 6 different rotational axes where each has a 5-fold rotational symmetry which is forbidden for any periodic crystalline structure. In the same year A. Mackay published the diffraction pattern of a Penrose tiling[128]. At this time the Penrose tiling was known only as a purely mathematical long-

range ordered structure. Mackay showed that the diffraction pattern of atoms arranged in such a tiling shows a non-crystallographic 5-fold rotational symmetry. Shechtman and the crystallographic community were not aware of the findings by Mackay. As a result Shechtman faced tough resistance against his interpretation of an ordered phase with non-crystallographic rotational symmetry. He was able to publish his findings finally in 1984 [177], two years after his discovery. After this publication the scientific community directed a lot of attention at this topic but still encountered a lot of opposition, in particular by the double Nobel prize winner L. Pauling [150]. The quasicrystalline alloy found by Shechtman was metastable and could be produced only by rapid quenching of the melt. The small grains of a few micrometer in size were difficult to study in detail. This situation changed in 1986 when the first stable quasicrystalline phase was found by Dubost et al. in an alloy of Al_6Li_3Cu [51]. At the end of the 80s the number of quasicrystalline phases in different alloys rapidly increased. As a reaction to the discovery of the quasicrystals the International Union of Crystallography changed its definition of a crystal to “any solid having an essentially discrete diffraction diagram” [36]. This definition is much wider than necessary for the incorporation of the first quasicrystals because it discards also the need for any rotational symmetry. Now quasicrystals are a commonly accepted particular state of matter. Shechtman has been rewarded the Nobel prize for chemistry for his discovery in 2011.

The physical properties of quasicrystals turned out to be different from conventional crystals as well as from disordered glass phases [94, 196]. Most quasicrystal materials are found in alloys of Al . But this could be an artifact of history of the discovery of quasicrystals. The Al rich quasicrystals are brittle, hard and poor conductors of heat and electricity. Because of their brittleness the search for technical applications concentrates on their usage as coatings or composites. For this purposes the surface properties of the quasicrystals are very important.

2.2 Quasicrystalline surfaces

2.2.1 Atomic surfaces

As the quality and size of the quasicrystalline samples has improved, the surface properties of such materials came in reach of scientific investigations [45, 56, 108]. In the beginning it was not clear whether quasicrystalline bulk structure also

appears at their surfaces. Fortunately one is now able to produce high quality quasicrystalline surfaces which can be used as templates for the growth of thin films or nanostructures[59, 132, 183, 184, 198]. The sizes of the samples vary between a few millimeters to 10cm. The main goal of forming such thin films on quasicrystalline surfaces is to force the atoms in the film into a quasicrystalline structure. This can result in quasicrystalline structures composed only from one single chemical element in contrast to natural quasicrystals which are composed of at least two different elements. Noble gases have a low chemical reactivity and were used to study the physisorption properties of various quasicrystalline surfaces[55, 200]. The experiments were accompanied by computational simulations of the noble gases[38, 46, 47, 174, 175]. The rare gases can retain the quasicrystalline structure if the length scale of the atomic bonds in their crystalline ordered phase matches the typical length scale of the quasicrystalline structures of the substrate like *Xe* on a quasicrystalline *AlNiCo* alloy. Experiments have been performed with metal elements like *Au*[181] and *Ag*[60] but also thin films of *Pb*[1, 42], *Bi* and *Sb*[63] lead to interesting results. Simulations of metal films helped to understand the experimental results like quasicrystalline clusters and locked crystalline domains[18, 140]. The competition of the quasicrystal template structure and the solid crystalline state of the film material can lead to fascinating new structures, e.g. the step structure of a *Cu* film on a *i - AlPdMn* interface follows a one-dimensional quasicrystalline sequence known as the Fibonacci sequence[115, 155]. *C*₆₀ molecules placed onto such *Cu* films show an unusual low mobility[185]. Chemically more reactive metals like *Fe* can also penetrate into the surface structure[213]. The low friction coefficient of quasicrystalline surfaces[57, 146, 147] raises questions about the interaction of the surfaces with lubricants commonly made from carbohydrates[39, 48, 133]. Quasicrystalline interlayers also may be a possibility to connect two crystalline materials with incommensurate periodicity[64]. Recently, also special adsorption sites on quasicrystalline surfaces have been identified. Due to the aperiodic nature of the surface multiple chemical decorations of a quasicrystalline surface are possible [202].

2.2.2 Colloidal systems

Colloidal systems are omnipresent in biological systems as well as in industrial applications. The motivation to understand the behavior of colloidal particles is not limited to those applications. They are also a model system for the understanding of atomic and molecular structures and dynamics[12, 216]. Due to their size they are easy to observe with microscopic devices working in the visible light spectrum. The time scales of their dynamical behavior are much longer than for atomic systems. This results in a good time resolution of dynamical processes where it is even possible to follow single particle trajectories. Colloidal particles can have almost arbitrary shapes and sizes[164]. It is possible to mix different colloidal particle species to investigate phenomena such as phase separation[102]. The interaction strength between particles is tunable over a wide range e.g. in systems with electrostatic interactions with different salt concentrations of the solution[218]. A very important feature of colloidal particles is their sensitivity to external fields introducing even more possibilities to force a colloidal system into a physical situation of interest. Colloidal particles are not only easy to probe in experiment but also easy to treat in theory and computer simulations[10]. This makes them a perfect model to study phase transitions or glass and gel formation.

Two-dimensional systems are particularly interesting. The phase behavior of particles confined to two dimensions is very different from the 3D case[195]. The KTNHY theory [110, 141, 220] is able to explain the two-dimensional melting as a disclination unbinding transition leading to a continuous phase transition in contrast to one first-order phase transition observed in 3D systems. In particular, the theory predicted a two stage melting in a system of spherical particles. First, a phase transition from the solid phase to a fluid hexatic phase can be observed where the bond orientational order of the solid is preserved only locally and the phase possesses no long-ranged order. Afterwards, in a second phase transition, the hexatic fluid phase melt and the system exhibits an isotropic phase. This two stage process could be investigated in an experiment with colloids in a 2D confined geometry[221]. Also simulations of confined systems show velocity[3, 50, 54] and angular momentum[207] autocorrelations with long positive tails. In early experiments with confined colloids[152, 153] the confining walls were structureless glass plates. In practical applications the substrates for a 2D colloidal film are

usually structured. Therefore, the substrates are able to induce an order in the colloidal monolayers[43]. That can be used to build template patterns which are able to not only order the first monolayer but also influence the order of the bulk in a technique named after its atomic counterpart as colloidal epitaxy[4, 92, 197, 203].

To model a wide range of different substrate patterns we make use of the sensitivity of colloidal particles to laser fields. Laser field experiments exploit the different dielectric constants of the solvent and the colloidal particle. The inverse of the laser frequency is much smaller than the relevant time scale of the motion of the particle. From the point of view of the particle the laser field is therefore of a static intensity. The particle is subject to two different contributions of the laser field. Those are easily derived for the force of the induced dipole moment of the particle [73, 96]:

$$\vec{F}_L = 0.5\alpha\nabla E^2 + \frac{\partial}{c\partial t}(\vec{E} \times \vec{B}) \quad (2.1)$$

with E the electric field, B the magnetic field and α the polarizability of the particle. The first term is the gradient force of the laser field and the second term is the scattering force describing the momentum transfer between the laser beam and the particle. In a two-dimensional system the scattering force points perpendicular to the plane and usually leads to a higher effective mass of the particle. To generate a substrate potential for colloidal particles the gradient force is the important part. This force is proportional to the gradient of the intensity. Depending on the particle shape the prefactors may be more complicated [9, 124, 199].

The most common applications of the influence of intense laser fields on colloidal particles are optical tweezers[77]. They are widely used instruments to confine and manipulate single particles. This tool is of a high scientific importance and its applications are the basis of many scientific developments of the past decades. In our focus, the usage of laser fields should not be limited to a single particle but to a system of interacting particles. Laser fields serve as a substrate potential in a two-dimensional system. Ordered structures of colloids which form under the existence of light fields are named optical matter[28]. The first investigated laser substrates where one-dimensional, periodic intensity profiles. The interference pattern of two laser beams consisted of parallel stripes. The colloids move to the high density regions and eventually crystallize to a state which is referred

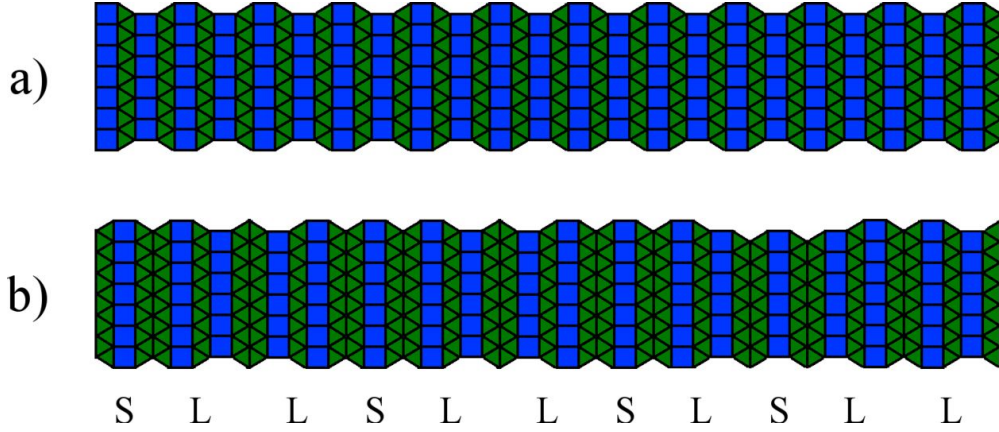


Figure 2.1: a) the Archimedian tiling $(3^3, 4^2)$ b) quasicrystalline modulated Archimedian tiling, the distances S and L between the double triangle rows follow a Fibonacci sequence.

to as laser induced freezing(LIF)[33, 124]. Later, it was found in theory and numerical simulations that such a system can undergo a second phase transition at even higher intensities. The crystalline phase melts again and this reentrant phase transition is called laser induced melting (LIM)[14, 30, 96, 212]. With the LIF and LIM transition the one dimensional periodic substrate shows a rich and surprising behavior.

With two-dimensional laser patterns one can form a periodic lattice of potential minima. At sufficiently high intensities the colloids freeze and occupy every potential minima with one particle. A special new phenomenon occurs if the number of colloids exceeds the number of potential minima. Two or three colloids are confined in one potential minimum to form a colloidal molecule[2, 23, 24, 53, 159]. One colloidal molecule is not spherical anymore but has an orientation. For interaction lengths longer than the distance between two potential minima the orientations between colloidal molecules of the whole system are able to couple and new forms of orientational order arises in a system of spherical particles.

2.2.3 Colloids on quasicrystalline surfaces

Laser fields could also used to create quasicrystalline substrates. The interference pattern of the laser beams can produce substrates belonging to arbitrary classes

of rotational symmetry[171]. The resulting intensity patterns are identical to the density functions in the phase field crystal model[163]. Most attention has been paid to the decagonal systems with a 10-fold rotational symmetry[170]. The decagonal symmetry is the most common symmetry found at quasicrystalline surfaces. On decagonal light substrates spherical colloids can order themselves into a quasicrystalline phase with 10-fold or 20-fold bond orientational symmetry. The most interesting discovery in the investigation of the phase diagram of the colloids is the occurrence of a phase with quasicrystalline Archimedian tiling[71, 137, 138, 139, 169] as shown in Fig. 2.1. This phase arises if the length scale of the bonds of the preferred hexagonal crystal is close to the typical length scale of the quasicrystalline decagonal substrate. The normal Archimedian tiling $(3^3, 4^2)$ consist of a periodical repetition of alternating rows of triangles and squares. The Archimedian tiling (3^6) consists of triangles only and the vertices belong to a triangular lattice. At high densities and without any substrate structure the colloidal particles form a hexagonal phase. If one draws the positions of the colloids as vortices and the bonds between nearest neighbors as edges, an Archimedian tiling (3^6) of triangles appears. A new phase emerges if one place the colloidal hexagonal phase onto a decagonal substrate with a length scale and an interaction strength matching the length scale and interaction strength of the bonds of the hexagonal phase. In this new phase, the bonds between the particles define a pattern of triangles and squares like in the Archimedian tiling $(3^3, 4^2)$. But in contrast to the normal Archimedian tiling the sequence of rows of triangles and squares is not periodic but follows a one dimensional quasicrystalline sequence known as Fibonacci sequence. To do so, the rows of triangles are doubled and the resulting tiling can be described as an alternating (3^6) and $(3^3, 4^2)$ Archimedian tiling.

There also have been investigations of the dynamical features of colloids on a decagonal substrate potential. Colloids on a quasicrystalline substrate find their potential minima similar to colloids on amorphous surfaces[168]. On a different decagonal substrate a directional locking of driven particles has been seen[158]. Quasicrystals do not only have translational modes. The dynamics of so called phasonic drifts which have no counterpart in periodical crystals have been investigated as well[111].

The experimental setup necessary for the creation of quasicrystalline substrates

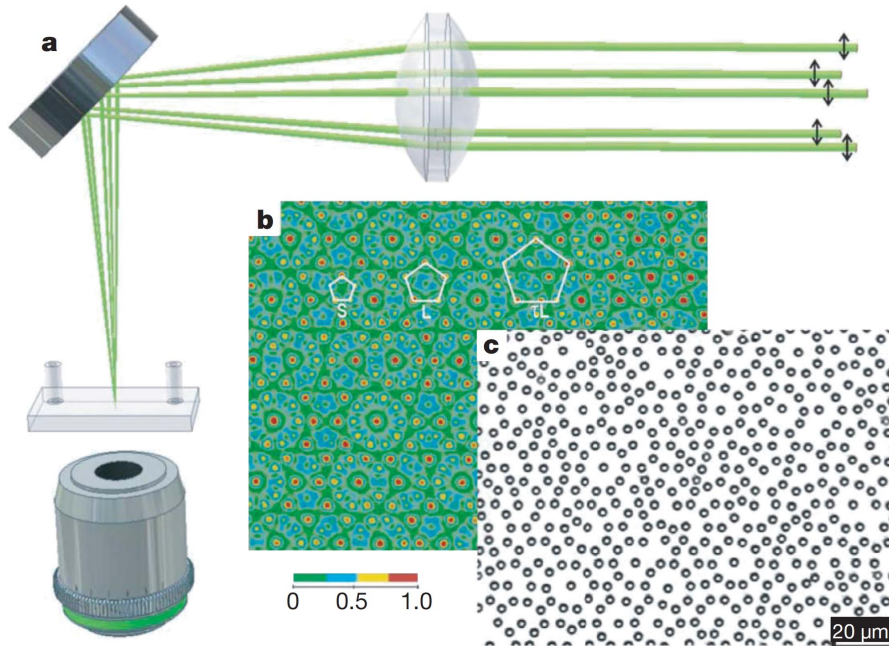


Figure 2.2: Experimental setup for the generation of a laser field substrate: a) Five linear polarized laser beams are focused into a sample cell. b) The decagonal interference pattern c) Configuration of spherical colloidal particles exposed to the interference pattern.[139]

is shown in Fig. 2.2. The setup consists of a laser beam which is split up into partial beams. The wave vectors of the laser beams are arranged along the n edges of a prism that is made of a perfect n -sided polygonal base. The laser beams interfere again in the plane of the sample which contains the colloidal suspension. The number and wave vectors of the beams determine the structure of the interference pattern. The wave vectors of the laser beams are arranged to form a rotational symmetric star. The rotational symmetry of the star is equal to the rotational symmetry of the interference pattern if the number of beams n is even. The rotational symmetry of the pattern is $2n$ if the number of wave vectors is odd.

As shown in Eq.(2.1), the potential acting on a colloid is proportional to the intensity of the electric field. For the average potential strength at a given point we have to integrate the interference of j laser beams over one period T defined by the inverse of the oscillation frequency of the laser beam ω :

$$\begin{aligned}
 V(\vec{r}) &\propto - \int_0^T dt \left\{ \sum_{j=0}^{n-1} E_j \cos(\vec{G}_j \cdot \vec{r} + \varphi_j + \omega t) \right\}^2 \\
 &\propto - \int_0^T dt \left\{ \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} E_i E_j \cos(\vec{G}_j \cdot \vec{r} + \varphi_j + \omega t) \cos(\vec{G}_i \cdot \vec{r} + \varphi_i + \omega t) \right\} \\
 &\propto - \int_0^T dt \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} E_i E_j \{ \cos((\vec{G}_j - \vec{G}_i) \cdot \vec{r} + \varphi_j - \varphi_i) \\
 &\quad + \cos((\vec{G}_i + \vec{G}_j) \cdot \vec{r} + \varphi_i + \varphi_j + 2\omega t) \}
 \end{aligned}$$

Where E_j is the amplitude and φ_j the phase and G_j is the wave vector of the laser beam. After integration over the time we get:

$$V(\vec{r}) \propto \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} E_i E_j \{ \cos((\vec{G}_j - \vec{G}_i) \cdot \vec{r} + \varphi_j - \varphi_i) \} \quad (2.2)$$

We are not interested in different phase shifts expressed by the term $\varphi_j - \varphi_i$. The general form of the potential reads then:

$$V(\vec{r}) = -\frac{V_0}{n^2} \sum_{j=0}^{n-1} \sum_{i=0}^{n-1} \cos[(\vec{G}_i - \vec{G}_j) \cdot \vec{r}] . \quad (2.3)$$

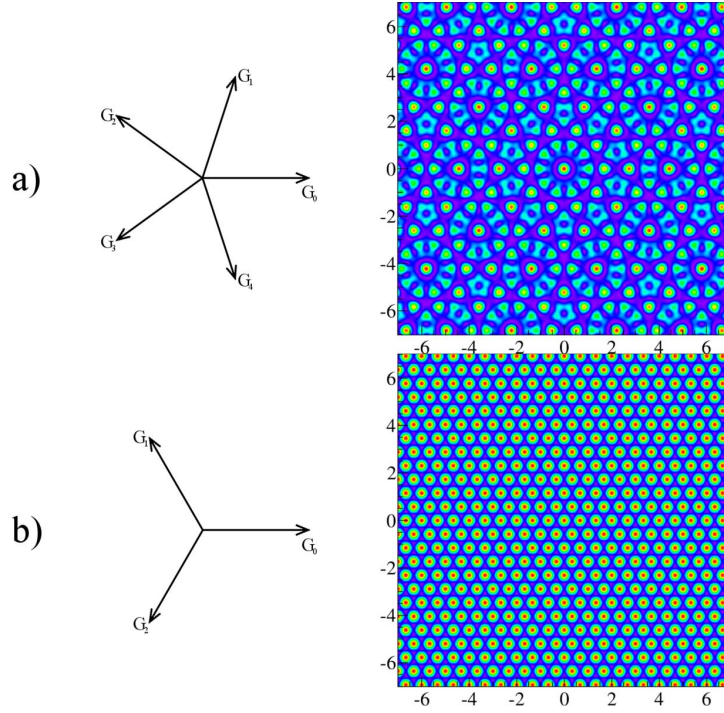


Figure 2.3: Star of wave vectors (left) and the resulting substrate potential (right) created from a) 5 laser beams and b) 3 laser beams.

The characteristic length scale of the structures of the potential is given by $a_V = 2\pi/|\vec{G}_i|$. Therefore we express all lengths in units of this length scale. The parameter V_0 gives the depth of the deepest minima. In our simulations we give V_0 in units of the thermal energy kT , where T is the temperature and k the Boltzmann constant. In Fig. 2.3 two different choices of a star of wave vectors $\vec{G}_i$ for $n = 5$ and $n = 3$ are shown. In Fig. 2.3 a) The five wave vectors $\vec{G}_i$ point to the vertices of a pentagon and generate a star of vectors with an angle $\phi = 2\pi/5$ between two neighboring vectors ($\vec{G}_i, \vec{G}_{i+1}$) the resulting potential has a decagonal quasicrystalline symmetry. In Fig. 2.3 b) the three wave vectors point to the vertices of an equilateral triangle. Right next to it the resulting triangular crystalline potential is shown. In the following we use the decagonal potential as our model for a quasicrystalline substrate potential.

2.3 Mathematical concepts of quasicrystals

Unlike crystalline matter the connection of the quasicrystalline order to its mathematical description is not straight forward[95, 119, 187]. We start with the three basic properties found in real material. Afterwards we explain quasicrystalline geometrical patterns in one and two dimensions.

The property of a long-ranged positional order leads to sharp peaks in the electron diffraction patterns of quasicrystals similar to crystalline matter. The most obvious property of quasicrystalline materials is the long range orientational order of the bonds of nearest neighbors. One can order the bond angles along a star of axis. The set of star axis can have a rotational symmetry. In most quasicrystals the rotational symmetry is non-crystallographic. That means that no crystalline order is able to have the same rotational symmetry. It is easy to picture this in two dimensions. Crystals with a unit cell shape of triangles, rectangles or hexagons have a 3, 4 or 6-fold rotational symmetry respectively. The quasicrystalline Penrose tiling consists of two different rhombic unit cells which edges are orientated onto a 5-fold rotational symmetry.

The second property is connected to the translational order of the atoms and atomic clusters. The density function can be decomposed into a sum of periodic functions. If the ratio of the periods of some of the functions is an irrational number those functions are called incommensurate. If a decomposition of a distribution into periodic functions exhibits also incommensurate functions the distribution is quasiperiodic. Quasicrystals possess a quasiperiodic translational order.

These two properties can be deduced from the electron diffraction patterns of the quasicrystals. One basic property is left to avoid unphysical mass distributions which can not be obtained in real materials. In real materials the atoms can not come arbitrary close to each other. Therefore there must be a minimal spacing between two atoms. There should also be a maximum spacing between two atomic sides. Otherwise the material can consist of arbitrary huge holes and gaps.

In the following we will use a further restriction for the quasicrystals mentioned

in this work. We always use quasicrystalline structures with non crystallographic rotational symmetries. This is a large restriction in mathematical terms but since nearly every known real quasicrystal material possesses such a rotational symmetry, the reduction of the mathematically possible quasicrystals leads to almost no constraints of the physical scope. This reduction gives us another important feature for most of the known quasicrystalline structures. Quasicrystals possessing rotational symmetry are self-similar. That implies the ability to construct quasicrystals with self-similarity transformations like inflation and deflation rules what is not possible for general aperiodic structures. In the next section we want to present some examples of quasicrystals and demonstrate the mentioned properties in detail.

2.3.1 Fibonacci sequences

A very important one-dimensional quasicrystalline set is the Fibonacci sequence[94, 119, 187]. It serves as an easy to understand toy model for more complicated cases of quasicrystalline structures. The Fibonacci chain is also very closely related to the Penrose tilings which we will discuss in the next section. In one dimension an rotational symmetry has no meaning so the construction of the Fibonacci sequence is only defined by the other two properties. The Fibonacci sequence consists of a quasiperiodic repetition of two spacings with different lengths. We denote the short length scale (s) and the long length scale (l). The spacings can be seen as the unit cells of the quasicrystalline structure which are repeated in a quasiperiodic order. In this way we satisfied the two conditions of an aperiodic translational order and a minimum and a maximum distance identical to the length scales of the unit cells. There are many ways to create this sequence exploiting different properties of an one dimensional quasicrystal. In general, one generates the sequence iteratively with construction or deflation rules. Both methods start with an initial sequence of spacings which grows with each step by a finite number of additional spacings. After each step, every obtained sequence is a finite patch of the infinite Fibonacci sequence which would be obtained for the step number $n \rightarrow \infty$.

A construction rule describes how to add configurations of the previous step to obtain a new longer sequence in the next step. A start configuration with the step

1	L								1
2	L				S				2
3	L			S		L			3
4	L		S	L		L		S	5
5	L	S	L	L	S	L	S	L	8

Figure 2.4: Subdivision of the upper box marked L into smaller parts using the deflation rule $S \rightarrow L$ and $L \rightarrow LS$ at each step. The fraction of the two distances always obey $L/S = \tau$. The step number is shown on the left and the number of sub boxes at each step is shown on the right.

numbers $n = 0, n = 1$ is defined by $S_0 = l$ and $S_1 = ls$. The construction rule for the Fibonacci sequence reads then $S_n = S_{n-1}S_{n-2}$. The recurrence relation for a Fibonacci number series is $F_n = F_{n-1} + F_{n-2}$ with the seed values $F_0 = 0$ and $F_1 = 1$. With this construction rule the similarity between the Fibonacci chain S_n and the Fibonacci series F_n become apparent. In particular the number of spacings in the patch of the Fibonacci chain N_n grow with $N_n = N_{n-1} + N_{n-2}$. The seed numbers of the Fibonacci sequence $N_0 = 1$ and $N_1 = 2$ are identical to the Fibonacci series steps $F_2 = 1$ and $F_3 = 2$. Therefore the number of spacings in every finite patch of S_n is the Fibonacci number $N_n = F_{n+2}$.

The deflation rules uses a given set of spacings and subdivide them into a new set of more spacings. In this way the lengths (s) and (l) cannot be preserved. In every step new lengths (s') and (l') are defined in a way such that the ratio between them stays constant and they differ from the previous lengths by only a constant factor. Because we are only interested in the sequence of the short and long lengths and not in their absolute value we will leave out the subscripts in the following. The easiest deflation rule substitutes in every step the spacing with $s \rightarrow l$ and $l \rightarrow ls$. In Fig. 2.4 the deflation is shown. The number of spacings after each step follows again the Fibonacci number series like in the construction rule above. The deflation rules show another very interesting symmetry if we introduce a dot as a marker in the initial step as $l.s$. The first 4 substitutions are shown in Fig. 2.5.

The sequence is despite of the first s and l exactly symmetric around the central dot. After each step the order of the inner asymmetric s and l is interchanged.

$$\begin{aligned}
& l.s \\
& ls.ll \\
& lsll.sls \\
& lsllsls.llslls \\
& lsllslsllsll.slsllslslls
\end{aligned}$$

Figure 2.5: First 4 deflations of the middle-C sequence.

This Fibonacci sequence around a central dot is called middle-C sequence [78]. This sequence plays an important role in the cartwheel tiling which we introduce in the next sections.

The deflation rule can reveal another connection of the Fibonacci chain to the Fibonacci number series. If we assign the probability of finding an l after step n at a certain position with $p_n(l)$ and a short distance with $p_n(s)$ we can express the probabilities of step n through the probabilities of the previous step $n - 1$ using the deflation rules. For the long distance the probability $p_n(l)$ reads :

$$p_n(l) = \frac{p_{n-1}(l) + p_{n-1}(s)}{2p_{n-1}(l) + p_{n-1}(s)} \quad (2.4)$$

With $p_n(l) = 1 - p_n(s)$ follows for the limit $n \rightarrow \infty$:

$$p_\infty(l) = \frac{1}{1 + p_\infty(l)} \quad (2.5)$$

$$p_\infty(l) = \frac{\sqrt{5} - 1}{2} = 1 - \tau \quad (2.6)$$

and therefore:

$$\frac{p_\infty(l)}{p_\infty(s)} = \tau \quad (2.7)$$

The number τ is known as the golden ratio and is also the limit $n \rightarrow \infty$ for the fraction of Fibonacci numbers F_{n+1}/F_n . Therefore the ratio of the number of long distances and the number of short distances in a infinite Fibonacci sequence is the golden ratio τ .

The Fibonacci sequence can also be obtained by a projection method. One can project a periodic regular square lattice onto a line with a slope of $1/\tau$. The

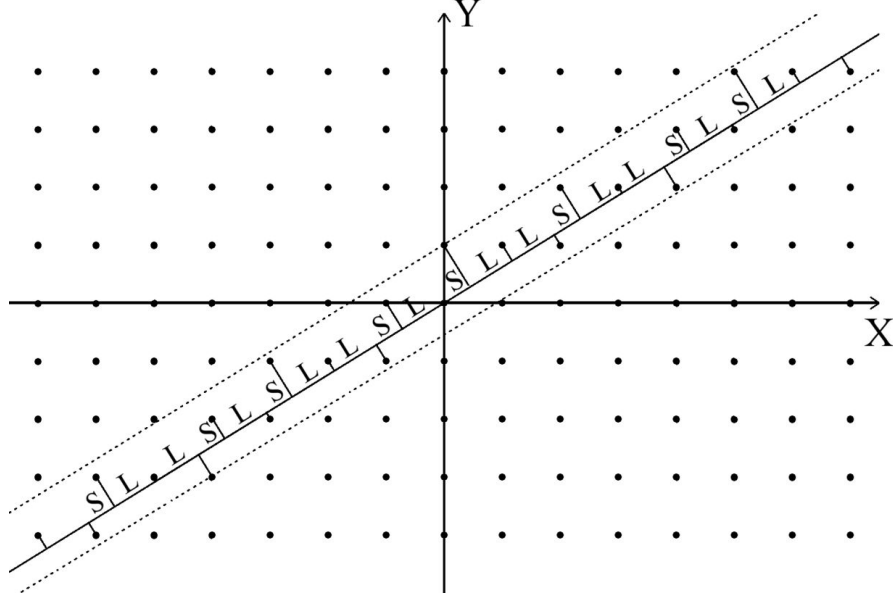


Figure 2.6: Construction of the Fibonacci chain via the projection method. The central black line has a slope of $1/\tau$. The dotted lines denotes the projection strip.

projection is done only for close points within a small environment around the line called the projection strip. There are only two different distances between the projected points which can be marked again as short s and long l . The sequences of the distances then follows the Fibonacci sequence. The size of the projection strip satisfies the condition of a minimum and maximum distance between two points in the Fibonacci sequence. The projection line don't have to cross the origin of the coordinate system and also the projection strip can be displaced as long as the width of the strip is preserved. Choosing the projection in the same way as shown in Fig. 2.6 we find again the exact sequences from the construction rules above. The sequence obtained with the deflation method is identical to the sequence starting from the origin of the coordinate system going into the negative direction. The symmetry center of the middle-C sequence is the cross section of the upper acceptance boundary with the Y axis.

2.3.2 Tilings

In the scope of this work we want to study a system of rod like particles on a quasicrystalline surface. Therefore the properties of two-dimensional quasicrystalline

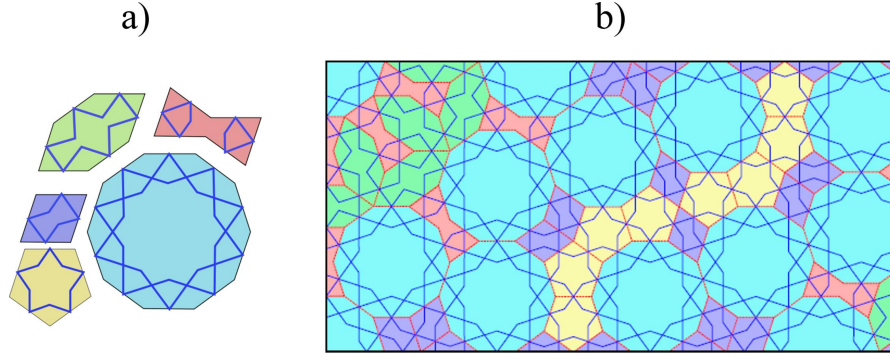


Figure 2.7: a) the tiles of a Girih tiling[37], b) a patch of a Girih tiling[126].

structures are important. As a mathematical model system we present the characteristics of quasicrystalline tilings of the plane. Tilings are well known geometrical structures based on a finite subset of topological discs which can be arranged to fill a two-dimensional space by periodic or aperiodic repetition. The first quasicrystalline tiling was found in ancient Islamic art about 500 years ago[126]. The tiling consist of so called Girih tiles as shown in Fig. 2.7. In Islamic art the Girih tiles are widely used as decorations until today, e.g. the portal of the Turkish embassy in Berlin is decorated with such a tiling. Most of these tilings are periodic but with a very large repeating patch. The most important quasicrystalline tiling related to our work is the Penrose[151] tiling which has a 5-fold rotational symmetry. The Penrose tiling was the first quasicrystalline tiling of the plane explored in modern mathematics. Therefore the features of the tiling are well known.

There are many possibilities to obtain a quasicrystalline two-dimensional structure by a tiling of the plane[8, 11, 161]. Quasicrystalline tilings consists of sets of two or more tiles which serves as unit cells of the tiling[187]. To be able to cover the whole plane without holes, one need in addition a special construction rule. There are different types of construction rules for a quasicrystalline tilings which can be classified as in the case of the one dimensional Fibonacci sequence. Most of them start from a single unit cell building an arbitrary huge patch. An easy to understood rule is a set of matching rules[120, 188] for the edges of the unit cells. The unit cells are decorated with markers which have to be matched by the neighboring unit cells. Starting with an arbitrary unit cell one can just add more cells and grow a patch which can cover the whole plane. Unfortunately

the matching rules alone are ambiguous. Every patch of a tiling must fulfill the matching rules but not every patch placed correctly with respect to the matching rules can be completed without defects to fill the entire plane. The importance of the matching rules arises from the fact that real quasicrystalline materials have to grow by local interactions between the atoms[34, 123]. This local interaction has to be reflected in the possibility to build a perfect quasicrystalline tiling with local matching rules for each tile[69]. Another problem is the building of two or more different tiles of the correct stoichiometric number out of an initial isotropic liquid state. This problem could be avoided by using one single prototile with a set of overlapping rules instead of different unit cell tiles with matching rules[196]. We will present these construction methods in the example of the Penrose tiling in the next section.

A different approach to obtain a tiling of the plane are deflation rules[119, 187]. The deflation rules describe how a tile can be subdivided into smaller unit cells. This method uses the self-similarity of many quasicrystalline tilings and is a two-dimensional analogon to the deflation rules of the Fibonacci sequence. One starts again with an arbitrary tile and subdivide it into a sub pattern. One repeats this subdivision until the needed size of the quasicrystalline patch is reached. This is a very reliable method which always produces perfect patches and is a vital approach for mathematical treatments. Obviously such a deflation can not serve as a model for the growth of real quasicrystals.

A more general way to obtain a quasicrystalline tiling of the plane is the multigrid method[68, 107, 189]. A grid is a countable, discrete set of parallel lines. The multigrid is a sum of many grids with different line directions. This method is analogue to the projection method of the Fibonacci sequences. One can identify the line directions with the symmetry axis of the system and regard them as projections of a higher dimensional hypercube on the two-dimensional plane. The crossing points of the lines can be regarded as dual to the positions of the unit cells of a tiling. Defining for every type of crossing points a corresponding tile, one can construct aperiodic tilings of the whole plane. This can lead to more general aperiodic tilings which can not be constructed by matching rules or deflation methods. This generalization can also introduce tilings without any rotational symmetry[186].

2.3.3 Penrose tiling

The Penrose tiling is an aperiodic tiling of the plane with a 5-fold rotational symmetry[151]. There are at least 3 popular different sets of unit cells[78]. We show them in Fig. 2.8. The Penrose set in Fig. 2.8 a) consist of six different unit cells which are four kinds of pentagons, a pentacle, a rhomboid and a half pentacle. This tiling has untypical many unit cells but displays the 5-fold rotational symmetry in the most understandable way. A very common set is the set of two different unit cells of kites and darts shown in in Fig. 2.8 b). The last set has also two unit cells, a skinny and a fat rhomboid, Fig. 2.8 c). The two unit cells of the last set turned out to be very useful also for the descriptions of other tilings with different rotational symmetries. The justification to call all of them a Penrose tiling stems from their equivalence under self-similar transformations. One can transform a perfect tiling of one set into a tiling of another set and vice versa. The Penrose tiling can be build from matching rules, deflation methods and a multigrid of 5 periodic grids in the symmetry directions of a pentagon. The matching rules of the rhomboid set are shown in Fig. 2.9 a). The rhomboids are marked with arrows. Two rhomboids are allowed to be placed side by side if the shared edges have the same number of arrows pointing in the same direction. The matching rules can be obtained from the projection of a 5 dimensional crystalline grid onto the 2 dimensional plane[40]. In Fig. 2.9 b) the deflation rules are shown. The rhomboids can be subdivided into a small sub patch of smaller rhomboids. The length of the edges shrinks by a factor of $1/\tau$. After each deflation one can inflate the obtained tiling by τ and obtain a bigger patch of a perfect tiling with the same edge lengths as in the initial patch.

Patterns with the same properties of an underlying tiling can be derived by the decoration of the unit cells[94]. One famous decoration of the fat and skinny rhomboids is the Ammann bar decoration[78, 119, 187]. The rhomboids are decorated with line segments which can also be used as markings for the matching rules. The marked tiles composing a Penrose tiling with the line segments merged into a set of parallel lines in every of the 5 symmetry directions. The Ammann bar decoration and the resulting tiling is shown in Fig. 2.10. In every set of parallel lines there are only two different distances, a short S and a long distance L which are ordered in a Fibonacci sequence. It is also possible to construct the

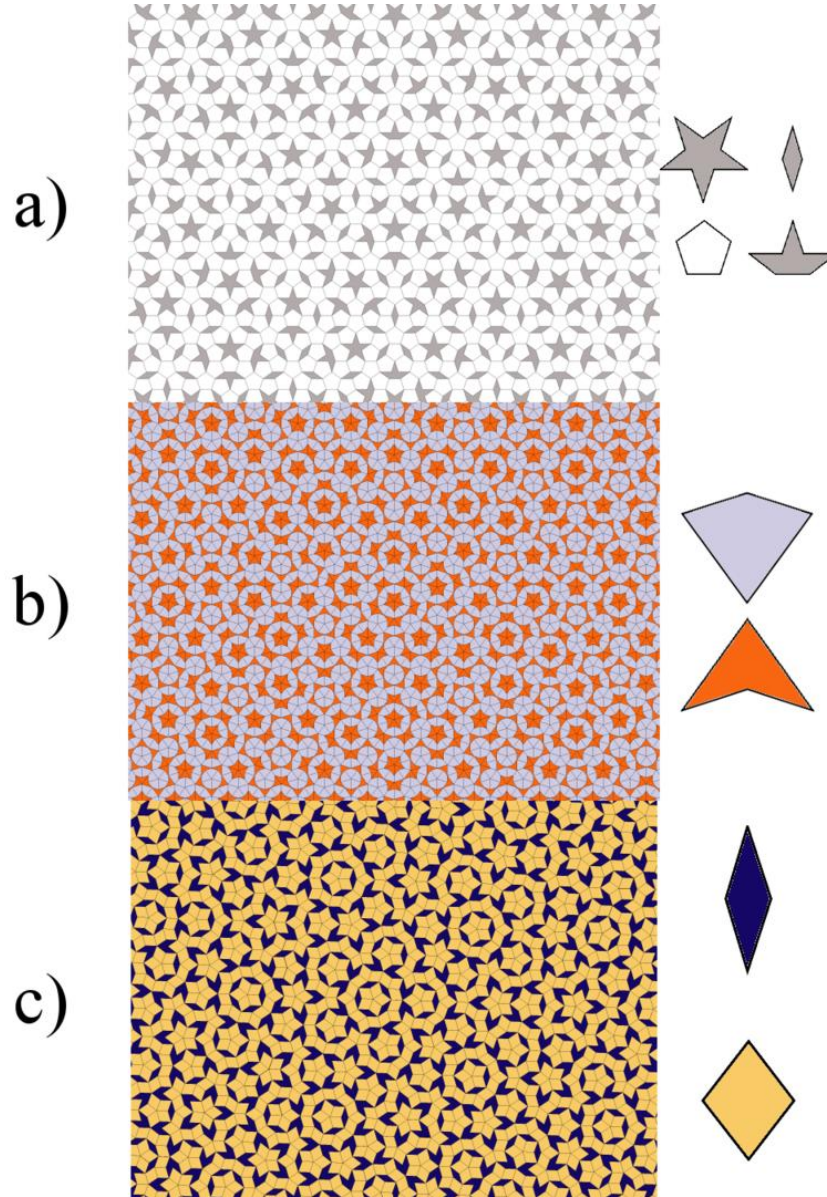


Figure 2.8: The 3 types of a Penrose tiling : a) Pentacles, rhomboids and pentagons, b) kites and darts, c) thick and thin rhomboids from [84]

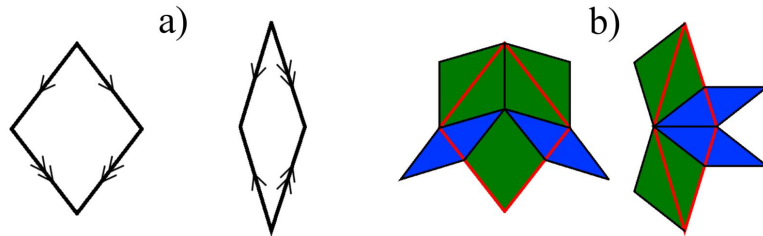


Figure 2.9: a) matching rules for thick and thin rhomboids. b) deflation of thick and thin rhomboids (red) into a smaller tiling.

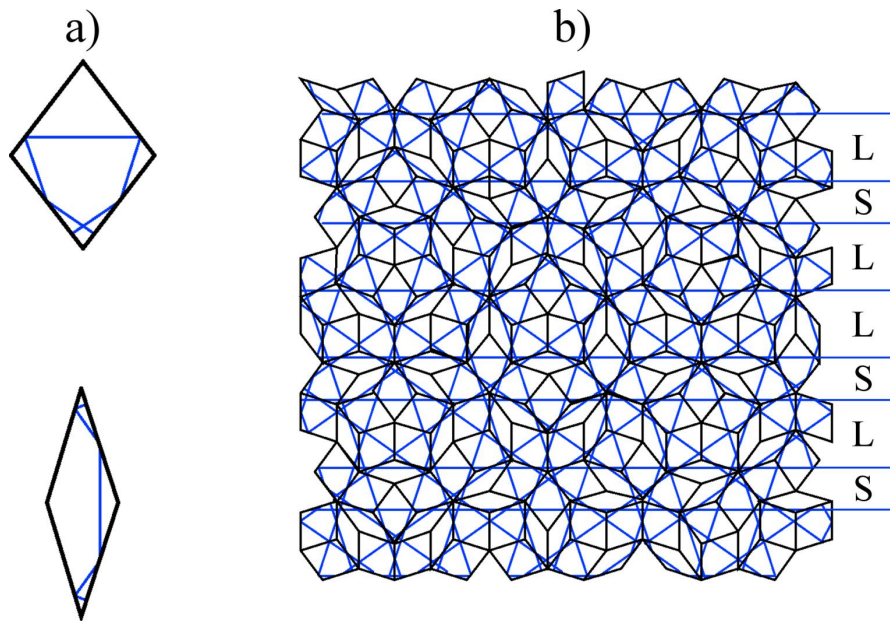


Figure 2.10: a) decoration of the tiles with Ammann bars b) resulting Penrose tiling with Ammann bars.

grid of parallel lines first and obtain the tiling stemming from the grid structure afterwards. If the lines have a sequence of long L and short S distances obeying $L/S = \tau$, following the Fibonacci sequence and the orientation of the lines is along the 5-fold symmetry directions of a pentagon, the grid is called Pentagrid. The Pentagrid is the underlying multigrid for all Penrose tilings. The intriguing property of the Ammann bar decoration is that it reveals the connection between matching rules, the multigrid method and the Fibonacci sequence in a Penrose tiling.

A quite sophisticated kind of deflation method for the kites and darts in a Penrose tiling is the cartwheel tiling[78]. Starting with a kite and two darts, a so called ace, and deflate this by the corresponding deflation rules, one gets sequentially growing patches. The patches with even numbers of deflations possess very interesting features. All patches have a mirror symmetry like the first ace. Furthermore, the even numbered patches consist of sub patches in the shape of a decagon. These patches are called cartwheels. A n th order cartwheel is a cartwheel after $2n$ deflations starting from the ace. In Fig. 2.11 the initial ace patch a) is shown. After two deflations one reaches the decagon patch b) with the ace in the middle. This decagon patch is the first order cartwheel. Two more deflations show a bigger decagon, displayed in Fig. 2.11 c). In the center of the big decagon is again the ace and the first order cartwheel. In the center of a cartwheel of n th order are always all cartwheels of the order $m < n$. One can show that every Penrose tiling consists of an infinite composition of cartwheels. Another important feature of the cartwheel tiling is the sequence of Ammann bars. The distances between the Ammann bars follow the middle-C sequence of the Fibonacci chain shown in the previous section.

The decoration of the unit cells is a widely used method to connect a tiling with actual quasicrystalline materials. The tiling together with a decoration which stands for the positions of the atoms can serve as an approximant of a real material. But the decoration of the tiling of a quasicrystal consisting of many unit cells remains unsatisfactory. These unit cells fall short in explaining how a real quasicrystal grows, especially how the single atomic bonds know the correct matching rules for a macroscopic quasicrystalline order without any defects and holes. An alternative approach inspired by the cartwheel tilings was given by the work of

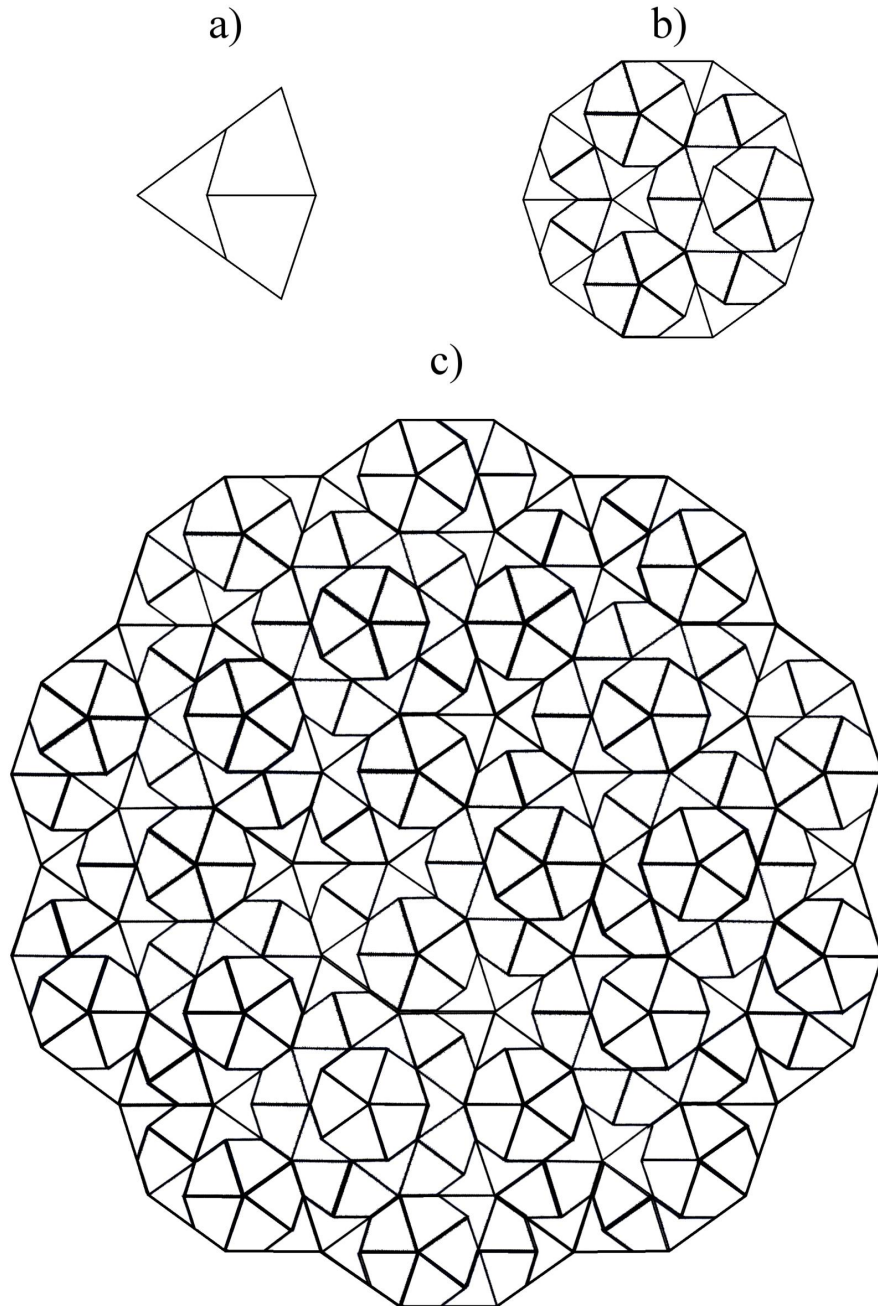


Figure 2.11: The cartwheel tiling derived by deflation rules. a) The central ace configuration b) the first order cartwheel c) the second order cartwheel.

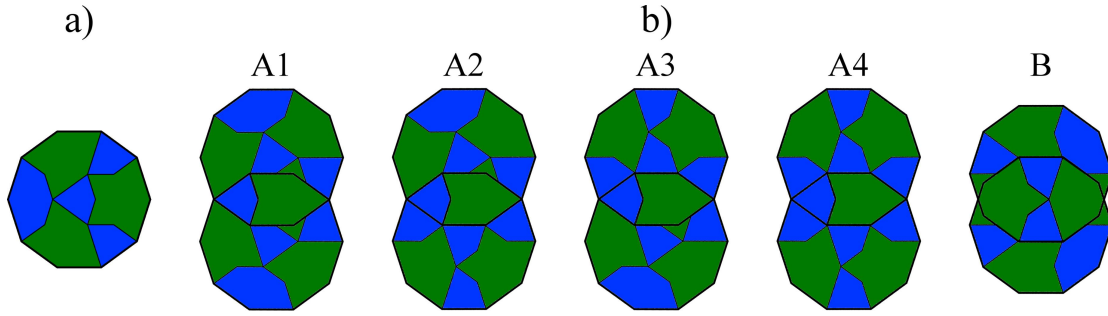


Figure 2.12: a) decagon prototile b) overlap rules for four small overlaps A and a big overlap B.

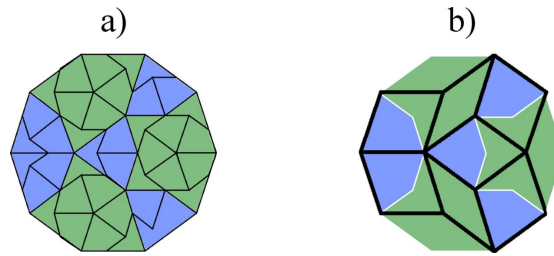


Figure 2.13: a) Cartwheel decoration of a Gummelt decagon b) Decoration of the decagon with a Jack.

Gummelt[66, 79, 80, 97]. The set of a few different unit cells is replaced by just one single quasi unit cell. The quasi unit cell for the Penrose tiling is a decagon. The decagons are allowed to cover parts of each other by a set of matching rules as displayed in Fig. 2.12. The benefit of this approach is that the matching rules of the decagon can be explained by the inner structure of the atomic clusters without the need of explaining how different building blocks are forming. A decoration of a decagon with the corresponding positions of the atoms reveals that the decagon clusters sharing just groups of atoms with each other[157, 192]. One group of atoms can belong to more than one decagon structure. The geometrical matching rules of the decagons correspond to the sharing possibilities of the atomic structures. Three dimensional quasicrystals can be build from the stacking of the two-dimensional clusters[135, 194]. One can derive the Penrose tiling from the Gummelt decagon easily by a decoration of the decagon as shown in Fig. 2.13. The kites and darts decoration is just the first order cartwheel tiling as shown in Fig. 2.11 b). The rhomboids tiling can be derived by adding a so called Jack configuration as a decoration of the decagon.

3 Nematic liquids

In this chapter we introduce first different kinds of liquid crystalline order. Afterwards we explain the special properties of phase transitions in two dimensions. Phase transitions can be described quantitatively by order parameters. The order parameters used in our work are shown in the third section of this chapter. In section 3.4 we display our particle models. Then we present the interaction of the hard rods with the substrate potential and choose the lengths of the rods.

3.1 Liquid-crystalline order

The mechanical properties and symmetries of liquid crystal phases are intermediate between a liquid and a crystalline state. They are therefore often referred to as mesophases. They were first discovered by Reinitzer[160] and shortly after named liquid crystals by Lehmann [118] in the 19th century. The components of liquid crystalline matter are anisotropic building blocks. The size of the building blocks range from small molecules up to the scale of colloidal particles. The most common shapes are elongated particles or disc-like particles. There are many different liquid crystalline phases which are categorized with regard to the order found in these phases[70]. The simplest phase is the nematic phase. In a nematic the particles are oriented along a common axis called the director. The particles can flow in every direction like in the liquid phase. The diffusion of the particles is usually different in the direction of the director and perpendicular to it. In the cholesteric phases the orientation of the director smoothly changes in space and has a helical structure around an axis perpendicular to the director. The period of the helix is called the pitch of the cholesteric. The pitch is typically much larger than the size of one particle. If the pitch is infinitely large we obtain the nematic phase. If the particles are positionally ordered in one dimension and the orientations are ordered along a common director like in a nematic phase the phase is called smectic. An one-dimensional spatial crystalline order defines two-dimensional layers in

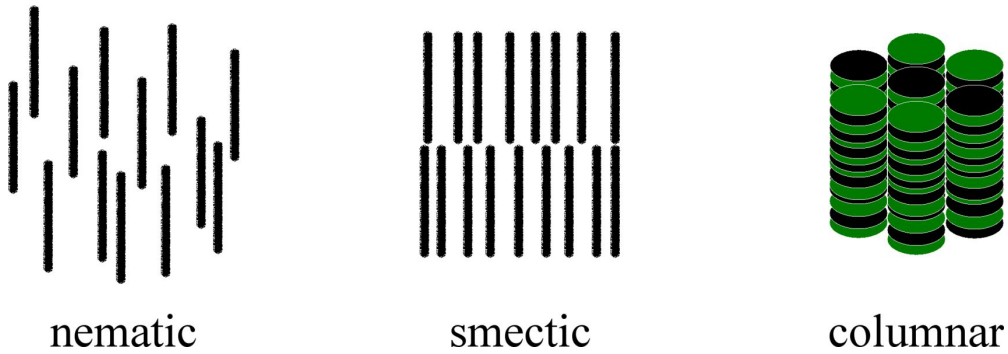


Figure 3.1: Schematic drawing of a nematic , smectic and columnar order.

which the particles can flow like a liquid. There are many different possibilities to build a smectic order so there is a large subgroup of smectic phases. The most common smectic phases are the smectic A where the layers are perpendicular to the director and the smectic C where the director is tilted with respect to the normal of the planes. The most ordered phase is the columnar phase. In this phase the particles are periodically ordered in two dimensions and liquid only in the third one. The name stems from the conformation of the particles into parallel columns. The particles are in a liquid state along the axis of the column only. Fig. 3.1 displays schematically the different phases. Another important classification of liquid crystals is how the matter approaches the liquid crystalline phase. Particles which undergo easily a phase transition into a liquid crystalline phase by a temperature change are called thermotropic. If the phase transition is density driven, the liquid crystal is called lyotropic.

Liquid crystals are nowadays most widely used in liquid crystal displays (LCD)[91]. The surface interactions play a very important role in the development of LCD systems. The direct interaction of an anisotropic molecule with a surface is called anchoring[99, 100]. The molecule can prefer to lie planar at the surface or have a specific contact angle. At the vicinity of the surface the liquid crystal can undergo a phase transition of the Kosterlitz-Thouless type[182]. The surface monolayer can induce a liquid crystalline order in the bulk[101, 130, 193]. The formation of an interfacial monolayer at a wall is strongly connected with the wetting behavior of the liquid[41, 173, 179, 191]. In LCDs the liquid crystals are usually confined between two parallel walls. Therefore the influence of the walls with and without a

substrate pattern raised a lot of attention[5, 32, 49, 76, 208]. Different techniques of patterning a surface are known, which can induce controlled phase behavior in the bulk phase[81, 106, 156, 219, 222]. The patterns can consist of topological gratings[26] or chemical structures [22]. Also patterns produced by laser fields are known[117, 127]. It has been shown that patterns with crystallographic symmetries can be used to build liquid crystal devices which have bistable or tristable nematic order[21, 105, 116]. The most interesting experiments for the scope of our work are nematogens in contact with crystalline surfaces. Some systems have already been investigated experimentally like alkene on graphite[88] or pentacen on SiO_2 [31], and through computer simulations[145].

Lyotropic hard core nematics are easy to model in computer experiments in the most general fashion. There are less lyotropic liquid crystals known than thermotropic but they have become more and more important also for practical applications. Many of the lyotropic nematics are anorganic rods[67, 165, 227] such as bohemite rods[27, 204, 205, 206, 215] sepiolite clay[217, 223] $LaPO_4$ rods [104], rodlike silica [112] or $\beta - FeOOH$ needles[129]. One of the oldest lyotropic liquid crystals is the tobacco mosaic virus[29, 144]. Because of its monodispersity it served as an ideal experimental model system[61, 74, 214] for a long time. The application of the self-organization of liquid crystals on crystalline surfaces raises scientific interest in other fields as well. For example, the self-assembly of nano rods can be used to build nanostructures on semiconductors[121, 122].

In the following we want to restrict ourself to the simulation of a two-dimensional system. The phase behavior of two-dimensional systems is quite different from the three dimensional bulk systems. We take two different models for the particles into account namely the hard needles and the hard spherocylinders.

3.2 Phase transitions in two dimensions

A phase transition occurs when a system changes its order from one state to another. The phase transition can be tracked quantitatively by a properly chosen order parameter. One can distinguish two basic types of phase transitions with respect to the behavior of the free energy function at the transition temperature

T_C . The transition is called first order if the first derivatives of the thermodynamic potential, e.g. the free energy, are discontinuous at the transition temperature. The size of the discontinuity is unimportant for this classification and can be arbitrary small or large in different systems. The transition is called continuous if the second or higher-order derivative of the thermodynamic potential exhibit a discontinuity.

Onsager predicted in 1949 a first order isotropic to nematic phase transition of a system of infinitely thin rods in three dimensions[143]. The phase transition is driven purely by the shape of the particles without the need of additional interaction potentials. This transition is well understood and experimentally confirmed. If one confines such a system between two plates, the first order phase transition gets lost as the distances between the two plates get narrower and the system becomes quasi two-dimensional. The phase behavior of a two-dimensional system is quite different from the three-dimensional case. The Mermin-Wagner theorem states that there is no long-range order in one or two-dimensional systems with short-ranged interactions between the particles[134]. This rigorous result can be extended to more complicated long-ranged potentials as shown by Bruno[25]. Nevertheless, phase transitions still exist, namely between an isotropic phase and a phase with long-ranged correlations which decay algebraically. In a two-dimensional system the nematic phase has no common director in the thermodynamic limit satisfying the Mermin-Wagner theorem. One can define the nematic director only locally for finite regions around every particle. Therefore the phase is called quasi-nematic. The nature of those phase transitions is of the KTNHY type[82, 110, 220]. Of special interest for our simulation of rods confined on a two-dimensional plane is the universality class of the two-dimensional XY model of freely rotating spins on a lattice. In this system the isotropic to quasi-nematic phase transition is continuous. Kosterlitz derived the critical exponents for this model quite early[109] but the simulation of this particular model turned out to be rather complicated and has been done more recently [58, 85]. In our simulations the long-ranged orientational correlations lead to a strong system size dependence of the the isotropic to quasi-nematic phase transition.

3.3 Order parameters

Order parameters are a vital tool to investigate the different states of matter and their phase transitions. In our system of rods confined to a plane in a quasicrystalline substrate several order parameters are necessary to describe its phase behavior. In the following we present the order parameters in detail.

We measure the existence of a nematic phase with the nematic order parameter S which is defined as

$$S = N^{-1} \left\langle \sum_{i=1}^N \cos(2\theta_i) \right\rangle, \quad (3.1)$$

where N is the particle number and θ_i is the angle of the i th rod with the nematic director.

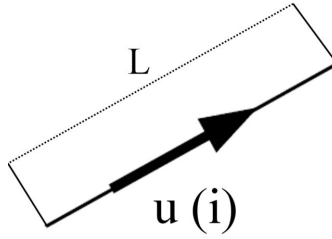


Figure 3.2: Rodlike particle with an length L and the attached orientational unit vector $\vec{u}(i)$.

In practice, it is more convenient to use the orientational tensor order parameter. For a configuration consisting of N rods it is defined as

$$Q_{ab} = N^{-1} \sum_{i=1}^N [2u_a(i)u_b(i) - \delta_{ab}] \quad , \quad (3.2)$$

where $\vec{u}(i) = [u_1(i), u_2(i)]$ is a unit vector indicating the direction of rod i as illustrated in Fig 3.2. Since $Q_{aa} = 0$, the two eigenvalues of Q_{ab} , Q and $-Q$ add up to zero and the nematic order parameter is the ensemble average $S = \langle Q \rangle$ over the positive eigenvalue of Q_{ab} .

Under the influence of the substrate potential the rods can form additional phases. They can be characterized by a bond-orientational or directional ordering in the plane. To describe a directional order where the rods are aligned along

the symmetry direction of the substrate we have introduced the directional order parameter for m -fold order :

$$\Phi_m = \langle \varphi_m \rangle \quad \text{with} \quad \varphi_m = N^{-1} \left| \sum_{j=1}^N e^{im\alpha_j} \right| \quad (3.3)$$

where α_j is the angle of the rod j with respect to an arbitrary axis.

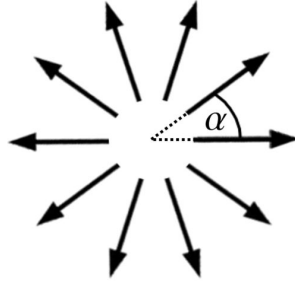


Figure 3.3: The decagonal directional order parameter Φ_{10} measures whether the angles α of all particles with respect to an arbitrary axis match onto a 10-fold rotational symmetric star.

In our decagonal substrate the important directional order is along the 10 symmetry directions of the substrate. To measure the occurrence of this directional order, we use Φ_{10} as displayed in Fig. 3.3. Like the nematic order parameter the directional order parameter measures only the existence but not the orientation of an ordered phase. One can obtain the orientation by taking the phase of the complex sum in Eq(3.3) despite of the absolute value. We note that this phase can also be measured if the system has a very low directional order which slightly prefers the symmetry directions.

Another kind of order observed in our system is a bond-orientational order of the rod centers. We measure this order quantitatively with the bond orientational order parameter which reads for a m -fold order :

$$\Psi_m = \langle \psi_m \rangle \quad \text{with} \quad \psi_m = N^{-1} \left| \sum_{j=1}^N n_j^{-1} \sum_{k=1}^{n_j} e^{im\theta_{jk}} \right| \quad (3.4)$$

where θ_{jk} is the angle of a bond between particle j and one of its n_j nearest neighbors k with respect to an arbitrary reference direction, see Fig. 3.4. The nearest

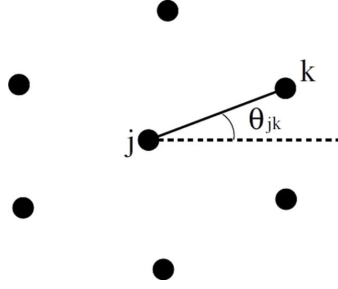


Figure 3.4: The bond orientational parameter uses the angle of a bond θ_{jk} between the particle j and its neighbor k with respect to an arbitrary axis.

neighbors are determined with the help of a Voronoi tessellation [167, 180]. At high potential strengths the rods form clusters. We define such clusters by the conditions that all nearest neighbors j of each particle i within a cluster stay below a maximum distance of $|r_i - r_j| < 0.4L$ where L is the length of the particle and in addition have a maximum difference in their orientation of $|\alpha_i - \alpha_j| < 0.2$. We tested different values for the definition of the clusters. The cluster structure turned out to be robust against changes. For each cluster one can define its position r_C by the center of mass and a orientation α_C by its director. We can define the order parameters for the clusters as before and denote the directional order parameter of the clusters Φ_{Cm} and the cluster bond orientational order parameter Ψ_{Cm} respectively. We are interested in the 10- and 20-fold bond orientational order of the particles and the clusters. We name the bond orientational order of a system after the bond orientational parameter with the highest value.

The localization of a phase transition by studying the relevant order parameter can be a difficult task. It is helpful to take a look at the fluctuations of the order parameter instead of the order parameter itself. The fluctuations become maximal at a phase transition and even show critical behavior in the vicinity of second-order phase transition [7, 190]. The fluctuations of the nematic order parameter is known as susceptibility, which is defined as the variance with respect to S [20, 142],

$$\chi_S = \beta N (\langle Q^2 \rangle - S^2) \quad (3.5)$$

with $\beta = 1/kT$. In the same way, we define the variance for fluctuations around

the directional order parameter and the bond orientational order parameter,

$$\chi_\Phi = \beta N (\langle \varphi_m^2 \rangle - \Phi_m^2) \quad (3.6)$$

$$\chi_\Psi = \beta N (\langle \psi_m^2 \rangle - \Psi_m^2) \quad (3.7)$$

Furthermore, we also look at the specific heat capacity, which is connected to fluctuations in the energy E of a rod configuration

$$c = \frac{\beta^2}{N} (\langle E^2 \rangle - \langle E \rangle^2) . \quad (3.8)$$

Another very useful tool to investigate the structure of a system are correlation functions. Of particular interest are the spatial distribution functions. The radial pair correlation function $g(r)$ gives the probability of finding two particles having a distance of r normalized to the probability of finding two particles with the same distance in a system with the same density but perfect random positions of the particles[6]. It is an important quantity since it can be also measured in scattering experiments. $g(r)$ can be determined in an ensemble average:

$$g(r) = \frac{1}{2\pi r \rho N} \langle \sum_i^N \sum_{i \neq j}^N \delta(r + |\vec{r}_i - \vec{r}_j|) \rangle \quad (3.9)$$

where $\vec{r}_i, \vec{r}_j$ are the positions of the center of mass of the rods and N is the number of particles in the system. In our system not only the radial distribution is of particular interest but the correlations in two dimensions. The two dimensional correlation can be measured with respect to different coordinate frames. We use the frame of the simulation box:

$$g_R(x, y) = \frac{1}{\rho N} \langle \sum_i^N \sum_{i \neq j}^N \delta(x + (x_i - x_j)) \delta(y + (y_i - y_j)) \rangle \quad (3.10)$$

where (x_i, y_i) and (x_j, y_j) are the coordinates of the rods with respect to the coordinate system of the simulation box. Sometimes the choice of a the local frame of each rod is more illuminating. In the pair correlation function of the local frame $g_R(r_\parallel, r_\perp)$, the axes of the local frame are oriented parallel and perpendicular to the director of the rod.

We also calculate the radial orientational correlation function:

$$g_S(r) = \langle \sum_i^N \sum_{i \neq j}^N \frac{\delta(r + |r_i - r_j|) \cos(2(\alpha_i - \alpha_j))}{\delta(r + |r_i - r_j|)} \rangle \quad (3.11)$$

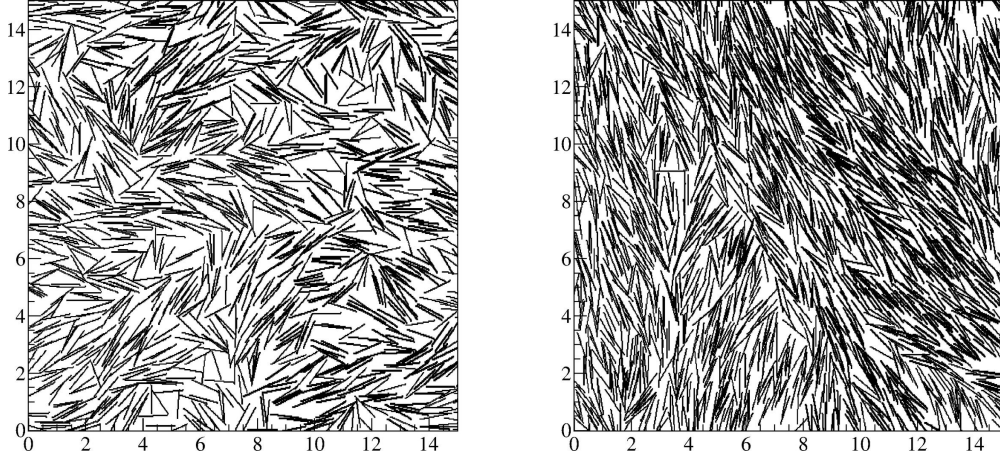


Figure 3.5: Left: Snapshot of a hard-needle system in the isotropic regime Right: Needles in a quasi-nematic phase

The orientational correlations can also be defined in two dimensions in the frame of the simulation box $g_S(x, y)$ and in the local frame of each rod $g_S(r_{\parallel}, r_{\perp})$ as defined for the spatial correlation functions before.

3.4 Particle models

3.4.1 Hard needles

Hard needles are particles with a finite length but without any lateral extension. The aspect ratio of the needle length to diameter is $L/D = \infty$. The needles interact with each other by a hard core repulsion potential V_I only. They are not allowed to cross each other that means $V_I = \infty$ if they cross and $V_I = 0$ otherwise.

Without any substrate the system was first investigated numerically by Frenkel and Eppenga[65]. The isotropic to quasi-nematic phase transition takes place at a number density of $\rho \approx 7 \frac{1}{L^2}$. In the quasi-nematic phase the orientational correlations decay algebraically. In computer simulations, the position of the phase transition and the value of the nematic order parameter strongly depend on the size of the simulation box. In our simulations the transition density is at $\rho \approx 6 \frac{1}{L^2}$ and the maximum value of the order parameter is between $0.8 < S < 0.9$. The critical exponents of the phase transition were investigated numerically by Vink[209]. They turned out to be consistent with the XY model. In Fig. 3.5



Figure 3.6: Hard spherocylinder with an aspect ratio of $L/d = 10$.

two snapshots from simulations of the isotropic and the quasi-nematic phase are shown.

3.4.2 Hard spherocylinders

In contrast to the hard needle model hard spherocylinders exhibit a finite aspect ratio. In two dimensions they consist of a rectangular rod with the diameter d and a length L with two half circular caps at each end. The diameter of the cap circles is also d . In Fig. 3.6 a spherocylinder with an aspect ratio of $L/d = 10$ is shown.

The phase behavior of the spherocylinders strongly depend on the aspect ratio. The model was investigated numerically first by Bates and Frenkel [13]. For low aspect ratios with $L/d < 7$ the rods exhibit only an isotropic phase for low densities and a solid phase at high densities. More slender rods with higher aspect ratios exhibit also a low density isotropic phase and a high density solid phase but at intermediate densities a quasi-nematic phase emerges. The properties of the isotropic to quasi-nematic phase transition are the same as for the hard needle model. The nature of the solid phase is still unknown. It looks almost smectic but it is very difficult to perform computer simulations in this density regime. In our simulations we stay at densities well below the transition to the solid phase. We use an aspect ratio of $L/d = 10$ to be able to simulate a system which possesses a nematic phase. At this aspect ratio the isotropic to quasi-nematic phase transition is expected to be at an area fraction of $\eta \approx 0.5$. In our simulations, the actual position of this phase depends again on the size of the simulation box. In Fig. 3.7 two systems of spherocylinders are shown in an isotropic and quasi-nematic phase

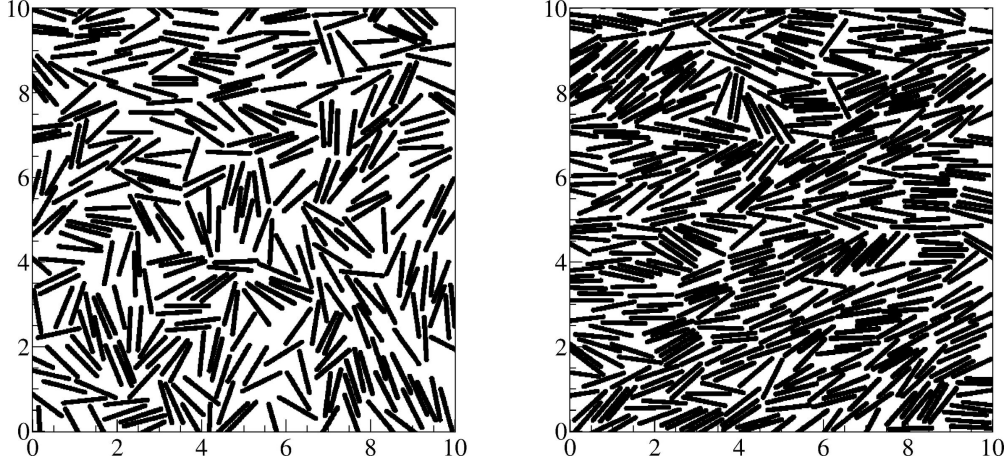


Figure 3.7: Left: Snapshot of a system of hard spherocylinders in the isotropic regime Right: Hard spherocylinders in a quasi-nematic phase

respectively.

3.5 Rod - substrate interaction potential

In this section we present the interaction of the rods with the substrate potential. We display the structural features of our substrate potential and choose the length of the rods. The substrate potential derived in Eq.(2.3) reads for a decagonal symmetry:

$$V(\vec{r}) = -\frac{V_0}{25} \sum_{j=0}^4 \sum_{i=0}^4 \cos[(\vec{G}_i - \vec{G}_j) \cdot \vec{r}] . \quad (3.12)$$

with the wave vectors $\vec{G}_i$ pointing to the vertices of a pentagon as shown in Fig. 2.3. The particles interact with the substrate by averaging the potential over their full length L :

$$V_R(\vec{r}, \vec{u}) = \frac{1}{L} \int_{-1/2}^{1/2} V(\vec{r} + lL\vec{u}) dl . \quad (3.13)$$

The potential V_R depends on the choice of the length L . We define the minimal potential energy of a rod at a given position $\vec{r}$ with respect to all possible orientations $\vec{u}$ of the rod:

$$V_M(\vec{r}) = \min_{\vec{u}} (V_R(\vec{r}, \vec{u})) \quad (3.14)$$

Fig. 3.8 displays $|V_M|$ for different choices of L . For $L = 0$ the substrate potential

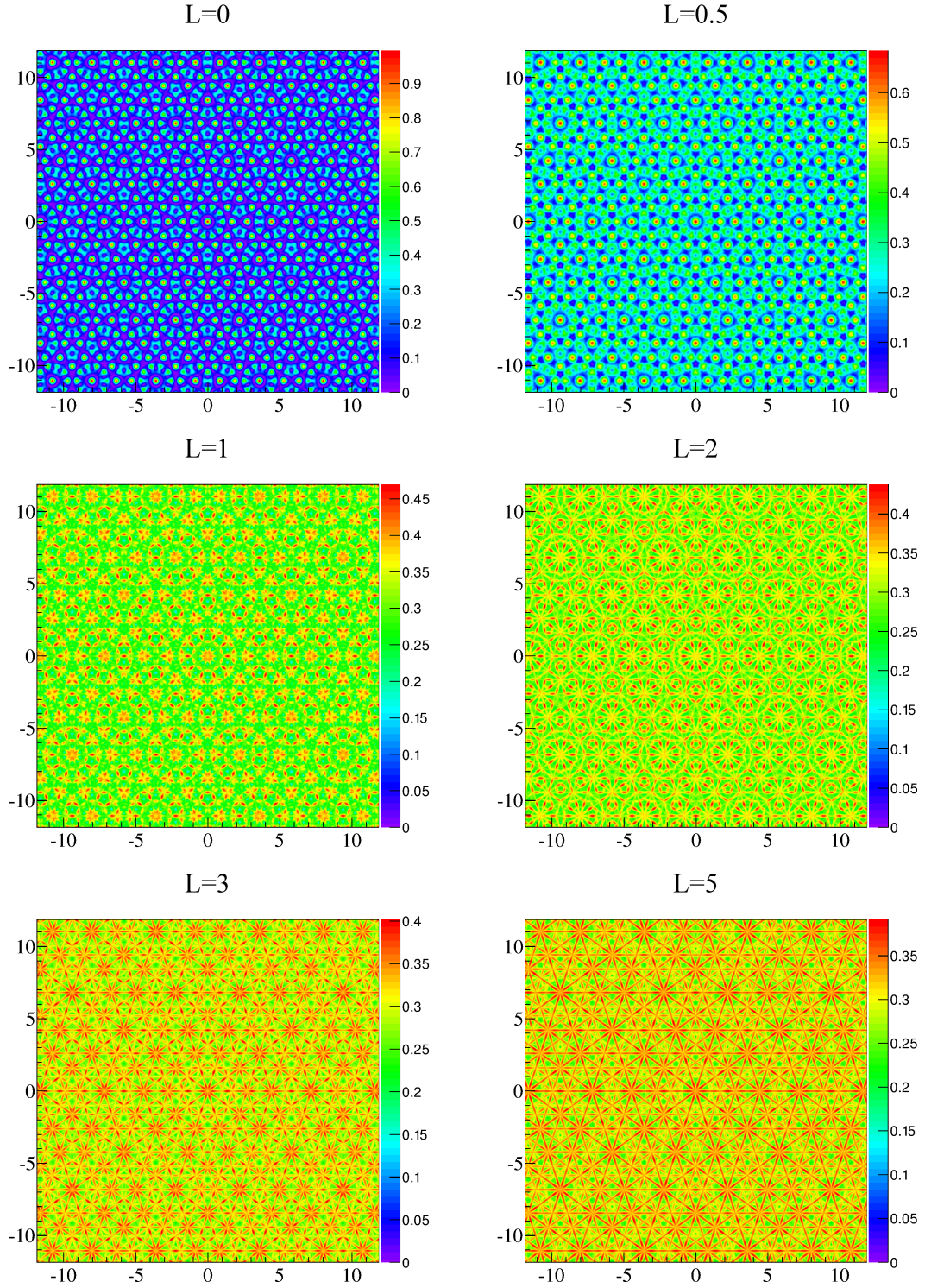


Figure 3.8: Maximum strength of the potential $|V_M|$ for different rod lengths L .

from Eq. (3.12) is recovered. If $L < 1a_V$ the particles are shorter than the typical distance of two potential minima. Therefore positions of the minima in V_M are the same as for V . Very short particles behave like point like particles despite averaging over a small length along the substrate potential. At $L = 1a_V$ the positions of the deepest minima change and the minima of V_M are located between two minima of the bare substrate potential V . The minima exhibit a elongated shape in contrast to the minima in the substrate potential V which possess a circular shape. The orientation of the long axis of the elliptical shaped minima is identical to the particle orientation with the lowest energy at this position. At a length of $L = 3a_V$ a pattern appears which consists of long lines of low potential energy connecting the minima. Because of the averaging in the definition of V_R the deepest minima of the resulting potential become shallower with increasing length of the particles. The depth of the deepest minima decreases from $V_{min} = -1$ for $L = 0$ to $V_{Rmin} = -0.38$ for $L = 5a_V$.

In the following we choose two lengths for our particles. The length of the short particles is $L = 1a_V$ and the length of the long particles is $L = 3a_V$.

Restricting the orientation to one of the symmetry directions, one can recognize a line pattern connecting all potential minima for both particle lengths. In Fig. 3.9 the orientation of the particles points along the X -axis. In the middle panel the projection of the potential of such aligned particles onto the Y -axis is shown. The projection onto an axis perpendicular to the orientation of the particles is independent of the particle length. One can identify characteristic distances between lines connecting the potential minima also seen in the distribution of the maxima in the projected potential. The distances between the lines of the deepest minima follow a Fibonacci sequence with a mirror symmetry at the center of the coordinate system. Taking also lines of shallower minima into account the Fibonacci sequence decomposes into two interwoven Fibonacci sequences of smaller distances which possess the same symmetry around the origin of the coordinate system as the Fibonacci sequence we have obtained by the projection method shown earlier in Fig. 2.6. We present a more through investigation of the origin of these line pattern in the Appendix of this work.

From the structure of V_M , we can derive the bond orientational order of the

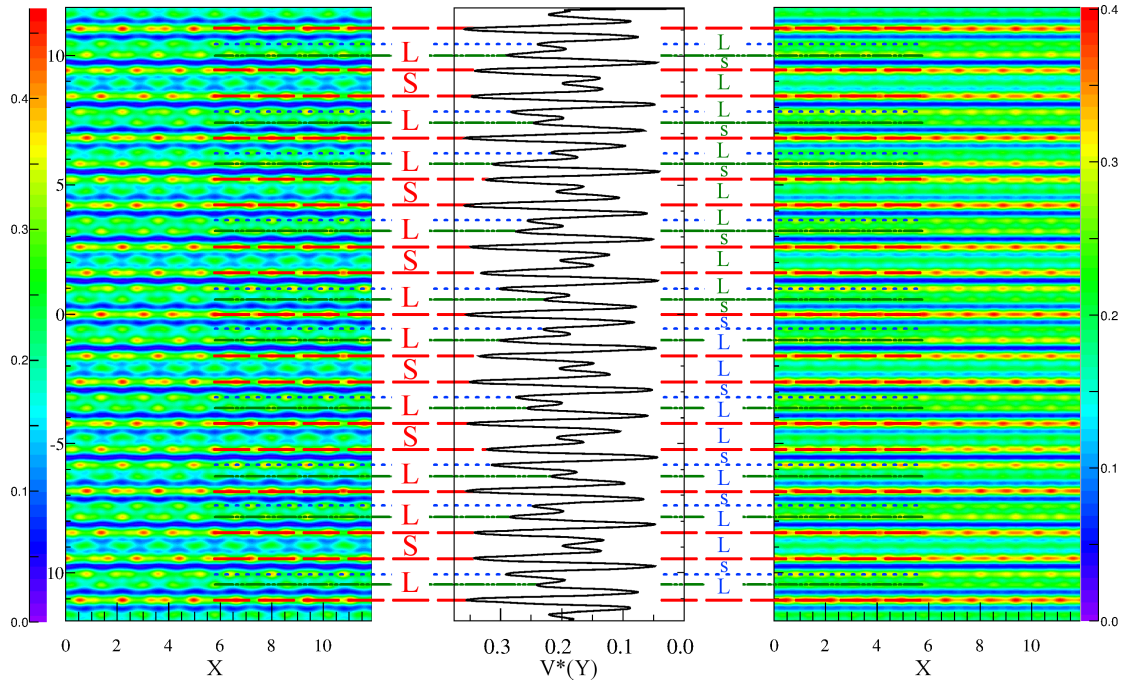


Figure 3.9: The potential $|V_R|$ for a particle which is oriented along the direction of the X -axis. Left panel for $L = 1$. Right panel for $L = 3$. In the middle panel the projection $V^*(Y)$ of both substrate potentials onto the Y -axis is shown together with the Fibonacci sequences which are defined by the distances between lines of deep minima.

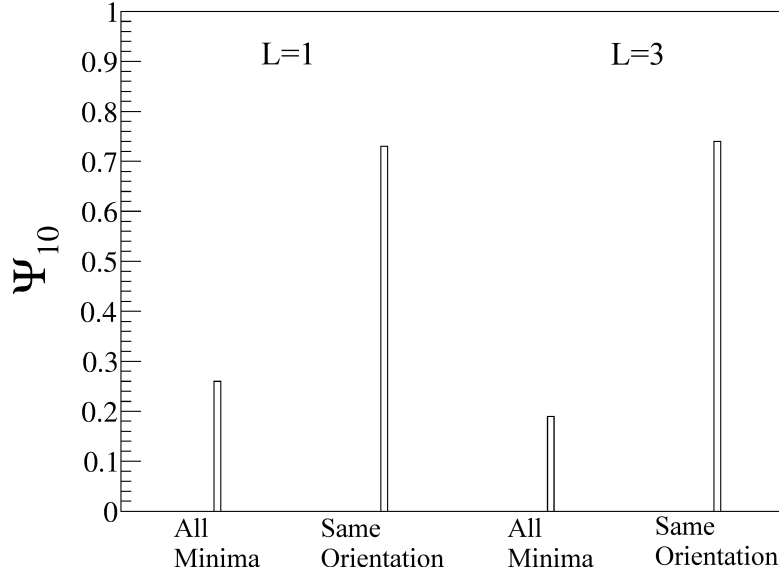


Figure 3.10: Bond orientational order parameter for the positions of the substrate minima for both length scales.

minima. The values of the bond orientational order parameter Ψ_{10} are shown in Fig. 3.10. For the calculation of Ψ_{10} we determined ≈ 20000 positions of the minima of V_M . For both particle lengths the bond orientational order is quite weak. The short particles have a slightly higher bond orientational order of $\Psi_{10} = 0.28$ compared to $\Psi_{10} = 0.26$ for long particles. At every minimum position of the potential V_M there is only one rod orientation for which the potential V_R exhibit this minimum. The rod orientations of every minima are aligned along one of the symmetry directions of the potential. If we divide the minima positions into groups of minima with the same orientation, the bond orientational order parameter of the minima in each group is significantly higher as for the sum of all minima. The bond orientational order parameter of every single group is for both particle lengths $\Psi_{10} \approx 0.75$.

4 Computational methods

In this chapter we present the basics of statistical mechanics necessary for our simulations and give the details of the algorithms used by our simulations.

4.1 Canonical ensemble

In statistical mechanics we characterize a macroscopic thermodynamic system by the weighted averages obtained from a complete set of its microscopic realizations[201]. We address the sets of microstates together with their statistical weights as ensembles. The weights depend on the interaction of the system with a reservoir and the ensembles are named accordingly. In our simulations we use the canonical ensemble. The canonical ensemble is described by its number of particles N its volume V and its temperature T . One can imagine such a system as a box with a fixed size in equilibrium in a heat bath with which it exchanges thermal energy to stay at a fixed temperature. We are interested in rods on a plane. Let $\vec{r}_i$ be the coordinate of the i -th particle, $\vec{u}_i$ a unit vector pointing in the direction of its long axis and $\vec{p}_i$ its momentum and $\vec{l}_i$ the angular momentum. The Hamiltonian for this system is given by:

$$H(\vec{r}, \vec{p}, \vec{l}) = \sum_i^N \frac{\vec{p}_i^2}{2} + \sum_i^N \frac{\vec{l}_i^2}{2I} + \sum_i^N \sum_j^N V_{\text{pair}}(\vec{r}_{ij}, \vec{u}_i, \vec{u}_j) + \sum_i^N V_{\text{substrate}}(\vec{r}_i, \vec{u}_i) \quad (4.1)$$

where I is the moment of inertia, V_{pair} is the pair potential and $V_{\text{substrate}}$ is the substrate potential. With the notation

$$d\Gamma = \frac{1}{h^{3N} N!} dr dp dl \quad (4.2)$$

the partition function can be written as:

$$Z = \int d\Gamma e^{\frac{-H(\Gamma)}{kT}} \quad (4.3)$$

Where k is the Boltzmann constant and h is Planck's constant.

It is an important feature of the partition function that one can split the function into the configurational parts and the kinetic parts[75].

$$Z = Z_K Z_R Z_V \quad (4.4)$$

Z_K is the translational kinetic term, Z_R the rotational kinetic term and Z_V the potential part. The integration of the different parts of the partition function can be done separately. The integral over the translational momenta can be carried out to:

$$Z_K = \frac{V^N}{N! \Lambda^{2N}} \quad (4.5)$$

where Λ the thermal de Broglie wavelength is given by:

$$\Lambda = \frac{h}{\sqrt{2\pi m k T}} \quad (4.6)$$

The rotational kinetic part reads:

$$Z_R = \frac{1}{\Lambda^N} \frac{I^N}{m^N} \quad (4.7)$$

The configurational part of the partition function is independent of the dynamics of the system. The Monte Carlo simulation takes only the configurational part into account. The translational and rotational kinetic part of the partition function add only as a prefactor. In the following we denote by Z the configurational part of the partition function only.

We want to derive the ensemble average of static properties in the canonical ensemble[19, 142]. Let $w_\mu(t)$ be the probability to find a discrete state μ in the system at a given time t . If we are interested in a quantity Q which is defined for every state the expectation value is :

$$\langle Q \rangle = \sum_{\mu} Q_{\mu} w_{\mu}(t) \quad (4.8)$$

In equilibrium the probability of finding a state μ is not time dependent, that is $\frac{dw_{\mu}}{dt} = 0$. For clarity, we denote the time independent w_{μ} by $p_{\mu} = w_{\mu}(0) = w_{\mu}(t)$. The value of the equilibration probabilities in a canonical ensemble are well known:

$$p_{\mu} = \frac{1}{Z} e^{-E_{\mu}/kT} \quad (4.9)$$

The expectation value $\langle Q \rangle$ now reads:

$$\langle Q \rangle = \frac{\sum_{\mu} Q_{\mu} e^{-E_{\mu}/kT}}{Z} \quad (4.10)$$

4.2 Monte Carlo simulation

In a Monte Carlo simulation we create a sample of configurations which is chosen in a way to be representative to the whole thermodynamic ensemble. We generate the new configurations with a Markov chain. If a system is in a given state μ it has the transition probability $P(\mu \rightarrow \nu)$ to move from this state to another state ν . The measurement of a quantity Q would then become an average over the visited states of the system. To generate a representative sample of a canonical ensemble in equilibrium, the transition probabilities have to satisfy certain conditions. The condition of ergodicity means that every possible state is part of the infinite Markov chain. The condition of detailed balance reads:

$$p_{\mu} P(\mu \rightarrow \nu) = p_{\nu} P(\nu \rightarrow \mu) \quad (4.11)$$

The total probability of being in state μ and visiting state ν is the same as the probability to be in the state ν and going to the state μ . These conditions are necessary to generate an equilibrium distribution. To guarantee that the equilibrium distribution is a Boltzmann distribution, the transition probabilities have to satisfy:

$$\frac{P(\mu \rightarrow \nu)}{P(\nu \rightarrow \mu)} = e^{-\beta(E_{\mu} - E_{\nu})} \quad (4.12)$$

We have still a lot of freedom for an algorithm which implements those conditions. The main focus of an algorithm is therefore to create a good sample of states in the most computational efficient way. The most popular and common Monte Carlo algorithm is the Metropolis algorithm. In this algorithm a small change is introduced in a given system for every simulation step. The transition probability is split in two parts:

$$P(\mu \rightarrow \nu) = g(\mu \rightarrow \nu) A(\mu \rightarrow \nu) \quad (4.13)$$

$g(\mu \rightarrow \nu)$ is the selection probability to chose the new state ν when the system is in the state μ . $A(\mu \rightarrow \nu)$ is the probability that the change is accepted and the

new state of the system is state ν . If the change is rejected the system stays in the state μ . The ratio between the trials and the accepted changes is the acceptance ratio. The rules to perform a change in the system satisfy the condition of detailed balance. The selection probabilities have to fulfill:

$$g(\mu \rightarrow \nu) = g(\nu \rightarrow \mu) \quad (4.14)$$

The information about the equilibration distribution is in the acceptance condition:

$$A(\mu \rightarrow \nu) = \min\{e^{-\beta(E_\mu - E_\nu)}, 1\} \quad (4.15)$$

In our simulations of rodlike particles the algorithm is implemented as follows. In every simulation step a random particle is chosen. The position $\vec{r}_N$ and angle α_N of the particle at step N are changed going to step $N + 1$ with :

$$\begin{aligned} \vec{r}_{N+1} &= \vec{r}_N + r_0 \Gamma \vec{e} \\ \alpha_{N+1} &= \alpha_N + \alpha_0 (1 - 2\Gamma) \end{aligned}$$

Γ is a random number between $0 \leq \Gamma \leq 1$ with a flat distribution. $\vec{e}$ is a unit vector with a random orientation. The values of r_0 and α_0 determine the maximum change in position and angle of the particle. The change in angle and position is made independent of each other to obtain the acceptance ratios of each configurational change separately. In an additional step a change in position and angle is made simultaneously to overcome energy barriers. The maximum values of the step sizes r_0 and α_0 are adjusted to a mean acceptance ratio of $\langle A \rangle \approx 0.5$. To help the simulation to resolve locked states in a more efficient way, we set the maximum step sizes to $r_0 = L$ with L is the lengths of a rod and $\alpha_0 = \pi$ at every 100th simulation step. Those steps have a very low acceptance ratio but account for a higher diffusion of the system through the configuration space.

4.3 Kinetic Monte Carlo

Monte Carlo simulations turned out to be quite efficient in systems with a complicated energy landscape to obtain the static properties of an thermodynamic equilibrated system. This high efficiency raised the question whether it is also possible to use the algorithm to get informations about the dynamical properties. It turned out that in the case of an overdamped Brownian systems it is possible to

use the Monte Carlo scheme with some minor changes only[103]. First we want to recall the term Brownian dynamics and than show how to apply the Monte Carlo scheme to this kind of system.

4.3.1 Brownian motion

The Brownian particles are placed in a surrounding medium with which it is in a thermal equilibrium[44, 131]. The particles interact with each other with an interaction force $\vec{F}_{\text{int}}$. The system can be influenced by an external field $\vec{F}_{\text{ext}}$. The influence of the medium is due to a friction force $\vec{F}_{\text{fric}}$ and a random thermal force $\vec{F}_{\text{therm}}$. The Langevin equation for a particle then reads:

$$m \frac{d}{dt} \vec{v} = \vec{F}_{\text{fric}} + \vec{F}_{\text{ext}} + \vec{F}_{\text{int}} + \vec{F}_{\text{therm}} \quad (4.16)$$

where m is the mass of the particle and v is its velocity. Regarding a one particle system without external forces only the friction force and the thermal force have to be taken into account. The friction force is proportional to the velocity of the particle $\vec{F}_{\text{fric}} = -\gamma \vec{v}(t)$, e.g. for a spherical particle according to Stoke's law $\gamma = 6\pi R\eta$, where R is the radius of the particle. The thermal force $\vec{F}_{\text{therm}}$ has a average of zero because the total system is at rest without a preferred drift direction. The components of the force are independent of each other. Both properties of the thermal force lead to[86]:

$$\langle F_{\text{therm},i}(t) \rangle = 0 \quad (4.17)$$

$$\langle F_{\text{therm},i}(t), F_{\text{therm},j}(t') \rangle = 2B\delta_{ij}\delta(t-t') \quad (4.18)$$

The Langevin equation is:

$$m \frac{d}{dt} \vec{v} + \gamma \vec{v} = \vec{F}_{\text{therm}} \quad (4.19)$$

The solution of this differential equation can be written as[83, 149]:

$$\vec{v}(t) = \vec{v}(0)e^{-\frac{\gamma}{m}t} + e^{-\frac{\gamma}{m}t} \int_0^t dt' \frac{1}{m} e^{\frac{\gamma}{m}t'} \vec{F}_{\text{therm}}(t') \quad (4.20)$$

We now can take a look at the mean square velocity given by:

$$\langle \vec{v}(t)^2 \rangle = \vec{v}(0)^2 e^{-2\frac{\gamma}{m}t} + e^{-2\frac{\gamma}{m}t} \int_0^t dt' \int_0^t dt'' \frac{1}{m^2} e^{\frac{\gamma}{m}(t'+t'')} \langle \vec{F}_{\text{therm}}(t') \cdot \vec{F}_{\text{therm}}(t'') \rangle \quad (4.21)$$

After integration, we derive in the long time limit $t \gg m/\gamma$:

$$\langle \vec{v}(t)^2 \rangle = \frac{nB}{m\gamma} \quad (4.22)$$

where n is the number of dimensions. From the equipartition theorem we know that $m \langle \vec{v}(t)^2 \rangle = nkT/2$ and therefore the strength of the fluctuations are related to the temperature:

$$B = \gamma kT \quad (4.23)$$

The particle diffuses with time. To quantify this diffusion process we take a look at the mean square displacement (MSD) in the long time limit:

$$\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle = \frac{1}{\gamma^2} \int_0^t dt' \int_0^t dt'' \langle \vec{F}_{\text{therm}}(t') \cdot \vec{F}_{\text{therm}}(t'') \rangle \quad (4.24)$$

$$= \frac{2nB}{\gamma^2} t \quad (4.25)$$

$$= 2nDt \quad (4.26)$$

The last equation is the definition of the diffusion constant D and it follows:

$$D = B/\gamma^2 \quad (4.27)$$

In the following we are not interested in the diffusion of a spherical particle but of elongated particles like spherocylinders. The diffusion of such a particle is not isotropic anymore[35, 93]. If we define a local coordinate system which is fixed to the symmetry axis and the center of each particle the diffusion process can be divided into a diffusion parallel to the long axis of each particle with a diffusion constant $D_{\parallel}$ and perpendicular to the long axis with a different diffusion constant $D_{\perp}$. In addition the particle can have an angular diffusion relative to the resting reference frame of the experiment defined by an angular diffusion constant D_R . In the case of spherocylinders we use the following approximate diffusion coefficients[125]:

$$D_{\parallel} = \frac{D_0}{2\pi} (\ln p - 0.207 + 0.980/p - 0.133/p^2) \quad (4.28)$$

$$D_{\perp} = \frac{D_0}{4\pi} (\ln p + 0.839 + 0.185/p + 0.233/p^2) \quad (4.29)$$

$$D_R = \frac{3D_0}{\pi L^2} (\ln p - 0.662 + 0.917/p - 0.050/p^2) \quad (4.30)$$

p is defined by $p = 1 + L/d$ where L is rod length and d is the diameter of the rod. The diffusion coefficients $D_{\parallel}$ and $D_{\perp}$ can be measured via the MSD in the co-moving frame:

$$\langle |r_{\parallel}(t) - r_{\parallel}(0)|^2 \rangle = 2D_{\parallel}t \quad (4.31)$$

$$\langle |r_{\perp}(t) - r_{\perp}(0)|^2 \rangle = 2D_{\perp}t \quad (4.32)$$

The total translational diffusion coefficient is then:

$$D_0 = 0.5(D_{\parallel} + D_{\perp}) \quad (4.33)$$

The mean square rotational displacement is connected to the angular correlation function :

$$\langle |\vec{u}(t) - \vec{u}(0)|^2 \rangle = 2(1 - e^{-D_R t}) \quad (4.34)$$

where $\vec{u}(t)$ is the unit vector oriented along the long axis of the particle. In the case of small simulation steps the angle α with respect to an arbitrary fixed axis shows the same diffusive behavior like the translational variables:

$$\langle |\alpha(t) - \alpha(0)|^2 \rangle = 2D_R t \quad (4.35)$$

A mean square displacement proportional to the time is usually found in simple systems such as a single particle without any external field for times much longer than the time scale of the fluctuations of the solvent. Interactions between particles, high densities and external fields can lead to a $\text{MSD} \propto t^{\nu}$ with $\nu \neq 1$. Those systems possess anormal diffusion. A coefficient $\nu < 1$ is called subdiffusive and a coefficient $\nu > 1$ is superdiffusive. A special case of superdiffusivity is the ballistic motion with $\nu = 2$. In the MSD one can distinguish the different time scales in which different kinds of diffusion occur. In a typical glassy system one can recognize a ballistic motion at very short time scales, which correspond to the mean free path of the particles, a subdiffusive motion at intermediate time scales where the particles are caged by its neighbors, and a long time normal diffusion for time scales greater than the mean caging time of a particle.

4.3.2 Simulation scheme

One usually uses the Brownian dynamics simulation scheme to solve the Langevin equation. In Brownian dynamics simulations the Langevin equation is discretized

and the computer solves the time evolution of the system. In such a simulation the calculation of forces can be the most time consuming part of the whole simulation. In particular for non-spherical particles which exhibit anisotropic friction forces and torques the computational effort to calculate one single time step can slow down a simulation. In a Monte Carlo simulation no forces have to be calculated at each simulation step. The Monte Carlo simulation takes only the potential energy into account. As a result a kinetic Monte Carlo simulation can be computationally much faster than a Brownian dynamics simulation. In this section we want to present the derivation of the kinetic Monte Carlo scheme and give the simulation details of our implementation.

To illustrate the functionality of the kinetic Monte Carlo scheme we consider a particle in an one-dimensional system[89, 90, 103]. The particle is at the position $x(t)$ within a potential $V(x)$. The Monte Carlo step chooses a new coordinate of the particle within an interval $[x - \delta x, x + \delta x]$ with a flat probability distribution. The potential is only slowly varying over the step interval so we can write the maximum change in potential energy $\pm\Delta V \approx \pm F\delta x$ with an approximate constant force F . We consider the potential to increase with x . In this way we only fix the direction of the movement. A change of position into the negative direction decreases the potential energy. The move is therefore always accepted. A step into the positive direction will be accepted with a probability of $e^{-\beta\Delta V} \approx e^{-\beta F\delta x}$ only. The mean displacement can be written as:

$$\langle\Delta x\rangle = \frac{\int_{-\delta x}^0 x dx + \int_0^{\delta x} x e^{-\beta F x} dx}{\int_{-\delta x}^{\delta x} dx} \quad (4.36)$$

We can now expand the exponential in the next two orders and integrate:

$$\langle\Delta x\rangle = \frac{\int_0^{\delta x} (e^{-\beta F x} - 1)x dx}{2\delta x} \quad (4.37)$$

$$\approx \frac{\int_0^{\delta x} (-\beta F x^2 + 0.5\beta^2 F^2 x^3) dx}{2\delta x} \quad (4.38)$$

$$\approx \beta F \frac{\delta x^2}{6} \left(1 - \frac{3\beta F \delta x}{8} + O(\delta x^2)\right) \quad (4.39)$$

The mean displacement in one time step is proportional to the strength of the force F corresponding to a drift of the particle. We can do the same expansion for the mean square displacement of one Monte Carlo step :

$$\langle \Delta x^2 \rangle = \frac{\int_0^{\delta x} (e^{-\beta F x} - 1) x^2 dx}{2\delta x} \quad (4.40)$$

$$\approx \frac{2/3\delta x^2 - \beta F \int_0^{\delta x} x^3 dx + o(\delta x^4)}{2\delta x} \quad (4.41)$$

$$\approx \frac{\delta x^2}{3} \left(1 - \frac{3\beta F \delta x}{8} + O(\delta x^2) \right) \quad (4.42)$$

The MSD is independent of F in the order of δx^2 . Comparing the MSD with the diffusion equation one can derive an equation for the size of the time step:

$$\langle \Delta x^2 \rangle = \frac{\delta x^2}{3} = 2D_0 \delta t \quad (4.43)$$

$$\delta t = \frac{\delta x^2}{6D_0} \quad (4.44)$$

The corrections of the order δx^3 are the same in the drift (Eq. 4.39) and in the MSD (Eq. 4.42). In simulations in more than one dimensions the higher order corrections can be approximated by the acceptance ratio A [166]. The final definition of the time step in our simulation is:

$$\delta t = \frac{A\delta x^2}{6D_0} \quad (4.45)$$

This procedure is straightforward for the isotropic diffusion of a spherical particle. However, a rod has different diffusion coefficients parallel and perpendicular to the rod axis and also performs rotational diffusion. Furthermore, the acceptance ratios for the different Monte Carlo steps within a Monte Carlo cycle can be different[148, 162]. Equation (4.45) then introduces three different time steps $\Delta t_{\parallel}$, $\Delta t_{\perp}$, and Δt_R for one cycle. To be consistent, they have to be the same. We therefore use as reference time step the diffusion time parallel to the rod axis, $\Delta t_0 = \Delta t_{\parallel} = r_{\parallel}^2 A_{\parallel} / (6D_{\parallel})$, and adjust the maximum step sizes for the other degrees of freedom so that $\Delta t_{\parallel} = \Delta t_{\perp} = \Delta t_R$. This procedure results in the maximum step sizes

$$r_{\perp} = \sqrt{\frac{A_{\parallel} D_{\perp}}{A_{\perp} D_{\parallel}}} r_{\parallel} \quad \text{and} \quad r_R = \sqrt{\frac{A_{\parallel} D_R}{A_R D_{\parallel}}} r_{\parallel}. \quad (4.46)$$

4.4 Wang Landau Monte Carlo

Monte Carlo simulations can lose efficiency if the system possesses a rough energy landscape with high energy barriers or in a system which is at the vicinity of a phase transition. There are many techniques to overcome high energy barriers but they are not always sufficient[113]. The so called Wang Landau Monte Carlo simulation method[114, 210, 211] is a quite recent approach to use the Monte Carlo scheme to derive the density of states (DOS) $g(E)$ where E is the internal energy of a state rather than to sample an ensemble at a fixed temperature. The algorithm was first used for lattice systems but can be applied to off lattice systems as well[154, 178, 226]. The acceptance criterion of the Monte Carlo simulation is modified to:

$$A(\mu \rightarrow \nu) = \min\left\{\frac{g(E_\nu)}{g(E_\mu)}, 1\right\} \quad (4.47)$$

With this acceptance ratio every state is visited with an equal probability. The density of states is the result of the simulation and is initially not known. We have to start with an arbitrary first guess of the shape of $g(E)$. One usually starts with histogram for $g(E)$ of a flat distribution giving every state the same weight, e.g. $g(E) = 1$. During the simulation every visited state changes the DOS by multiplying $g(E)$ with a constant factor $f > 1$. The more often a state is visited the larger the corresponding $g(E)$ and the less probable is a further visit of the same state. We record in a second histogram $H(E)$ the absolute number of visits of every state. As soon as the shape of the initial $g(E)$ converges to the real $g(E)$ the histogram of the number of visits becomes flat. The finite value of f determines the strength of the fluctuations of $g(E)$ and is therefore an upper limit of the accuracy of the obtained DOS. On the other hand a small value of f slows down the convergence of $g(E)$ and wastes a lot of computation time. To deal with this problem one splits the simulations into many single runs with different values of f . In the first simulation the modification factor f_1 is chosen to be $f_1 > 1$. The simulation is done until a reasonable flatness in the histogram for the visits of states is reached. After that a second simulation is started with the outcome of $g(E)$ from the previous simulation as the initial shape of the DOS. The next simulation has a modification factor of $f_2 = f_1^{0.5}$. Again the simulation is performed until the histogram of the visited states is sufficiently flat. The scheme is repeated and the modification factor is converging $f_n \rightarrow 1$ for $n \rightarrow \infty$. One can stop the simulation when the desired accuracy of the shape of $g(E)$ is gained[224].

In our simulations we use a refinement of this iteration scheme. We do not use many simulations with fixed f_n but slowly lowering $f(\tau)$ with increasing simulation time τ . If the modification factor scales down with $f \sim 1 + 1/\tau$ the convergence time can get shorter and we reach $g(E)$ with a higher accuracy[15, 16, 17, 225]. The exact values of the start factor f and the timescale τ are subject to a fine tuning which have to be done for every individual system separately. The edges of the histograms are defined by the energy range we are interested in. To avoid boundary effects trial moves which lead to configurations outside the preferred energy range were treated like discarded moves from the acceptance criterion[172].

With the DOS we can calculate the configurational part of the partition function:

$$Z_{conf} = \sum_{conf} e^{-\beta E} = \sum_E g(E) e^{-\beta E} \quad (4.48)$$

Because we modify in the simulation scheme only the shape of $g(E)$ its absolute value differs by a constant factor from the real $g(E)$. We still can get a lot of information from this by normalizing this equation. We get the statistical weight of the states with a given temperature and a given energy by:

$$P(E, T) = \frac{g(E) e^{-\frac{E}{kT}}}{\int g(E) e^{-\frac{E}{kT}} dE} \quad (4.49)$$

We can record in a simulation run the distribution of any observable as a function of the energy $O(E)$ and get its mean value at a given temperature with:

$$\langle O \rangle_T = \int P(E, T) O(E) dE \quad (4.50)$$

In particular, the internal energy U can be obtained by:

$$U(T) = \langle E \rangle_T = \int P(E, T) E dE \quad (4.51)$$

In some systems it is possible that the complex configurational landscape is not only a function of the energy but also of additional parameters like an order parameter. We can extent the density of states $g(E)$ to a joint density of states (JDOS) as a two dimensional function of a parameter O and the energy that reads $g(E, O)$. The modification of the simulation scheme is straight forward.

The histograms for $g(E, O)$ and the histogram of visits $H(E, O)$ become two dimensional. The acceptance criterion modifies to:

$$A(\mu \rightarrow \nu) = \min\left\{\frac{g(E_\nu, O_\nu)}{g(E_\mu, O_\mu)}, 1\right\}. \quad (4.52)$$

We obtain the statistical weight with respect to only one of the variables by integrating over the other:

$$P(E, T) = \frac{\int g(E, O) e^{-\frac{E}{kT}} dO}{\iint g(E, O) e^{-\frac{E}{kT}} dE dO} \quad (4.53)$$

$$P(O, T) = \frac{\int g(E, O) e^{-\frac{E}{kT}} dE}{\iint g(E, O) e^{-\frac{E}{kT}} dE dO} \quad (4.54)$$

This can be extended in principle to any number of variables. Because of the high computational costs most of the Wang Landau simulations are done for only one or two variables. We use the JDOS Wang Landau simulation with the energy and the nematic order parameter S to obtain an expression for $g(E, S)$.

4.5 Simulation details

In our simulation we use periodic boundary conditions [83, 136]. Since the quasicrystalline potential is not periodic, discontinuities at the boundaries of the periodically repeated simulation boxes occur. To minimize the discontinuities, we choose special box sizes following Ref. [167]. For the decagonal potential the edge lengths of the simulation box have to be $X = 2na_V$ and $Y = ma_V/\sin(\pi/5)$, where n and m are Fibonacci numbers. The periodic repetition of quasicrystalline subpatches leads to a crystalline structure called a crystalline approximant[72]. Since we fix the box sizes to discrete values, we vary the particle number to realize different densities.

As initial conditions we choose two different particle configurations. The first consists of a random distribution of both the particle positions and orientations. With such isotropic starting conditions one can study whether the particles are able to build up nematic order. In the second configuration the positions of the particles are randomly distributed but they all align along an arbitrarily chosen common direction. Starting with such an ideal nematic order, we investigate how stable the nematic phase is.

Details of hard needle simulations

Most of our simulations of the needle system are performed in simulation boxes with $n = 3$, $m = 5$ for short needles and $n = 13$, $m = 21$ for long needles. The particle number varies between 232 and 654 for the short needles and between 331 and 886 for the long needles to realize an appropriate density range. The limitations on the possible box sizes also makes it difficult to perform finite size analysis. The next larger box size for the long needles needs 776 needles at the lowest and 2318 at the highest simulated density. Because of the very long computation time, we performed a search for finite-size effects only for two densities of the two needle lengths. We confirmed results from Ref. [65] that in the two-dimensional needle system the position of the isotropic-to-quasi-nematic transition depends on the system size. However, for the onset of the decagonal directional order, which is mainly determined by the substrate potential, we do not find a finite-size effect. In the following, we measure the needle density ρ in units of the square of the needle length, $1/L^2$. In this way, the isotropic-nematic phase transition always occurs at the same value of the reduced density ρ independent of needle length L .

To equilibrate the system, we use a few 10^5 Monte Carlo sweeps at low densities and low potential strengths up to a few 10^6 sweeps for high densities and high potential strengths. One Monte Carlo sweep consists of the number of particles times a single Monte Carlo cycle for each particle. At least 10 simulation runs with independent initial conditions are performed for each initial condition and each density.

We performed Wang Landau simulations to derive $g(E, S)$. The Wang Landau simulations are performed in systems of box sizes with $n = 3$, $m = 5$ for short needles and with $n = 13$, $m = 21$ for long needles. The number of short needles varied between 232 and 403. Two densities of the long-needle system with 623 and 886 particles have been investigated. For every particle density 6 Wang Landau simulations are performed in parallel. After $\approx 10^7$ simulation sweeps the resulting histograms for $g(E, S)$ were averaged. The obtained average $g(E, S)$ was used as an initial shape for the density of states in the following simulation runs. This simulation scheme was repeated until the modification factor f reached $f = 1.0005$ for the short needles and $f = 1.0025$ for the long needle system. The Wang Landau

simulations give the resulting order parameter as functions of the temperature T of the system for a constant potential strength. Because the interaction with the potential is the only energy scale in our system, we can transform the results of the Wang Landau simulation for a given temperature into the results of a system with a constant temperature but a given potential strength.

Details of hard spherocylinder simulations

For the short-rod system we use a box size with $n = 8$, $m = 13$ and a particle number between 100 and 637 to realize low densities and a box size with $n = 5$, $m = 8$ with a particle number between 245 and 776 to realize high densities. The long-rod system is simulated in a box with $n = 34$, $m = 55$ and particle numbers varying between 229 and 1431. All particle densities are quantified by the area fraction η which the rods occupy relative to the total area.

To equilibrate the system, we use at least 10^6 Monte Carlo sweeps for the low densities and $3 \cdot 10^6$ sweeps for the high densities. For the short-rod system we perform at least ten independent simulation runs at every density, potential strength and initial condition. For the long-rod systems the number of runs is at least four.

When we perform kinetic Monte Carlo simulations, we use the normal Monte Carlo scheme to equilibrate the system. Then we start the kinetic Monte Carlo scheme where we rescale the maximum step sizes until the time steps t_R and $t_\perp$ converge to $t_\parallel$. One Monte Carlo sweep goes consecutively through all the particles to avoid unphysical double moves or stops of one rod. The sequence of the particles is altered randomly between the sweeps.

The step size $r_\parallel$ should be well below the smallest characteristic length scale one wants to resolve. In our case, it is given by the diameter of the rod d . We therefore set $r_\parallel < 0.1D$ but also verified that $r_\parallel < 0.01d$ does not change our simulation results. Our choice of $r_\parallel < 0.1d$ is well suited to resolve the dynamics of the rod on a time scale it needs to diffuse a diameter d .

To obtain the single particle diffusion we average over 2500 particle trajectories. The MSD of the rods in an ensemble is an average over at least 7 different

simulation runs.

5 Hard needles

In this chapter we show our results of the investigation of the hard-needle model. First, we start with the short-needle system and then we present our investigation of the long-needle system. At the beginning of every section we give a short introduction of the phase diagram and thereafter we explain the different phases in detail. Most results of this chapter are published in [A].

5.1 Short needle system

5.1.1 Phase diagram

The phase diagram of the short needles in Fig. 5.1 can be divided into four regions. The most important transition separates surface-induced directional or decagonal order at high substrate strength from a region at low or zero strength. Here the substrate does not influence the typical phase behavior where below a density of $\rho \approx 5.9$ we observe an isotropic phase followed by the quasi-nematic phase as already reported for this system size by Frenkel and Eppenga [65]. Above the main transition line also two regions exist. In the low-density region a pure decagonal phase exists without any nematic order. In the region at high densities, the realized ordering depends on the initial condition. In particular, it is possible to freeze in a starting configuration with nematic order in addition to the surface-induced decagonal order. Now, we give a detailed account of our results.

5.1.2 Decagonal directional order

In Fig. 5.2 we plot the decagonal order parameter Φ_{10} and its susceptibility χ_Φ as a function of the potential strength V_0 . The maximum of the susceptibility coincides with the inflection point of the decagonal order parameter at a value of $\Phi_{10} \approx 0.2$. We find this behavior at all simulated densities. Therefore, we

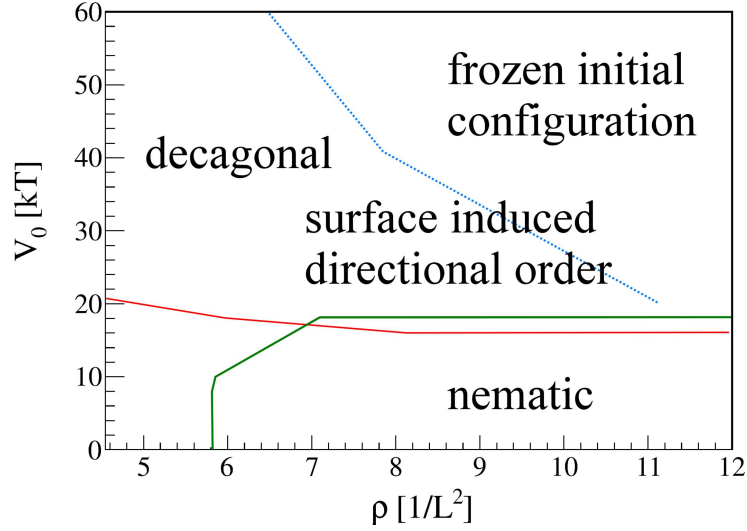


Figure 5.1: Phase diagram for the short needles.

let the decagonal directional phase of the needles start at $\Phi_{10} \approx 0.2$. Figure 5.3 shows the decagonal order parameter versus V_0 for different densities. In the short-needle system, all these curves look similar and there is no pronounced density dependence. Only for low densities, decagonal ordering needs a higher potential strength to develop. Accordingly, the transition line in the phase diagram 5.1 slightly bends upwards at low densities. The minimum potential strength for observing the decagonal phase is about $V_0 = 15$ at high densities. Despite the clear maximum in the susceptibility, we do not observe a maximum in the heat capacity at the same position in the phase space. This is reminiscent to the work of Frenkel and Eppenga [65]. They only observed a weak maximum in the heat capacity shifted against the actual transition from the isotropic to the nematic phase. For comparison a infinite dilute system $\rho = 0$ is also shown in Figure 5.3. The directional order of such a dilute system is substantially lower than for higher densities. This can be understood by the different mechanism of directional ordering.

The snapshots of Fig. 5.5 show the short-needle system at a density $\rho = 8.3$. In the left panel the substrate potential has a strength of $V_0 = 10kT$ just below the phase transition. The system is in a nematic phase but one can already recognize a weak modulation of the density of the needles induced by the substrate. The modulation leads to bundles of needles within the nematic phase. In the right

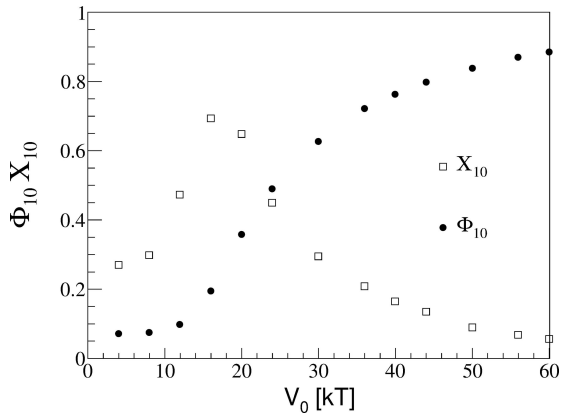


Figure 5.2:

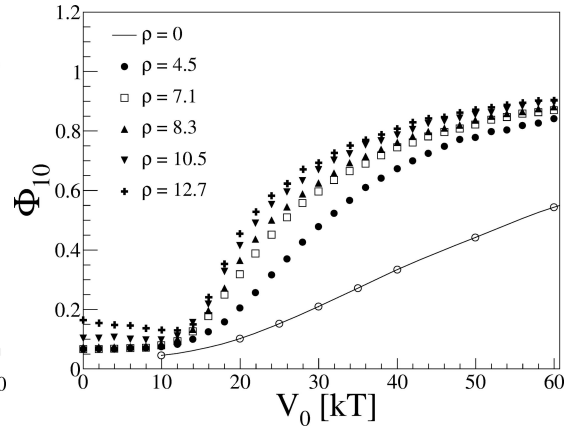


Figure 5.3:

Left: Decagonal directional order parameter Φ_{10} and its susceptibility χ_{Φ} at $\rho = 8.3$.

Right: Decagonal directional order parameter Φ_{10} for different densities.

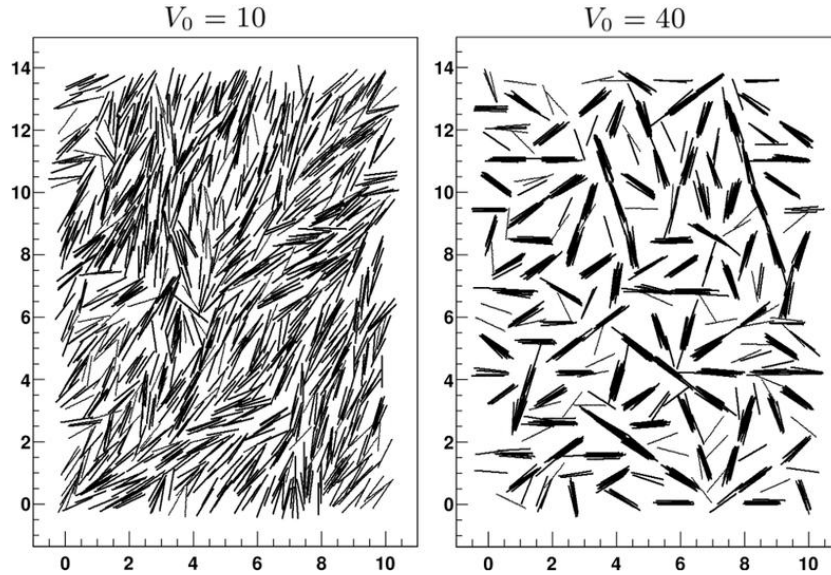


Figure 5.5: Snapshot of a short needle system at a density of $\rho = 8.3$. Left : at a potential strength of $V_0 = 10kT$, right : $V_0 = 40kT$

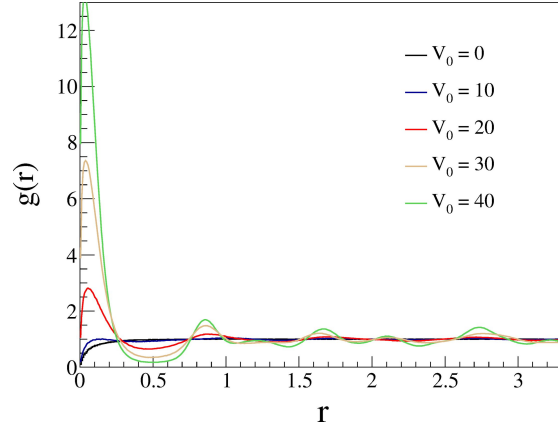


Figure 5.6: Pair correlation function $g(r)$ for short needles at a density of $\rho = 8.3$ for different potential strengths V_0 .

panel of Fig. 5.5 the strength of the substrate potential is $V_0 = 40kT$. The needles are confined to clusters at the minima positions of the substrate. The needles in a cluster are parallel and are ordered along the symmetry directions of the substrate. The pair correlation function for $V_0 = 40$ in Fig. 5.6 shows the dense packing within the clusters through the large first maximum very close to $r = 0$. One recognizes the isolated clusters by the deep and broad first minimum at $r = 0.5$. The pair correlation function exhibit no pronounced maximum at $V_0 = 10kT$ but one can identify a weak density modulation in comparison with the substrate free case $V_0 = 0kT$. We conclude that the formation of clusters strongly enhance the directional order through a local nematic phase within every cluster. The weak density dependence in the simulated range shown in the phase diagram stems from the minimum potential strength to confine a single needle at a minimum. Finally, we note that the profiles for the decagonal order parameter in fig. 5.3 do not change by increasing the number of needles from approximately 600 to 1200. So there is no size dependence. This is in agreement with the fact that the decagonal order is due to the local values of the substrate potential.

5.1.3 Nematic order

The isotropic to quasi-nematic transition has already been discussed extensively [65, 209]. We now discuss the transition from the nematic phase into the region with surface-induced directional order for increasing V_0 . Figure 5.7 plots the nematic

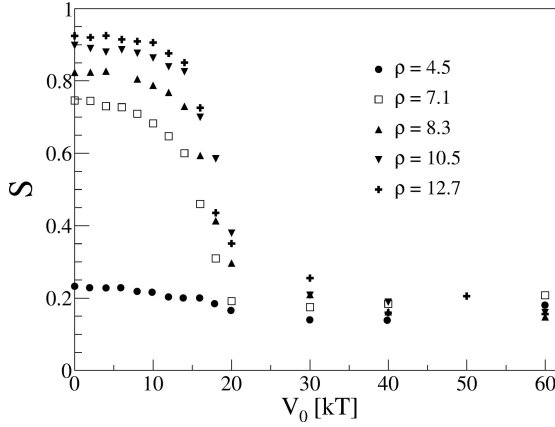


Figure 5.7:

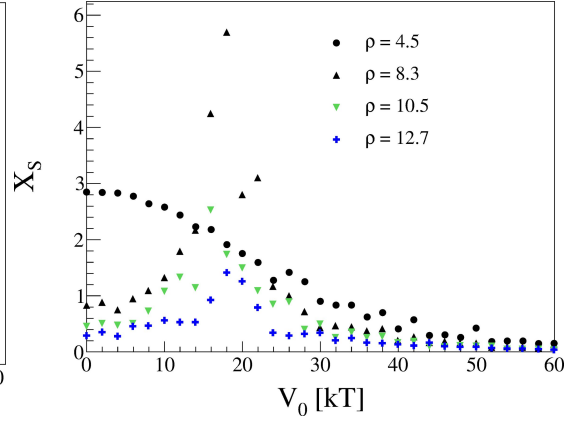


Figure 5.8:

Left: Nematic order parameter S as a function of the potential strength V_0 for different densities ρ .

Right: Nematic susceptibility χ_S as a function of the potential strength V_0 for different densities ρ .

order parameter profile for different densities. The nematic order first decreases slowly until a potential strength of about $V_0 = 18kT$ where the surface-induced decagonal order sets in. Now, local needle clusters form that isolate the needles against each other. This leads to a sharp drop of the order parameter to $S \approx 0.2$ and nematic order vanishes. So the loss of nematic order is strongly correlated with the appearance of decagonal directional order. The nematic susceptibility plotted in Fig. 5.8 for various densities indicates the loss of nematic order with a pronounced maximum at the transition line. For comparison the nematic susceptibility in the isotropic phase at $\rho = 4.5$ does not exhibit such a maximum. The fourth region in the phase diagram of the short needles in Fig. 5.1 is named frozen initial configuration. The plot of the nematic order shown in Figure 5.7 results from simulations which started with a random distribution of both the needle positions and orientations. After the equilibration of the system we find a decagonal orientated phase where the needle clusters oriented along the symmetry directions of the substrate potential with an equal probability for each direction. In the region of frozen initial configurations situated at high potential strengths and high densities the outcome of the simulation depends on its initial configuration. When we prepare the initial configuration to be in a nematic phase and there-

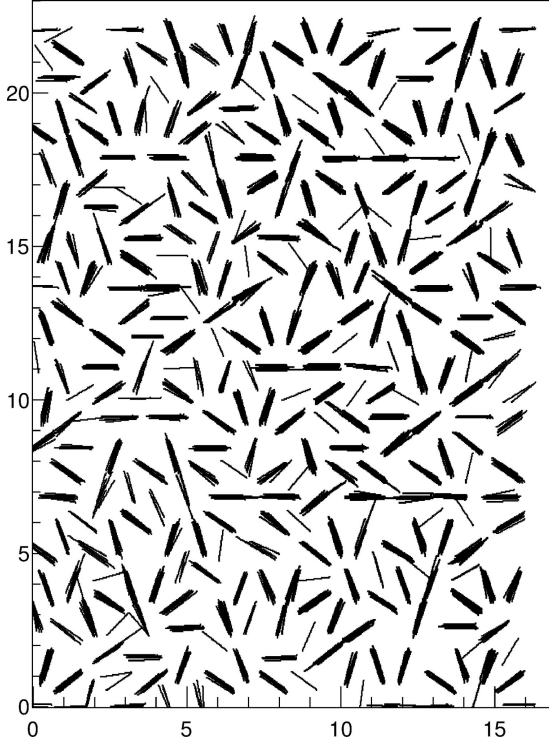


Figure 5.10:

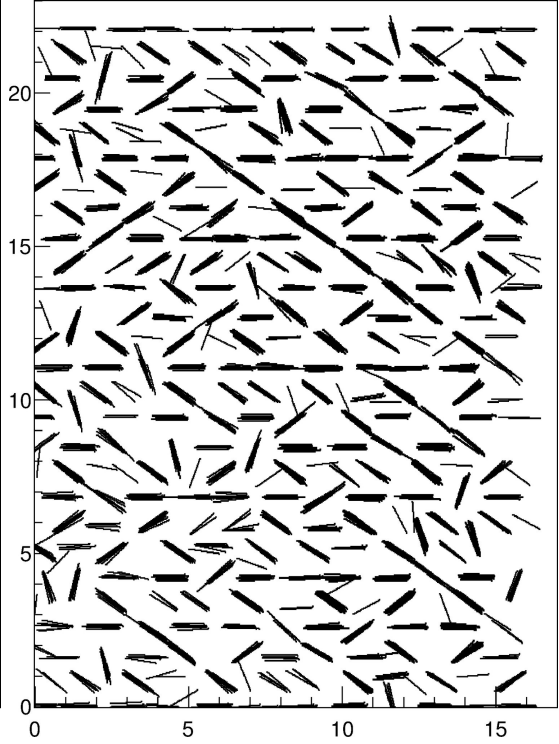


Figure 5.11:

Left: Snapshot of a short needle system at a density of $\rho = 8.3$ and a potential strength of $V_0 = 60kT$ with a frozen nematic order of $S \approx 0.1$.

Right: Snapshot of a short needle system at a density of $\rho = 8.3$ and a potential strength of $V_0 = 60kT$ with a frozen nematic order of $S \approx 0.6$.

fore exhibit an common director the resulting system remains in a nematic order after equilibration. We have confirmed this behavior by doubling the simulation time normally needed for equilibrating the system. Two snapshots of simulations with different nematic order are shown in Fig. 5.10 and Fig. 5.11. In Fig. 5.10 in initial isotropic initial configuration is frozen and as a result the nematic order parameter is $S \approx 0.1$. One can recognize a flower like structures of the clusters which is reminiscent of the overlapping decagons of potential minima in the substrate potential. Fig. 5.11 shows a system with a high nematic order parameter of $S \approx 0.6$. The needle clusters are ordered onto lines following the Fibonacci line structure of the potential. In Figure 5.13 the different results of the nematic order parameter for the different initial configurations at a density of $\rho = 8.3$ are

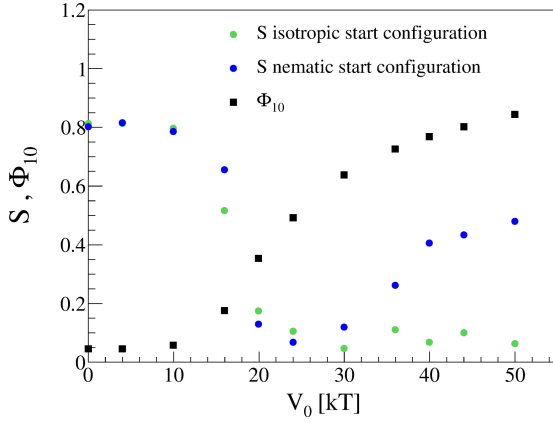


Figure 5.13:

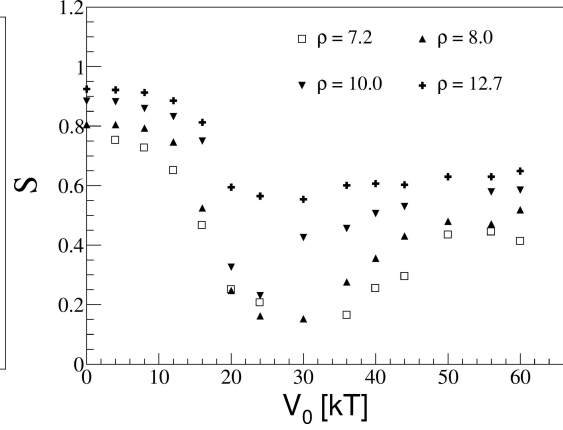


Figure 5.14:

Left: Nematic order parameter S as a function of the potential strength for isotropic and nematic starting configuration respectively and the decagonal directional order parameter Φ_{10} at a density of $\rho = 8.3$.

Right: Nematic order parameter S as a function of the potential strength for different densities ρ from nematic initial starting configurations.

shown. Below a potential strength of $V_0 = 36kT$ the results are independent of the initial configuration. Needle clusters with the same orientation order along the Fibonacci lines as expected from the structure of the substrate potential (Fig. 3.9). In between needle clusters with different orientation occur. In our simulations the order parameter never exceeds $S \approx 0.7$ since between clusters oriented along neighboring Fibonacci lines always clusters with different orientations can be inserted. Therefore, in a frozen nematic state we always observe at least two of the five possible cluster orientations and the nematic order is never perfect. In Fig. 5.14 the dependency of the frozen nematic order on the density is shown. The higher the density the lower the potential strengths necessary to freeze an initial nematic order of the system. At the highest simulated density of $\rho = 12.7$ there is almost no gap of low nematic order between the region of the nematic system and the region of the frozen initial configurations. The direct transition from a nematic to a frozen nematic system is accompanied by a very low maximum in the nematic susceptibility as already shown in Fig. 5.8.

For a further investigation of the nature of the frozen nematic order we performed Wang Landau simulations. A comparison of the Wang Landau results

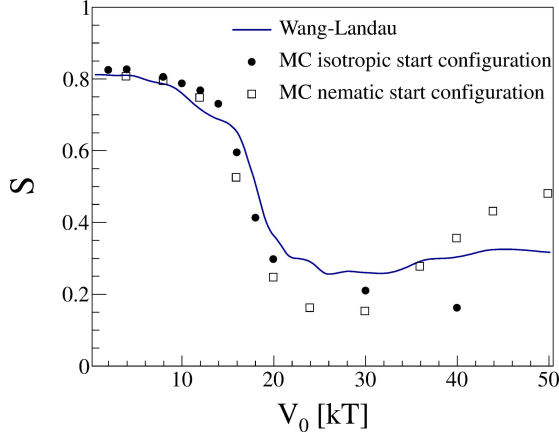


Figure 5.16:

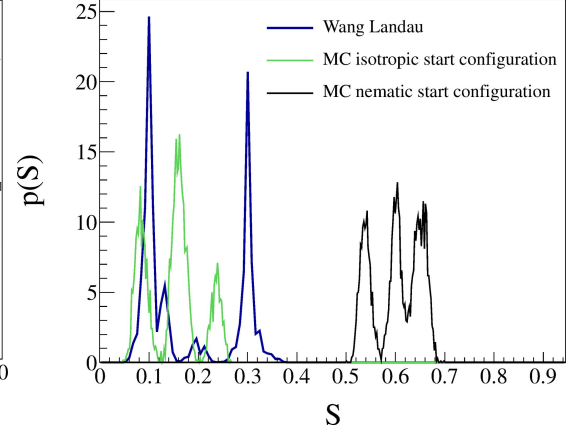


Figure 5.17:

Left: The nematic order parameter S at a density of $\rho = 8.3$ as a function of the potential strength V_0 in a comparison between the Wang Landau MC simulation and the Metropolis MC scheme.

Right: Distribution of the nematic order parameter $p(S)$ at a density of $\rho = 8.3$ and a potential strength of $V_0 = 60kT$ for different simulations.

with the results from the Metropolis Monte Carlo scheme are plotted in Fig. 5.16 for $\rho = 8.3$. The nematic order derived from the Wang Landau simulation is in good agreement with the Metropolis simulations. The nematic order decreases with increasing potential strength. In the region of the frozen nematic configuration the Wang Landau simulations prefer a low nematic order of $S \approx 0.3$ which is higher than the frozen isotropic configuration but much lower than the maximum frozen nematic order. In Fig. 5.17 the distribution of the nematic order parameter at a potential strength of $V_0 = 60kT$ for the different simulations is shown. The peak structure indicates frozen systems with a different degree of nematic order. In the region of frozen initial configuration, the energy of the system, the decagonal order, and the heat capacity do not depend on the degree of nematic ordering. So, configurations with different frozen nematic order just seem to constitute different possible realizations of the same decagonal order which corresponds to a highly degenerate ground state.

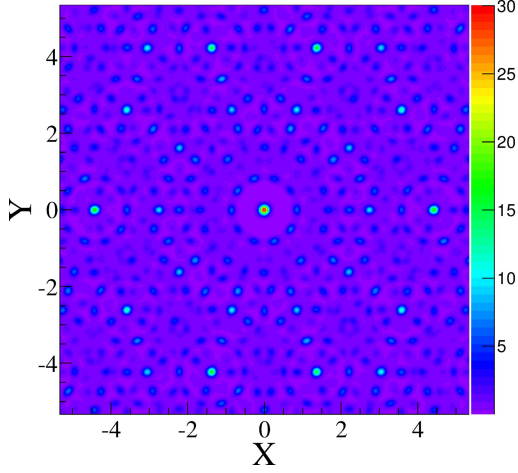


Figure 5.19:

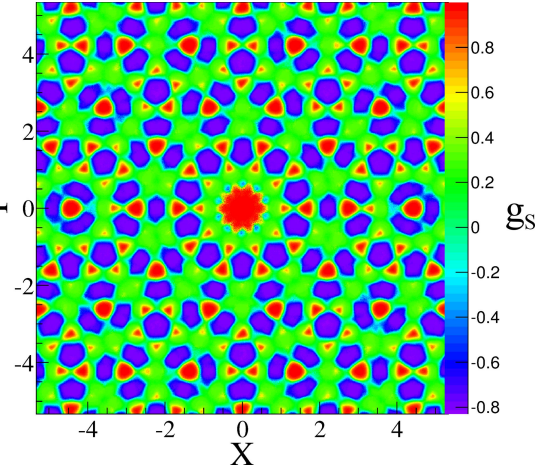


Figure 5.20:

Left: Two dimensional pair correlation function $g_R(x, y)$ for a short needle system with a density of $\rho = 4.5$ and a potential strength of $V_0 = 60kT$.

Right: Two dimensional order correlation function $g_S(x, y)$ for a short needle system with a density of $\rho = 4.5$ and a potential strength of $V_0 = 60kT$.

5.1.4 Positional and Bond-orientational order

At high potential strengths the needles are well ordered in clusters at the positions of the potential minima. The two-dimensional pair correlation function $g_R(x, y)$ in Fig. 5.19 shows the quasicrystalline order. The two-dimensional orientational correlation function $g_S(x, y)$ of the same system is shown in Fig. 5.20. Figure 5.20 displays a central spot surrounded by 10 red spots which indicate directions in space along which clusters assume the same orientation as the central cluster. In between, the blue spots give directions with perpendicular orientation. The pattern in Fig. 5.20 displays the same decagonal symmetry and positional order as the substrate potential. Therefore, parallel needle clusters exhibit the same long-range positional and orientational order as the substrate potential. The relative positions of non-parallel clusters can be identified as peaks in the pair correlation function in Fig. 5.19 which do not match any red areas in the orientational correlation function in Fig. 5.20. The definition of the positions of the clusters at the vicinity of the transition into the substrate induced order is difficult. The system undergoes huge fluctuations which is indicated by the huge standard deviation of the number of clusters found in the simulated systems at $V_0 < 20kT$ shown in Fig.

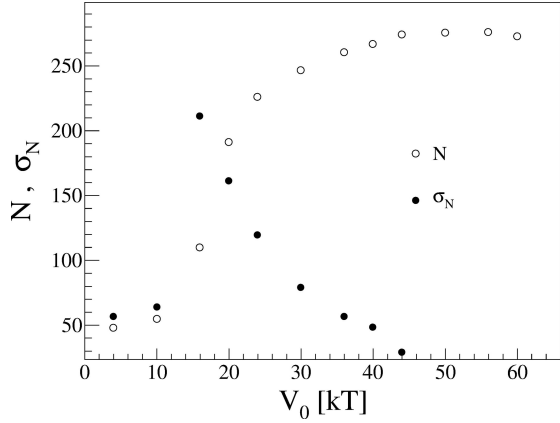


Figure 5.22:

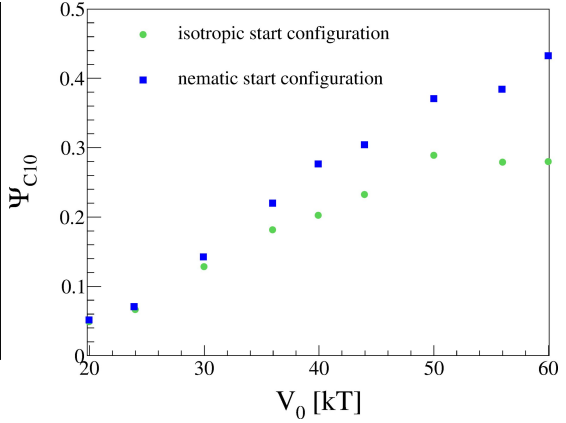


Figure 5.23:

Left: Absolute number of clusters N in the simulation box and its standard deviation σ_N as a function of the potential strength V_0 at a density of $\rho = 8.3$

Right: Decagonal bond-orientational order parameter Ψ_{C10} for the center of mass of the clusters as a function of the potential strength V_0 at a density of $\rho = 8.3$ for nematic and isotropic initial configurations.

5.22. Therefore, we define the bond-orientational order of the cluster centers Ψ_{C10} only from potentials strengths above $V \approx 20kT$. The bond-orientational order of a system with $\rho = 8.3$ is shown in Fig. 5.23 for the different initial configurations. In the region of the frozen initial configuration the bond-orientational order of the nematic systems is significantly higher than for a frozen isotropic order. In this region a high nematic order is coupled with a high bond-orientational order.

5.2 Long needle system

5.2.1 Phase diagram

The phase diagram of the long needles in Fig. 5.25 can be divided into five regions and exhibits pronounced differences compared to the short-needle system and its phase behavior in Fig. 5.1. The most important division line marks again the onset of surface-induced decagonal order with $\Phi_{10} > 0.2$ for increasing substrate strength V_0 . However, whereas for short needles this line is more or less horizontal, it now tilts towards smaller V_0 when density ρ increases. Below the decagonal transition

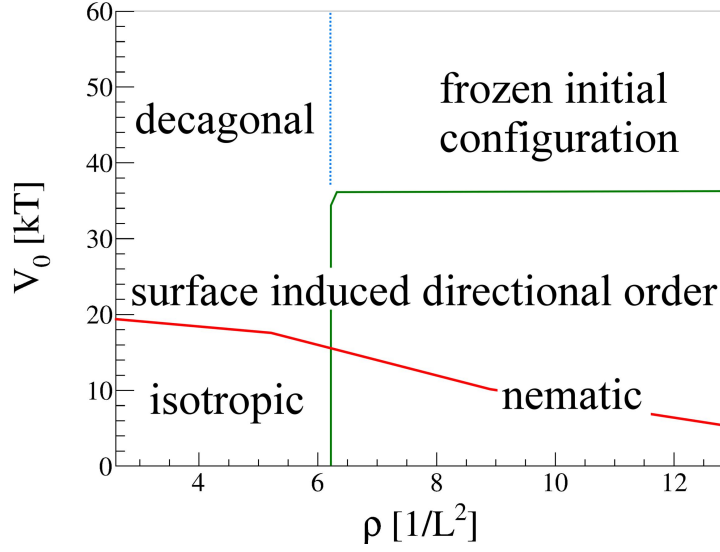


Figure 5.25: Phase diagram of the long needle system

line, one observes again the isotropic and quasi-nematic phase with the transition located at $\rho \approx 6.2$ for the simulated system size. Interestingly and in contrast to short needles, the transition at $\rho \approx 6.2$ extends beyond the main decagonal transition line to larger V_0 , where now three different phase regions exist. At densities below $\rho \approx 6.2$ the system assumes pure decagonal order without any nematic ordering. At densities larger than $\rho \approx 6.2$ a phase with both nematic and decagonal order exists up to a substrate strength of $V_0 \approx 35kT$. In the short-needle system, such a phase does only occur in a very narrow region of V_0 . For $\rho > 6.2$ and $V_0 > 35kT$, the starting configuration again freezes in. Now, we describe the phase behavior in more detail and try to explain it.

5.2.2 Decagonal directional order

We first discuss the decagonal ordering of the long needles as illustrated by the decagonal order parameter Φ_{10} plotted versus V_0 for several densities in Fig. 5.26. Most properties of Φ_{10} are the same as in the short-needle system. The maximum of the susceptibility χ_Φ when plotted as a function of V_0 occurs again when the decagonal order parameter assumes the value $\Phi_{10} = 0.2$ and the heat capacity does not show any maximum at this position. However, in contrast to short needles, the potential strength V_0 necessary to induce decagonal ordering strongly decreases

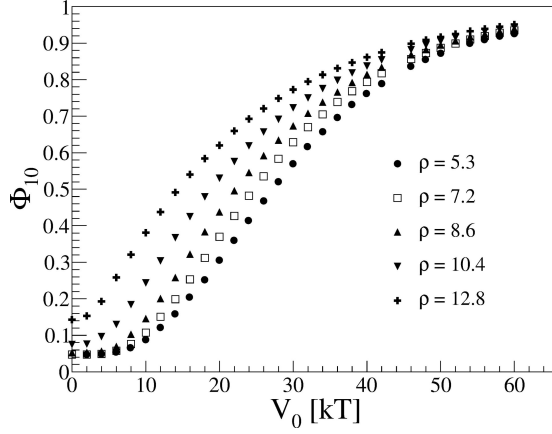


Figure 5.26:

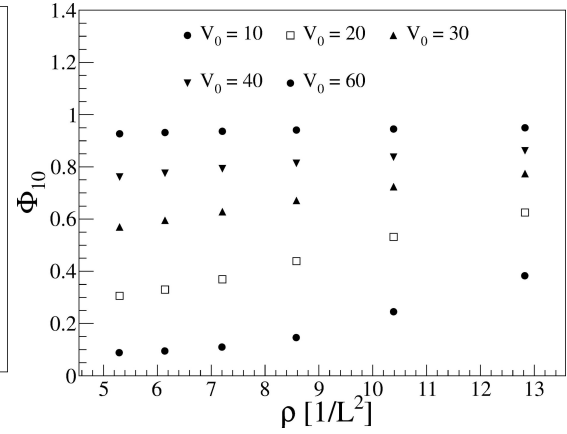


Figure 5.27:

Left: Decagonal directional order parameter Φ_{10} as a function of the potential strength V_0 for different densities ρ .

Right: Decagonal directional order parameter Φ_{10} as a function of the density ρ for different potential strengths V_0 .

with increasing density. In Fig. 5.27 the order parameter is plotted against the density. We understand such a behavior qualitatively. With increasing V_0 , short needles tend to form compact clusters of the size of one needle length when they connect two potential minima. The clusters are well separated from each other regardless their density. In contrast, long needles connect several minima and even share one or two of them. Now, clusters with the same orientation form elongated domains which have a length equal to several needle lengths (Fig. 5.29). The widths of the domains oriented along one of the decagonal directions also extend beyond one needle length since geometrically it is simpler to align clusters. For larger densities, we expect such domains to form more easily which explains the behavior of the decagonal transition line.

5.2.3 Nematic order

At low densities $\rho < 6.2$ the needles show surface-induced decagonal order without any nematic ordering. Similar to Fig. 5.29 the needle clusters form aligned domains that are equally distributed in all 10 decagonal directions. Above $\rho = 6.2$ the formation of the needle clusters does not destroy nematic order since the clusters

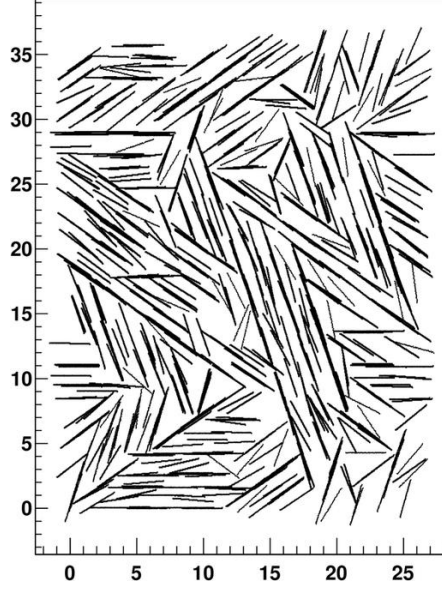


Figure 5.29: Snapshot of a long needle system at a density of $\rho = 8.6$ and a potential strength of $V_0 = 40kT$.

overlap with each other as explained in the previous paragraph. As a result the phase region with both stable nematic and decagonal order in the phase diagram of Fig. 5.25 occurs. Figure 5.30 demonstrates that for each density the nematic order parameter is nearly constant as a function of V_0 . One recognizes a slight increase when the decagonal order is established and a decrease beyond $V_0 = 40kT$ in the region of frozen initial configuration. Finally, in the region termed frozen initial configuration in the phase diagram of Fig. 5.25, the mobility of the needles is so small that the system is not able to change an initial configuration. Like short needles, long needles are able to freeze in an initial nematic order. However, if the simulation starts without any orientational order, nematic ordering does not develop during equilibrating the system. Figure 5.31 shows how the nematic order parameter S depends on the starting configuration. The energy, heat capacity, and decagonal order are the same whether the system freezes in the nematic or isotropic state. In the isotropic system needle clusters are aligned within domains the orientations of which are distributed equally on all ten decagonal directions.

In Fig. 5.31 the nematic order parameter in the simulations with isotropic start configurations does not drop immediately but decreases between potential strengths of $V_0 = 40kT$ till $V_0 = 60kT$. We believe this is an artifact of the

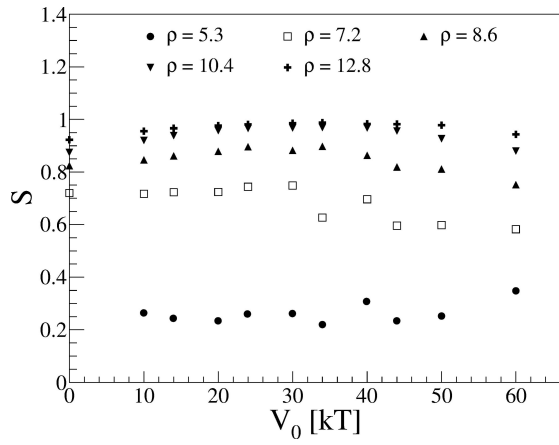


Figure 5.30:

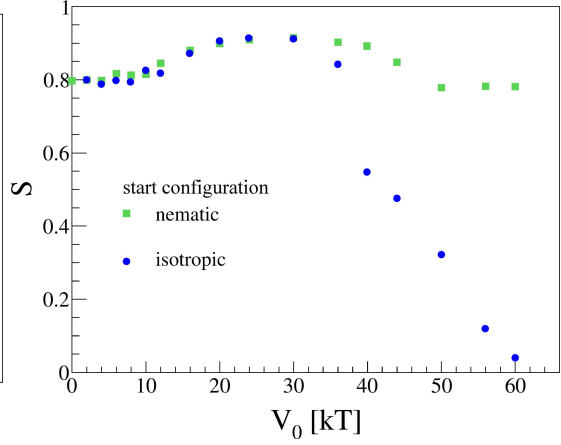


Figure 5.31:

Left: Nematic order parameter S as function of the potential strength V_0 for different densities ρ .

Right: Comparison of the nematic order parameter for different initial configurations as a function of the potential strength V_0 at a density of $\rho = 8.6$.

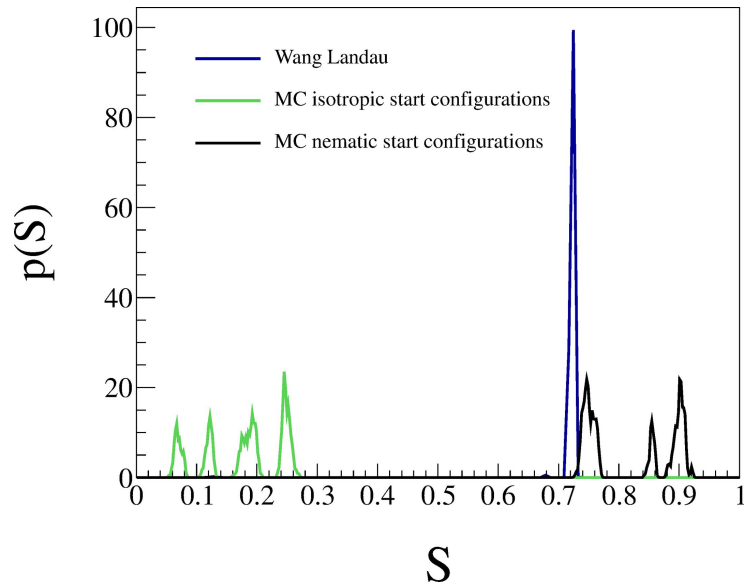


Figure 5.33: Distribution of the nematic order parameter at a density of $\rho = 8.6$ and a potential strength of $V_0 = 60kT$ obtained from different simulation schemes and initial conditions.

simulation scheme. In the Monte Carlo simulation scheme, the equilibration run corresponds to a fast cooling of the system. Just above the limit potential strength of $V_0 = 40kT$ the system can increase its nematic order while equilibrating. This results in an increased nematic order above $S = 0$ even if started with an isotropic configuration. The nematic order drops with increasing potential strength until finally the equilibration is fast enough to perfectly freeze in an initial non-nematic order at $V_0 = 60kT$. Artifacts of the equilibration run also freeze in when starting in an initial nematic order. Fluctuations of the nematic phase freeze in for $V_0 > 40kT$. In the equilibration run the fluctuations are introduced in two different ways. The first source of fluctuations is the initial isotropic positional order of the system. The simulation scheme creates fluctuations while finding the proper minima of the needles. The second source of fluctuations are the thermal fluctuations of needles around their director which are also usually seen in the case of zero potential strength. The strength of the fluctuations of the substrate free case are the upper limit for the simulation scheme at high potential strengths and the nematic order drops to the nematic order of the substrate free system.

A comparison of the results at a density of $\rho = 8.6$ and a potential strength of $V_0 = 60kT$ between Monte Carlo simulations with different initial nematic order and the Wang Landau simulations is shown in Fig. 5.33. In contrast to the short needle system the Wang Landau simulation results favor a high nematic order of the long needles in the region of frozen initial configurations. In the common nematic - decagonal directional ordered phase the nematic director is oriented along one of the symmetry direction of the substrate. In Fig. 5.34 we show a typical needle snapshot of the combined nematic and decagonal order at $\rho = 8.6$ and $V_0 = 18$. One clearly recognizes an average direction of the needles along the director, which points along one of the decagonal directions. The single needle orientations fluctuate around the director. The fluctuations of the orientations of the needles with respect to the nematic director prefer the neighboring decagonal directions of the potential. One can identify such fluctuations in the snapshot Fig. 5.34a) as bundles of needles. The corresponding orientational distribution function of the needles is plotted in Fig. 5.34(b). Besides the orientation of the director at $\alpha = 2\pi/5$, two weaker maxima appear at the neighboring decagonal directions at $\alpha = \pi/5$ and $3\pi/5$. Increasing density, these maxima become weaker in agreement with the increasing nematic order parameter S . All three maxima

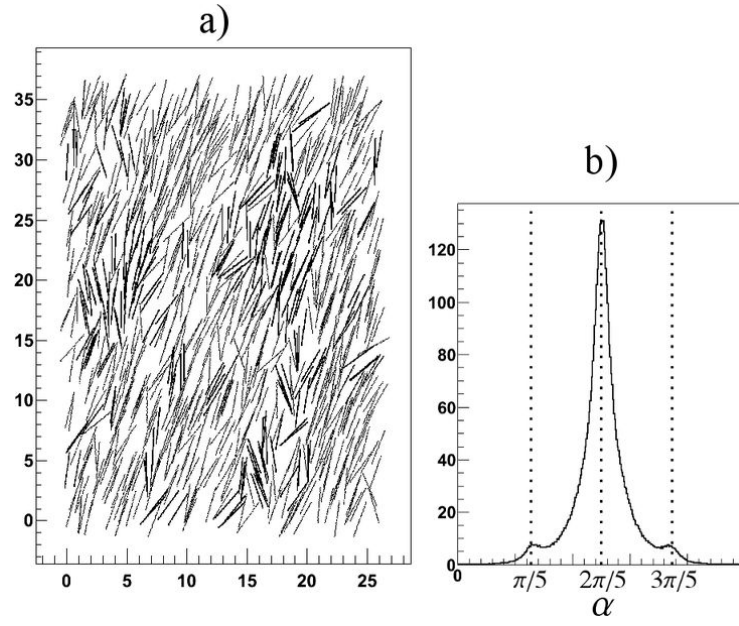


Figure 5.34: a) Snapshot of a long needle system at a density of $\rho = 8.6$ and a potential strength of $V_0 = 18kT$ in a nematic and decagonal directional ordered phase. b) Corresponding orientational distribution function for the needles. The angle α is measured with respect to the horizontal.

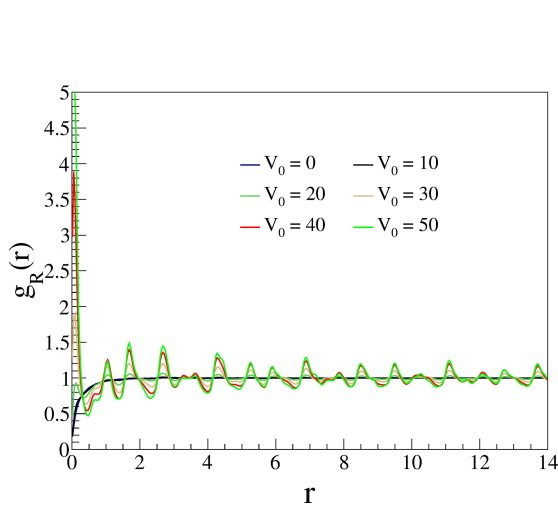


Figure 5.35:

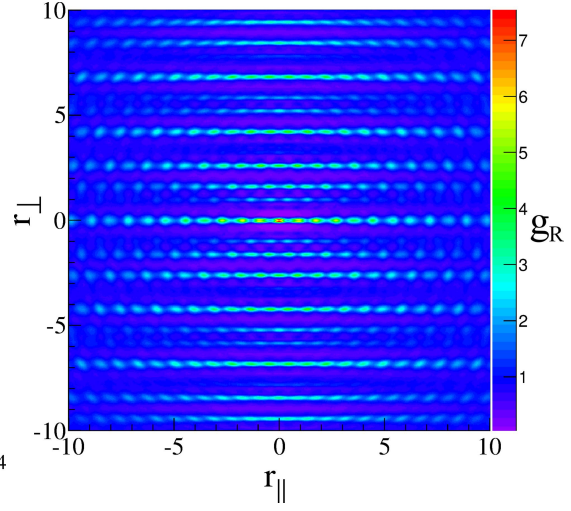


Figure 5.36:

Left: Pair correlation function for the center of mass of the long needles at a density of $\rho = 8.6$ for different potential strengths V_0 .

Right: Two dimensional pair correlation function with respect to the axis parallel $r_{\parallel}$ and perpendicular $r_{\perp}$ to the director of each long needle at a density of $\rho = 8.6$ and a potential strength of $V_0 = 60kT$.

become sharper when V_0 increases restricting the needles more and more to the decagonal directions of the substrate potential. In the short needle system the needles form isolated clusters and therefore the angular correlation is finite and the effect of directional enhancement is confined to the needles within a cluster. In the long needle system the nematic phase remains fluid. Despite the restriction of the system to a finite number of directions the phase may be still quasi-nematic.

5.2.4 Positional order

In the vicinity of the transition to the decagonal directional order the positional order of the long needles is not as pronounced as for the short needles. In Fig. 5.35 the pair correlation function for different potential strengths of a dense system with $\rho = 8.6$ is shown. The growth of first maximum denotes the creation of clusters under the influence of the potential. The maximum stays below 1 even at a potential strength of $V_0 = 20kT$ which is already in the region of decagonal directional order. The maximum becomes sharper with higher potential strengths

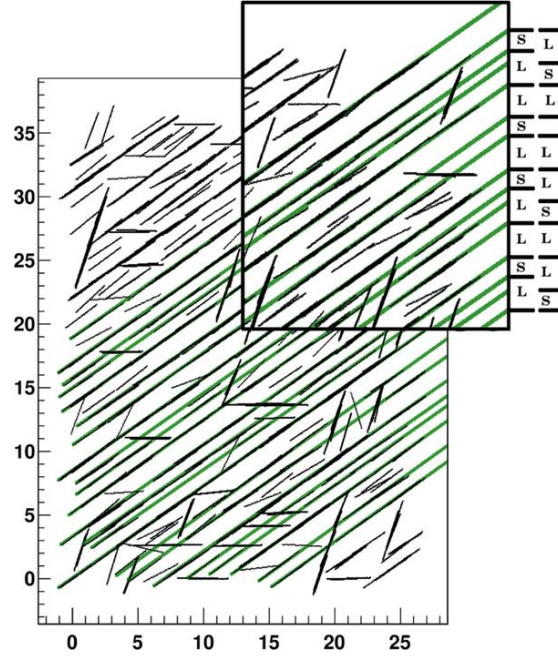


Figure 5.38: Snapshot of the long-needle system at a density of $\rho = 8.6$ and a potential strength of $V_0 = 60kT$ in the region of frozen initial configuration. Blow-up: One-dimensional quasicrystalline positional order of the needle clusters on two Fibonacci chains.

and the line structure of clusters begin to form. For a large substrate strength of $V_0 = 60kT$ this is illustrated in Fig. 5.38. The needles form again clusters which are mostly aligned along one decagonal direction. Some needle clusters deviate from the nematic director and point along other decagonal directions reducing the nematic order parameter below $S = 1$. Still the directional order parameter indicates decagonal ordering. The blow-up of one region of the snapshot in Fig. 5.38 reveals that the positions of the needle clusters possess one-dimensional quasicrystalline order perpendicular to the nematic director. This leads to a pronounced line structure in the two-dimensional pair correlation function as displayed in Fig. 5.36. The pair correlation function $g_R(r_{\parallel}, r_{\perp})$ shows the positional correlations of the needles center of mass with respect to the coordinate system whose axes are parallel to the long and short axes of each individual particle. The order is characterized by the two interwoven Fibonacci chains, which we identified in the substrate potential as illustrated in Fig. 3.9.

6 Hard spherocylinders

In this chapter we discuss the simulation results for the short- and long-spherocylinder system, separately. We present the phase diagram and then discuss more details of the phase ordering. In the last section, we show the results from the kinetic Monte Carlo simulations for the mobility of the rods. Most of our findings presented in this chapter are published in [B].

6.1 Short-spherocylinder system

6.1.1 Phase diagram

The phase diagram of the short rods in Fig. 6.1 exhibits several phases which differ by their bond-orientational, their directional, and orientational order. Below the horizontal black line at a potential strength $V_0 \approx 30kT$, the system of spherocylinders displays the usual phase sequence isotropic-nematic with increasing area fraction η which one observes without any substrate potential. With increasing V_0 the isotropic-nematic phase transition shifts to larger η . Above the potential strength of $V_0 \approx 30kT$ the phase diagram is divided into regions A-D with different bond-orientational order to be discussed below. In addition three characteristic density ranges exist. At very low area fractions of $\eta < 0.12$ (region A and B) the single rods display surface-induced bond-orientational order as well as pronounced directional order with non-zero order parameter Φ_{10} . In the regime of intermediate area fractions $0.12 < \eta < 0.35$ (regions C and D) the rods form well separated clusters under the influence of the surface potential. Now, the clusters display bond-orientational and directional order similar to the single rods in the dilute regime. At large area fractions of $\eta > 0.35$ the clusters touch each other. While the directional order parameter falls below $\Phi_{10} = 0.2$, still a delicate directional order is observable as we explain below. In particular, in the gray shaded region the preferred directions of the rods lie between the symmetry

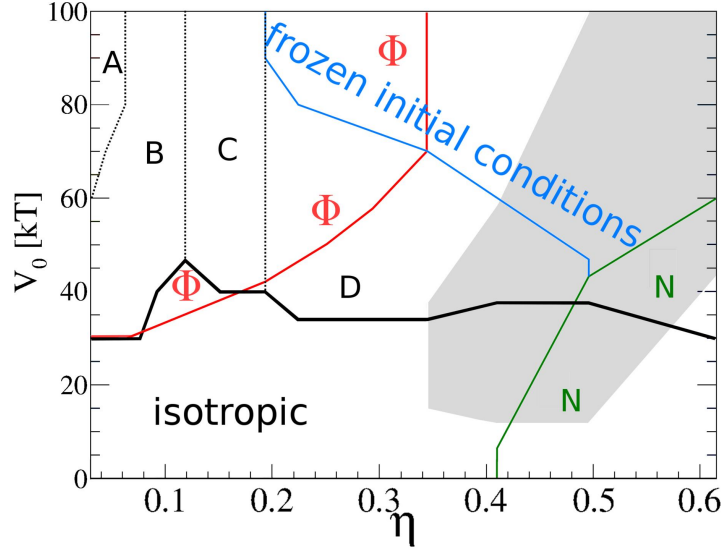


Figure 6.1: Phase diagram of the short rods system.

directions of the surface potential. Finally, at area fractions above $\eta = 0.19$ and sufficiently large potential strength V_0 , an initial isotropic state or nematic order remains after equilibration. We now discuss the different regions in more detail.

6.1.2 Bond-orientational order

The maximal fluctuations in the bond-orientational order parameter occur already at about $\Psi_m \approx 0.1$, so we identify bond order for $\Psi_m > 0.1$. In Fig. 6.2 we plot bond-orientational order parameters for rods (Ψ_{10} , Ψ_{20}) and the center of mass of rod clusters (Ψ_{C10} , Ψ_{C20}). Below an area fraction of $\eta = 0.12$ most rods are well separated from each other and only a few clusters exist. At very low area fractions $\eta < 0.08$ and large potential strengths $V_0 > 60kT$ a 20-fold bond-orientational order dominates (region A in Fig. 6.1). It occurs since the system is so dilute that nearest neighbors also occupy minima which lie in directions between the 10 symmetry directions of the substrate potential. 10-fold bond-orientational order forms at lower potential strengths down to $V_0 = 40kT$ and for area fractions up to $\eta = 0.12$ (region B).

For $\eta > 0.08$ most of the minima in the rod potential V_R are occupied and clusters of rods start to form. This is already visible in Fig. 6.3 at an area frac-

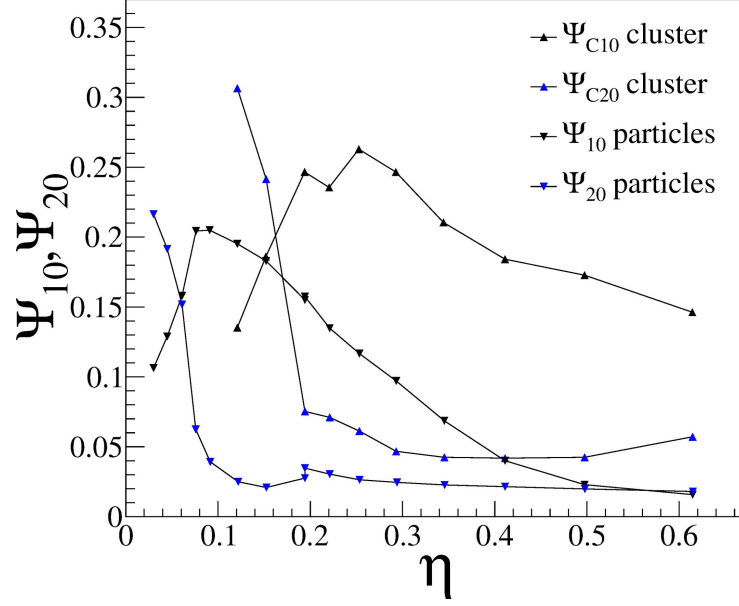


Figure 6.2: Bond orientational order parameter of a 10-fold and 20-fold symmetry for the center of mass of rods and the center of mass of clusters of rods versus area fraction at a potential strength of $V_0 = 80kT$.

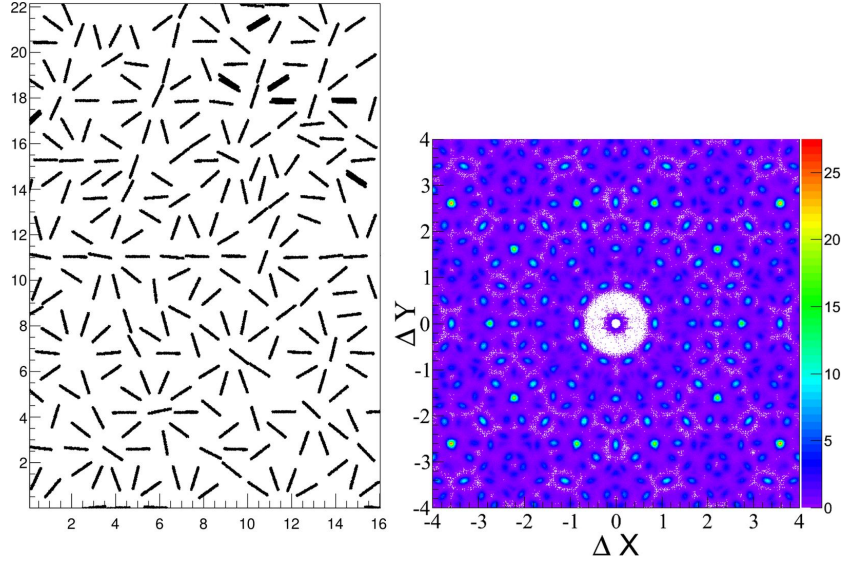


Figure 6.3: Snapshots (left) and 2D pair correlation functions of the center of mass of the clusters (right) for the short-rod system at $V_0 = 100kT$ and $\eta = 0.08$ in region B.

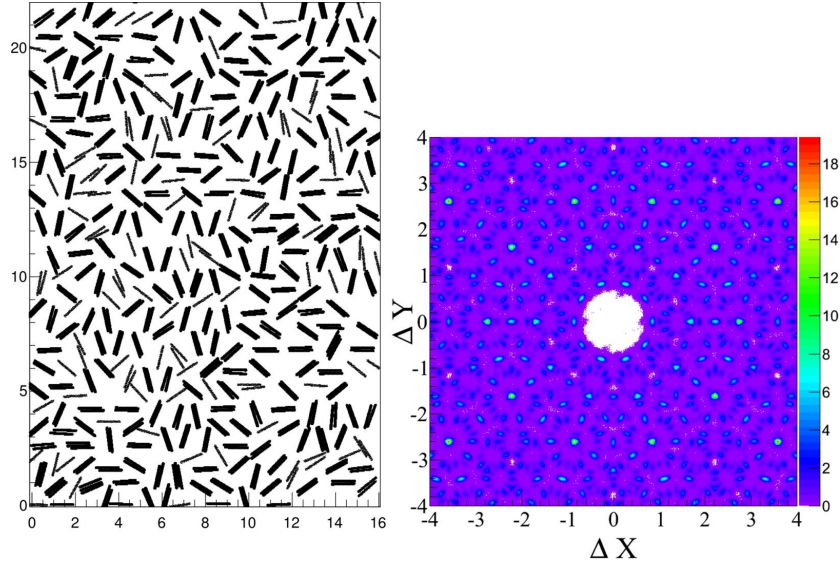


Figure 6.4: Snapshots (left) and 2D pair correlation functions of the center of mass of the clusters (right) for the short-rod system at $V_0 = 100kT$ and $\eta = 0.19$ in region C.

tion $\eta = 0.08$. The rods form a pattern of decagonal flower structures and the sharp maxima in the pair correlation function indicate the long-range positional order with decagonal symmetry induced by the surface potential. At area fractions above $\eta = 0.12$ the number of rods well exceeds the number of deep minima in V_R . Within one cluster two or more rods start to occupy the same minimum in V_R or, differently speaking, they connect two to three minima in the substrate potential $V(\vec{r})$. These clusters behave now like single rods in the very dilute regime. When the cluster density is low (region C in Fig. 6.1), they exhibit 20-fold bond-orientational order as indicated by $\Psi_{C20} > \Psi_{C10}$ in Fig. 6.2 in the range $\eta = 0.12$ to 0.19.

Then, further increasing the area fraction η 10-fold bond-orientational order dominates in region D which extends to large densities. In Fig. 6.4 we show the snapshot of a rod system at $\eta = 0.19$ and $V_0 = 100kT$ together with the pair correlation function of the center of mass of the clusters. As in the single-rod case, the pair correlation function for the clusters shows sharp maxima. The bond-orientational order of the clusters decays quite slowly with increasing area fraction (Fig. 6.2). The 10-fold order parameter Ψ_{C10} stays above 0.1 for $V_0 > 40kT$ and

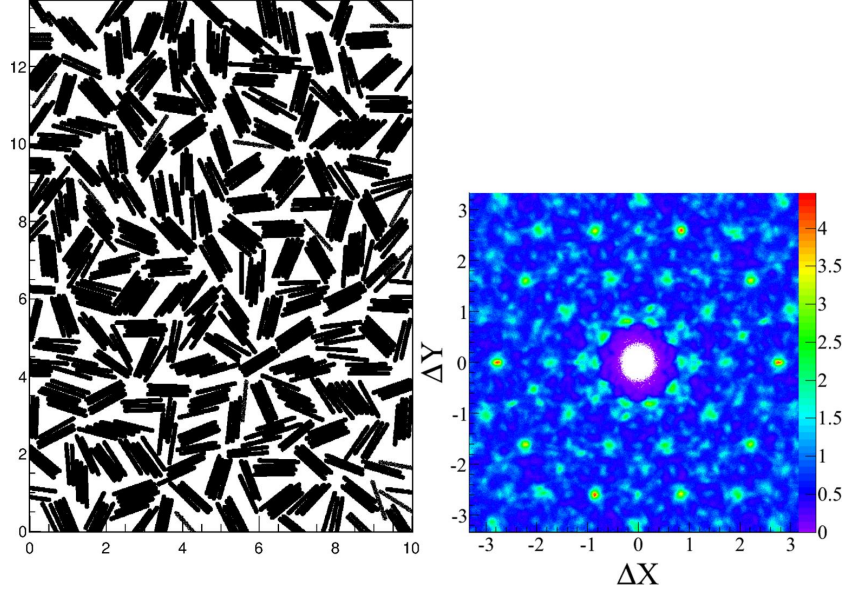


Figure 6.5: Snapshots (left) and 2D pair correlation functions of the center of mass of the clusters (right) for the short-rod system at $V_0 = 100kT$ and $\eta = 0.5$ in region D.

all simulated area fractions $\eta > 0.19$.

In Fig. 6.5 we show a high-density system with $\eta = 0.5$. Even though the clusters are not separated from each other anymore, one can still identify flower-like structures formed by the densely packed clusters. In these structures, the clusters are oriented more along directions in between the symmetry directions of the substrate potential, which we will investigate further below. In contrast to the previous cases, the cluster pair correlation function now displays broader peaks which we attribute to the following observation. The clusters connect two to three minima of the substrate potential (for a schematic see Fig. 6.8). This creates a broad potential well for the rods in which they perform thermal motion resulting in the broadened peaks.

6.1.3 Decagonal directional order

As in the hard-needle system we find the maxima of the fluctuations of the decagonal directional order parameter χ_Φ at an approximate value of $\Phi_{10} \approx 0.2$ independent of the system parameters. Figure 6.6 shows the decagonal directional order parameter Φ_{10} as a function of the potential strength V_0 for different area

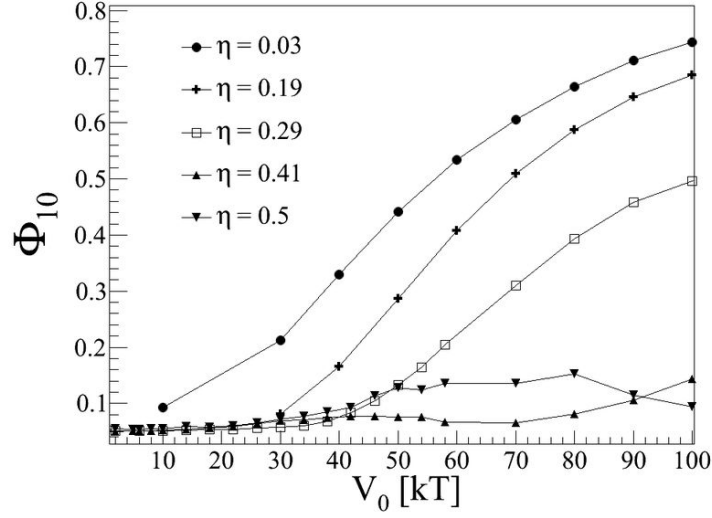


Figure 6.6: Decagonal directional order parameter Φ_{10} plotted versus V_0 for different area fractions.

fractions. With increasing η decagonal directional order is reduced. Finally, at $\eta = 0.42$ and larger area fractions the directional order parameter Φ_{10} always stays below 0.2 for all simulated potential strengths. However, the substrate potential still affects the orientations of the rods.

In Fig. 6.7 we plot their full directional distribution function $f(\alpha)$ for three different area fractions and potential strengths. At a low area fraction of $\eta = 0.19$ and low potential strength $V_0 = 26kT$ (isotropic phase), the substrate potential only induces a small modulation of the isotropic distribution. The maxima coincide with the 10 symmetry directions of the decagonal substrate potential. The directional order parameter stays below $\Phi_{10} = 0.1$. The difference between maxima and minima in $f(\alpha)$ grows with increasing V_0 until a directionally ordered phase with $\Phi_{10} \geq 0.2$ is established. The locations of the maxima and minima stay the same. This changes when the area fraction is increased. At $\eta = 0.35$ and low potential strength $V_0 = 26kT$, the preferred directions are located between the 10 symmetry directions. In the phase diagram of Fig. 6.1 the gray shaded region marks the parameter space where such a shift in the directions occurs. At the highest simulated potential strength $V_0 = 90kT$ the rod system exhibits directional order with $\Phi_{10} > 0.2$ and the preferred directions agree again with the

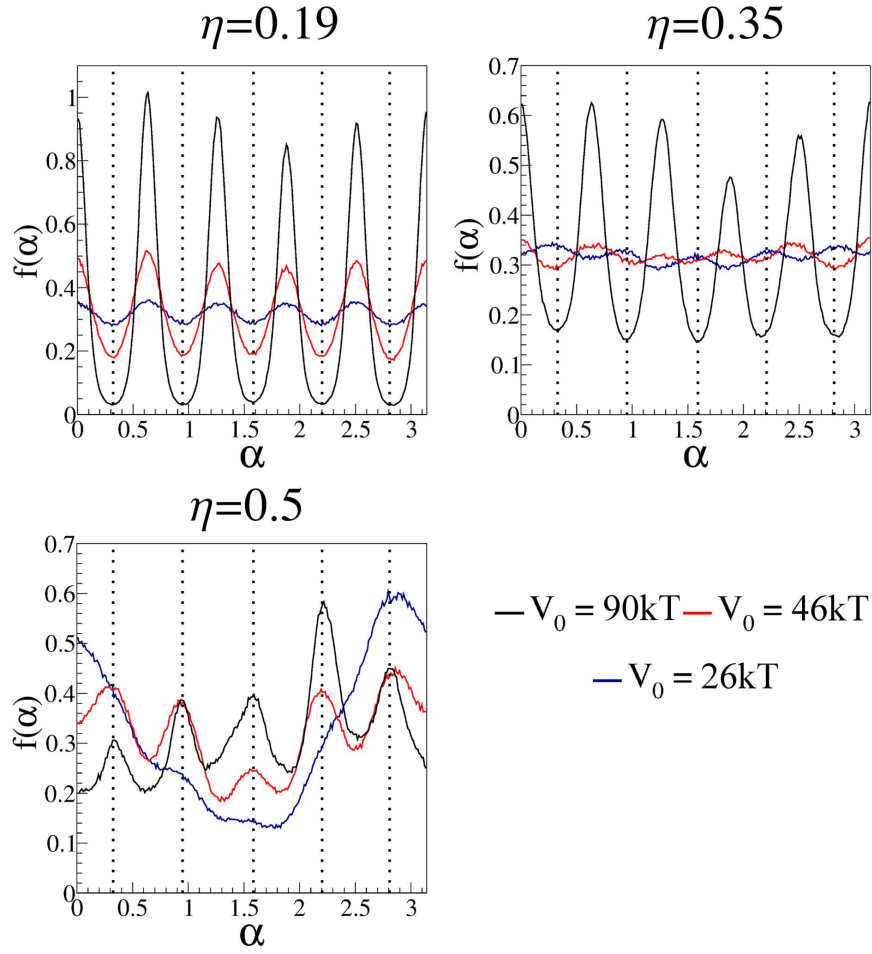


Figure 6.7: Directional distribution function $f(\alpha)$ for three area fractions η and three potential strengths V_0

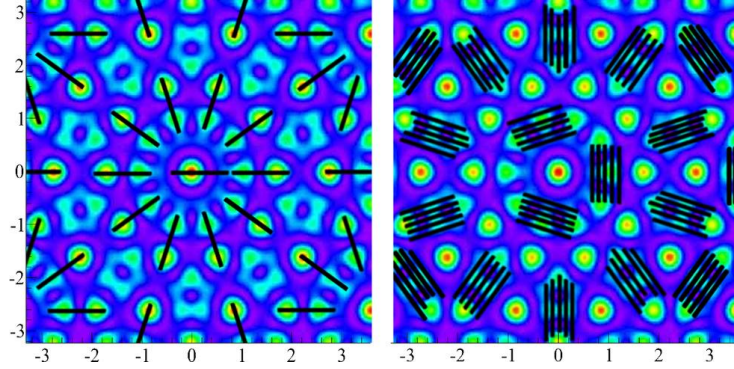


Figure 6.8: Single rods and small clusters (left) occupy different positions and directions in the substrate potential than larger clusters (right) which gives rise to the gray shaded region in the phase diagram of Fig. 6.1 (schematic drawing).

symmetry directions. In dense rod systems with a large area fraction the preferred directions of the rods remain shifted at large potential strengths V_0 . We illustrate this in Fig. 6.7 for $\eta = 0.5$. However, even at $V_0 = 90kT$, where the maxima are pronounced does the directional order parameter stay below $\Phi_{10} = 0.2$. Note that at a potential strength of $V_0 = 26kT$ the rod system is in the nematic phase and the director aligns along one of the shifted preferred directions. These directions occur when the size of the rod clusters increases from small clusters with up to three rods per cluster to larger clusters.

The schematic drawing of Fig. 6.8 illustrates the preferred directions. Single rods and clusters of up to three rods (Fig. 6.8, left) connect two deep minima of the substrate potential. However, clusters consisting of four rods and more (right) connect more shallow minima since they occupy more area which the deep minima cannot provide. So their preferred directions lie between the symmetry directions of the substrate potential. The mean energy of a rod in a three-particle cluster is always below the respective value in larger clusters. So, in the high-density regime starting at $\eta = 0.35$ the rod system consists of a mixture of small and big clusters with a rising fraction of big clusters at larger area fractions. Hence, there is no sharp transition from one set of preferred directions to the other set. Finally, we find it remarkable that the gray shaded region in Fig. 6.1 indicating the shifted preferred directions includes the isotropic and nematic phase, but also regions with bond-orientational order and with frozen initial conditions. As illustrated in

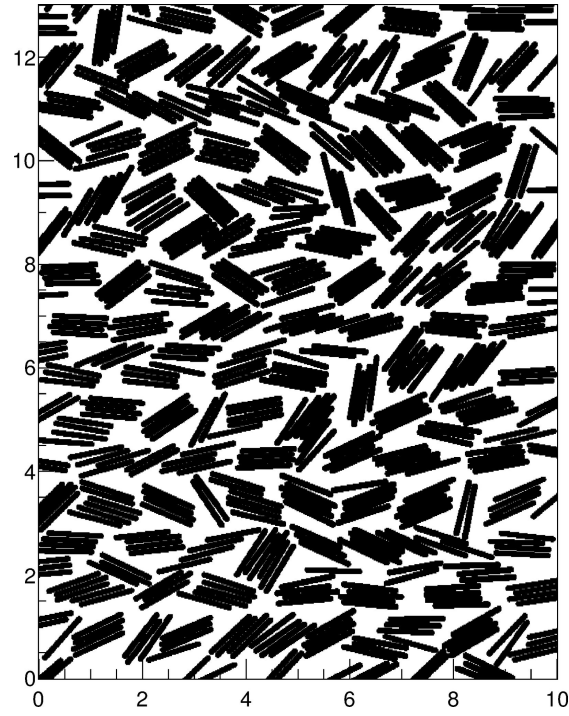


Figure 6.9: Snapshot of a short rod system at $V_0 = 100kT$ and $\eta = 0.5$ with a frozen nematic order.

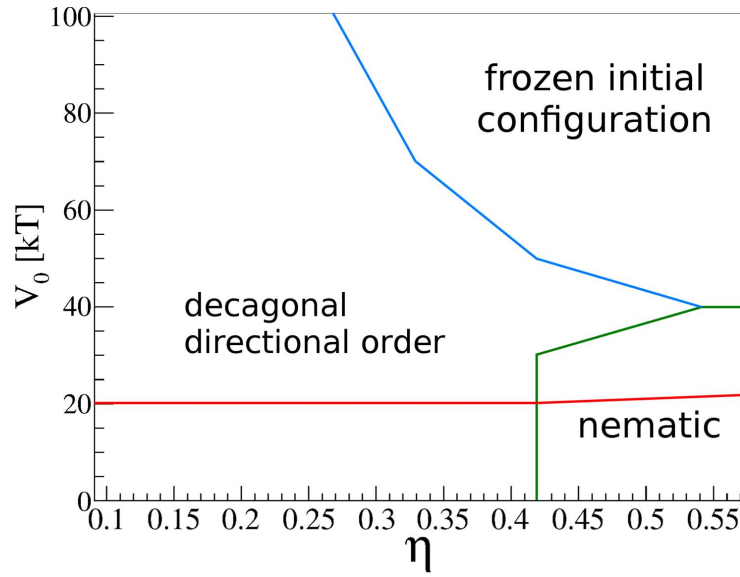


Figure 6.10: Phase diagram of the long rods.

Fig. 6.9 a certain degree of an initial nematic order can be frozen in. As in the short needle system the maximum nematic order parameter is limited due to the distribution of possible cluster positions with a common orientation.

6.2 Long-spherocylinder system

6.2.1 Phase diagram

Figure 6.10 shows the phase diagram of long rods which looks much simpler than the one for short rods. Below the potential strength $V_0 = 20kT$, one observes the typical isotropic-nematic phase transition completely unaffected by the substrate potential. Above $V_0 = 20kT$, spherocylinders with length $3a_V$ connect several minima of the surface potential (see Fig. 2.3) and therefore become mainly oriented along one of the symmetry directions. For this reason, one obtains directional order with decagonal symmetry that extends along the whole range of area fractions in contrast to the short-rod system. Figure 6.11 demonstrates that the directional order parameter plotted versus V_0 only weakly depends on the area fraction η . Since the rods can slide to a certain degree along the minima, which they occupy, the positional order is not sufficient to generate a pronounced

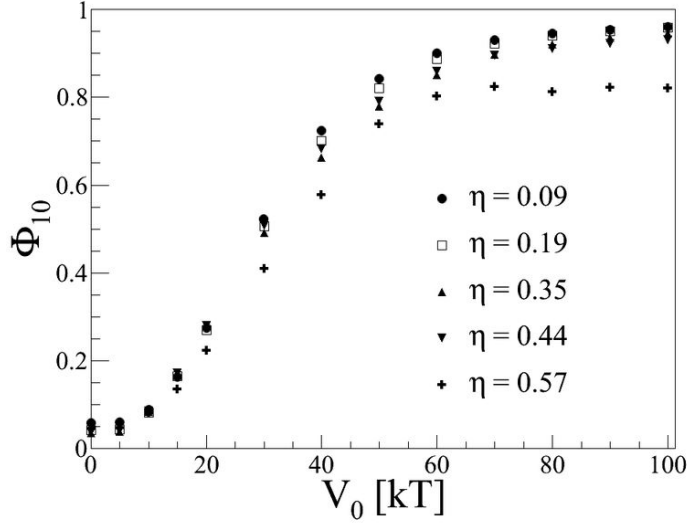


Figure 6.11: Decagonal directional order parameter Φ_{10} plotted versus potential strength V_0 for different area fractions η .

bond-orientational order as observed for short rods. The bond-orientational order parameter Ψ is always below 0.1. Nevertheless, as we will see below, in the pair correlation function one can identify preferred positions of the rods as dictated by the substrate potential. Furthermore, rod clusters that form at increasing area fraction show a delicate short-range order. As in a long-needle system the nematic phase extends into the region of decagonal directional order. Finally, at higher potential strengths the initial configuration, for example, a nematic order, can be frozen in.

6.2.2 Positional order

We now study in more detail positional order with the help of the two-dimensional pair correlation function which we determine in the local frame of the rod. So we describe positional correlations of the rod's center of mass with respect to the coordinate system whose axes are parallel to the long and short axes of each individual rod, respectively. Figure 6.12 shows the snapshot of a low-density system at area fraction $\eta = 0.19$. The pair correlation function in the local rod frame exhibits peaks according to the substrate potential but they are broadened due the motion of the rods. One also clearly recognizes a stripe pattern parallel to the local rod on which the peaks lie interrupted by blue bands with low positional correlations.

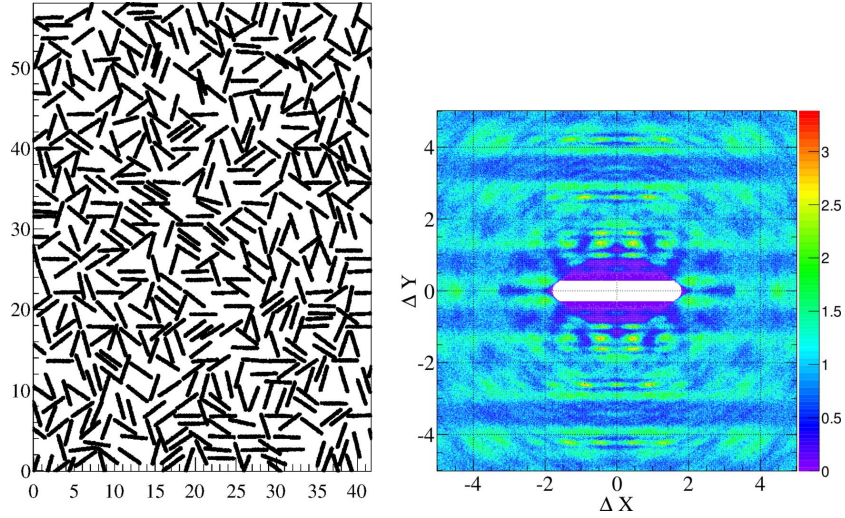


Figure 6.12: Snapshots (left) and 2D pair correlation functions in the local rod frame (right) for the long-rod system at $V_0 = 60kT$ and $\eta = 0.19$

They belong to the Fibonacci sequence from the substrate potential. However, our analysis shows that nearest-neighbor minima on this Fibonacci sequence are not occupied due to thermal motion of the rods so the pronounced stripes occur. At increasing density clusters of rods form and positional order still exists. Now, the nearest-neighbor minima are filled up and the pronounced stripe pattern vanishes as indicated in Fig. 6.13. Unlike short rods, the long rods cannot cluster together in the same line of potential minima since their diameter approximately equals the width of the minima. Each rod is trapped in a different line of minima. In the snapshot of Fig. 6.13 one can clearly see spaces between parallel rods. Indeed the corresponding pair correlation function exhibits a correlation hole between the excluded volume of the central rod (in white color) and the nearest neighbors. As the relevant maxima indicate, the bond between nearest neighbors is not along their common short axis but points along the symmetry directions of the potential at angles $\pm\pi/5$ relative to the central rod. Hence, the clusters in the snapshot exhibit their typical rhombic shape. The distance of neighboring rods is the smallest distance of the Fibonacci sequences associated with the substrate potential. Compared to short rods, which at comparable area fraction [see Fig. 6.4] form well separated clusters in a close side-by-side configuration, the behavior of long rods with the same aspect ratio is quite different. Increasing the area fraction further, the whole system is compressed so that the rods start to touch

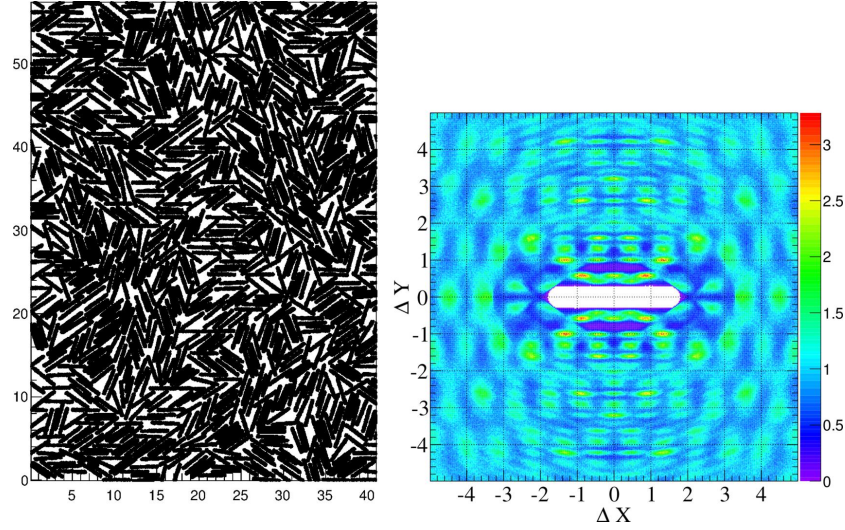


Figure 6.13: Snapshots (left) and 2D pair correlation functions in the local rod frame (right) for the long-rod system at $V_0 = 60kT$ and $\eta = 0.44$.

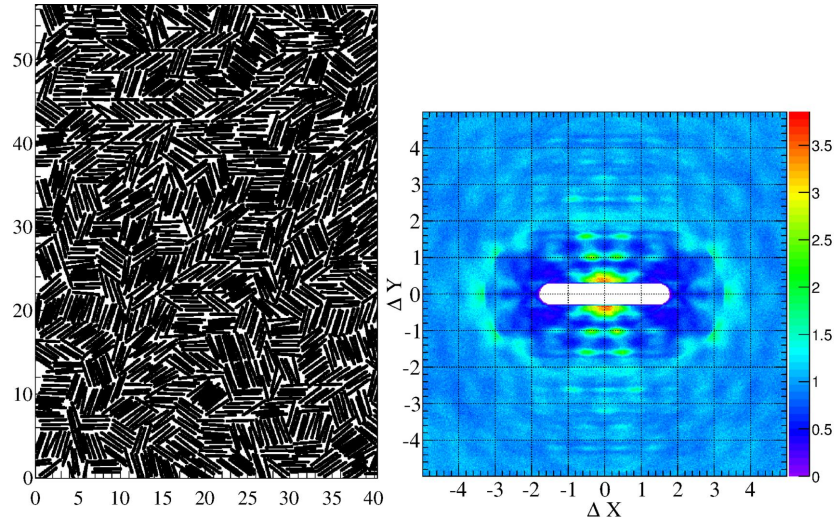


Figure 6.14: Snapshots (left) and 2D pair correlation functions in the local rod frame (right) for the long-rod system at $V_0 = 60kT$ and $\eta = 0.57$.

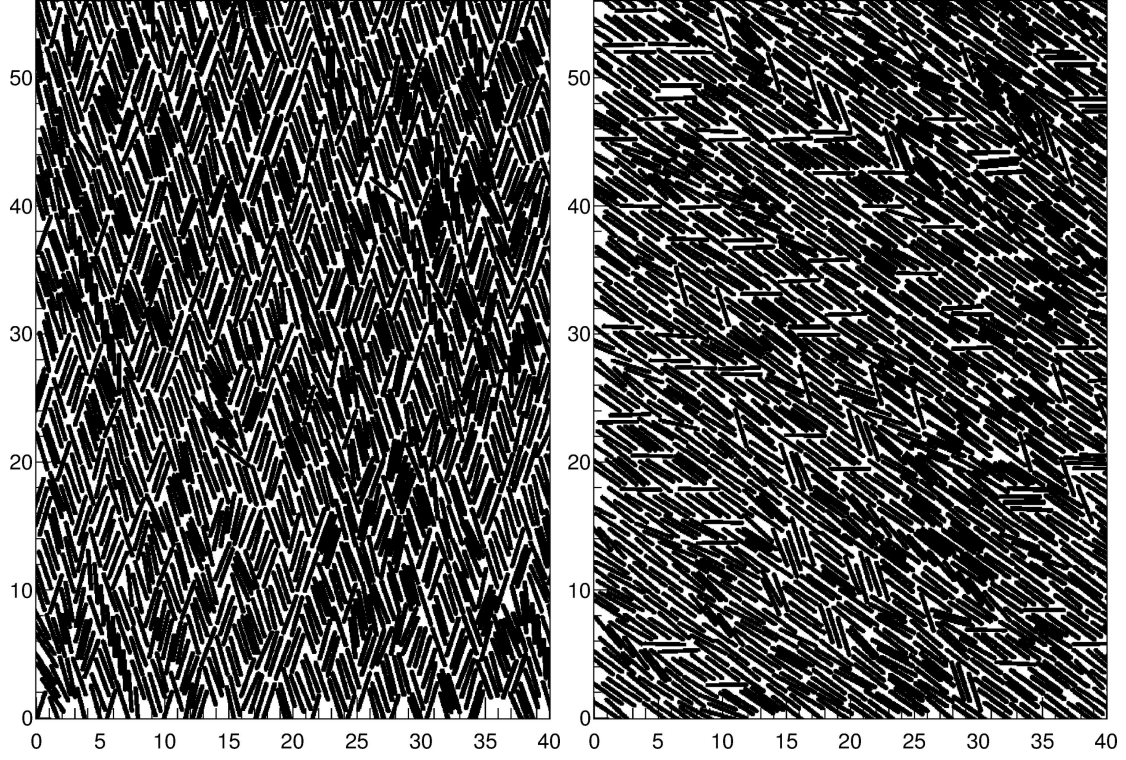


Figure 6.15: Snapshots from two systems at an area fraction of $\eta = 0.57$ and a potential strength of $V_0 = 90kT$ with frozen nematic order. Left: with two main orientations and $S = 0.85$. Right: Almost perfect nematic order with $S = 0.93$.

each other. This is indicated in the pair correlation function of Fig. 6.14, where the nearest-neighbor maximum is located at the border of the excluded volume. Furthermore, the surface-induced positional order has vanished almost completely since the rods fill the whole space quite uniformly. Partially, they form elongated clusters by ordering side by side and head to tail. Finally, decagonal directional order is still very high since the rods strictly align along the symmetry directions. Frozen nematic states can exhibit very high degrees of nematic order because of this strict alignment of the rods. In Fig. 6.15 the frozen nematic order is illustrated with two snapshots of a system at an area fraction of $\eta = 0.57$ and at a potential strength of $V_0 = 90kT$. The rods are aligned along one or two symmetry directions of the substrate. In contrast to the long needle system the order of the rods onto the Fibonacci lines of the substrate is lost.

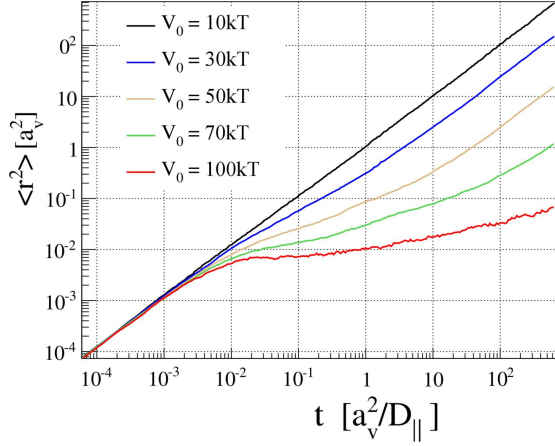


Figure 6.16:

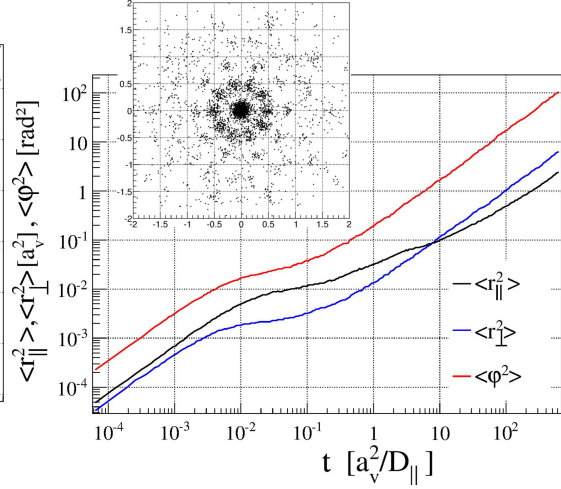


Figure 6.17:

Left: Mean square displacement $\langle r^2 \rangle$ of a single short rod in units of a_V^2 for different potential strengths V_0 . Time is measured in units of $a_V^2/D_{\parallel}$, where $D_{\parallel}$ is the single-rod diffusion coefficient parallel to the rod axis [see Eq. (4.28)].

Right: Angular mean square displacement $\langle \varphi^2 \rangle$ and accumulated mean square displacement parallel ($\langle r_{\parallel}^2 \rangle$) and perpendicular ($\langle r_{\perp}^2 \rangle$) to the rod axis at $V_0 = 70kT$. The inset shows a snapshot of the rod positions at $t = 500a_V^2/D_{\parallel}$.

6.3 Dynamics of hard spherocylinders

6.3.1 Short spherocylinders

We now present the results of our kinetic Monte Carlo simulations on the mobility of the rods both for single and multi-particle systems. Figure 6.16 shows the mean square displacement of a single short rod for different potential strengths. At $V_0 = 10kT$ the mean square displacement is nearly the same as without substrate potential. With increasing V_0 the rod becomes trapped in a pair of deep potential minima and can only leave them by thermal activation. As a result, a subdiffusive regime develops before the rod performs normal diffusion. At $V_0 = 100kT$ the rod stays trapped in its potential minima and the regime of normal diffusion is not reached within the simulation time. In Fig. 6.17 we plot the angular mean square displacement $\langle \varphi^2 \rangle$ and the accumulated displacements parallel ($\langle r_{\parallel}^2 \rangle$) and perpendicular ($\langle r_{\perp}^2 \rangle$) to the rod axis for $V_0 = 70kT$. Interestingly, $\langle \varphi^2 \rangle$ and $\langle r_{\perp}^2 \rangle$

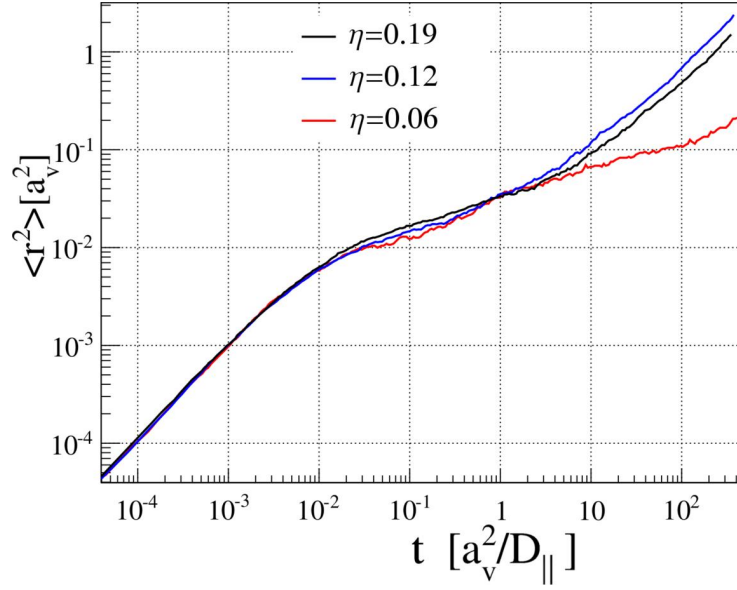


Figure 6.19: Mean square displacement of a short-rod system for different area fractions at $V_0 = 70kT$.

enter the diffusive regime at the same time whereas $\langle r_{\parallel}^2 \rangle$ becomes diffusive more than two decades later. The reason for this behavior is the following. Whereas one end of the rod stays trapped in its potential minimum, the other end moves/rotates into a neighboring minimum like a clock hand by thermal activation. This motion contributes to both $\langle \varphi^2 \rangle$ and $\langle r_{\perp}^2 \rangle$. To perform a motion parallel to the rod axis, both ends of the rod have to leave their potential minima and normal diffusion sets in later. This also explains why the total mean square displacement in Fig. 6.17 follows $\langle r_{\parallel}^2 \rangle$.

The mobility of the short rods changes dramatically when a whole ensemble of rods is considered. In Fig. 6.19 we plot the mean square displacement at $V_0 = 70kT$ for different area fractions. In the dilute regime at $\eta = 0.06$, $\langle r^2 \rangle$ behaves similar to the single-rod system and does not reach normal diffusion within the simulation time. As soon as the rods start to cluster (region C in the phase diagram of Fig. 6.1), their mobility rises and normal diffusion is observed. The outer rods of a cluster are more weakly bound to the trap and can more easily leave their potential minima by thermal activation. Nevertheless, the diffusion coefficient is much smaller than for free diffusion by a factor of ca. 100. Most particles stay in their potential minima and only a few move from cluster to cluster. Further

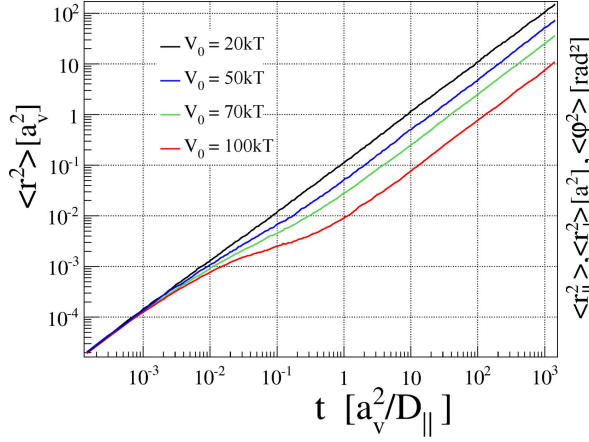


Figure 6.20:

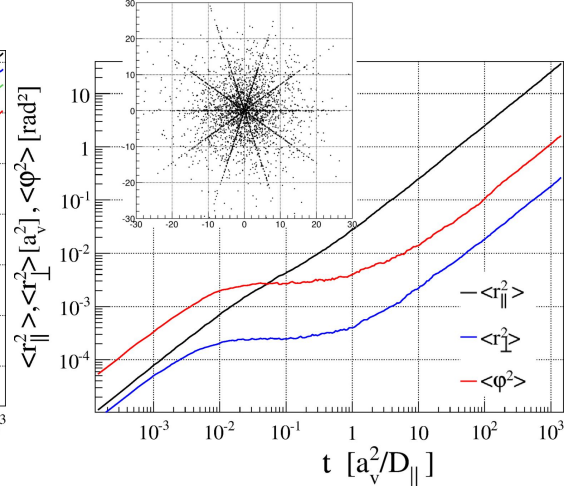


Figure 6.21:

Left: Mean square displacement $\langle r^2 \rangle$ of a single long rod in units of a_v^2 for different potential strengths V_0 .

Right: Angular mean square displacement $\langle \varphi^2 \rangle$ and accumulated mean square displacement parallel ($\langle r_{||}^2 \rangle$) and perpendicular ($\langle r_{\perp}^2 \rangle$) to the rod axis at $V_0 = 70kT$. The inset shows a snapshot of the rod positions at $t = 500a_v^2/D_{||}$.

increasing the area fraction decreases the mobility again since the space between clusters becomes more and more crowded.

6.3.2 Long spherocylinders

Compared to short rods, long rods are much more mobile when the substrate potential is switched on and the mobility is much less affected by the strength of the potential. The mean square displacement for a single long rod in Fig. 6.20 shows normal diffusion at long times even at a potential strength as high as $V_0 = 100kT$. The subdiffusive regime is always quite short. The high mobility arises from the motion of the rods along the lines of minima. They act as rails along which the rods can easily slide. To leave a rail, the rod changes its direction and occupies another rail. This picture is confirmed by Fig. 6.21. Now the accumulated mean square displacement along the rod axis, $\langle r_{||}^2 \rangle$, drastically exceeds $\langle r_{\perp}^2 \rangle$ and determines translational diffusion. The ten symmetry directions for the rails are clearly visible in the snapshot of Fig. 6.21. Compared to short rods, $\langle \varphi^2 \rangle$ is smaller

by a factor of ten. In an ensemble of long rods the usual crowding occurs and in contrast to the short rods a density-induced mobility enhancement is not visible.

7 Conclusion and outlook

We determined the phase behavior of hard rods confined in two dimensions under the influence of a decagonal substrate potential. We took two different particle models into account. The hard needle model illustrates the phase behavior of very slim rods. The influence of a finite width of the rods is demonstrated using the hard spherocylinder model. The interaction of the rods with the substrate strongly depends on the ratio of the length of the rod L and the typical length scale of the substrate potential a_V . We identified different rod - substrate interactions for three different rod lengths. If the length of the rod is much smaller than the length scale of the potential, $L < a_V$, the interaction of the rod-like particle with the substrate does not differ much from the interaction of spherical particles with the substrate. Rods with a length comparable to the length scale of the substrate potential, $L \approx a_V$, can connect two minima of the substrate and find the positions of their minimum potential energy in between the minima of the substrate potential. Rods with a length of a few a_V can connect more minima at the same time. With increasing rod length, a grid structure of lines connecting the potential minima is the most important feature of the quasicrystalline substrate. The lines are oriented along the symmetry directions of the potential. We could explain the grid structure from the basic features of an underlying decorated Penrose tiling. In our simulations we took two rod lengths into account. The short rods have a length of $L = 1a_V$. The long rods are three times longer with $L = 3a_V$.

In the short-needle system the quasi-nematic order is destroyed with increasing potential strength. The system exhibits directional order where the needles gradually form disconnected clusters located between two potential minima and oriented along the symmetry directions of the decagonal potential. As a result, the needle clusters exhibit the same long-range positional order as the substrate and their relative orientations also display long-range order. Finally, at sufficiently high densities and potential strengths it is possible to freeze in nematic order up

to an order parameter of $S = 0.7$. In the region of frozen initial configurations a high nematic order also results in an increased bond-orientational order.

Long needles tend to connect several potential minima with increasing potential strength and to form clusters that interact with neighboring clusters. In contrast to short needles, extended domains of uniformly oriented clusters along the decagonal directions form. At larger densities the interaction between needles enforces directional order to set in at lower potential strengths compared to the short-needle system and to stabilize the nematic phase also in regions of surface-induced directional order. For densities above the isotropic-nematic phase transition, the needle clusters position and orient themselves along lines defined by the potential minima. These lines follow a one-dimensional quasicrystalline order that is described by two interwoven Fibonacci chains. The effect becomes very pronounced for large potential strengths, where one can again freeze in nematic order with any value of the order parameter S .

In both systems of hard spherocylinders we observe characteristic positional and directional order with decagonal symmetry that sets in when the strength of the surface potential exceeds a threshold value. Short spherocylinders connect two deep minima and orient along the symmetry directions of the substrate potential similar to short needles. At low area fractions this enforces directional order together with 10- and 20-fold bond-orientational order. With increasing area fraction rods form clusters. When the cluster size exceeds three rods, they leave the deepest minima and connect more shallow minima. This destroys directional order along the ten symmetry directions. The directional distribution function reveals a shift by $\pi/10$ for the preferred cluster directions. For the whole range of area fractions, the pair correlation function shows pronounced positional order induced by the substrate potential.

Long spherocylinders connect several minima and therefore slide more easily along their long axis. This results in only weak positional order and precludes any bond-orientational order for the center of mass of the rods. Pronounced directional order sets in at lower potential strength compared to the short-spherocylinder system. With increasing area fraction, long spherocylinders also cluster but due to their width they occupy separate lines of minima. Further increase of area fraction

compresses the clusters whereby the rods are pushed out of their lines of minima. Still they stay oriented along the ten symmetry directions and the directional order parameter hardly changes with increasing area fraction. When the clusters are compressed, the weak positional order vanishes completely.

We have also investigated the mobility of the spherocylinders. The mobility of short spherocylinders decreases with increasing potential strength since they are trapped in their pair of minima. They leave this trap by rotating one end into a neighboring minimum. However, translational diffusion is determined by the hindered mobility along the rod axis. When the rods form clusters at increasing area fraction, the rod mobility increases drastically since outer rods of the clusters are more weakly bound so they leave their traps more easily. Long rods can slide along their lines of minima, therefore their mobility is much less affected by the substrate potential. Their diffusive motion is determined by the sliding while motion perpendicular to the rod axis is strongly hindered by the substrate potential.

The combination of a hard-rod system, which tends to form a quasi-nematic phase in two dimensions, and a quasicrystalline substrate potential leads to fascinating patterns of clustered rods especially for large potential strengths. We found new phases with quasicrystalline directional order and quasicrystalline bond-orientational order and new fascinating structures which exhibit a nematic and a quasicrystalline order at the same time. It would be very interesting to perform experiments with the help of quasicrystalline light patterns as in Refs. [138, 139, 169] using systems of rodlike colloidal particles. The broad diversity of rod-like colloids and the possibility to tune the characteristic length scales of the substrate potential should make this experimental setup an ideal testing ground for our findings.

Another interesting experimental setup for the realization of our findings are quasicrystalline atomic surfaces as substrates for monolayers of organic rod-like molecules of alkenes or aromatic hydrocarbons like pentacene[87]. In atomic systems it is more difficult to find substrates and particles with the correct ratio of length scales than in colloidal systems. First detailed simulations of hexane and octane have been performed for a quasicrystalline approximant [39, 176]. With growing density an interesting stripe pattern appears in the first monolayer.

It is also appealing to use the resulting two-dimensional rod adsorbate as template to build three-dimensional structures and to explore how well the quasicrystalline cluster phases extend into the third dimension. The growth of films on patterned substrates is the basis for many applications like coatings or electronic devices from epitaxial overlayers.

In our work we left out the possibility of phasonic defects of the quasicrystalline potential. Such defects are very common in real quasicrystals and can also be created with laser fields. A phasonic defect introduces a break and shift in the Fibonacci line structure of the substrate. Phasonic drifts can initiate fascinating dynamics of adsorbed particles[111]. A phasonic drift leads to a movement of the Fibonacci lines of the potential perpendicular to their orientation. Every line drifts with a different velocity depending on the phason mode. That may lead to locked nematic states of rods placed onto the drifting substrate. Further computer simulations may reveal a deeper understanding of phasonic defects and drifts of quasicrystalline structures and its applications.

Appendix : Decomposition of the potential into a tiling

As shown in Fig. 3.9 all deep potential minima can be ordered along straight lines and the distances of the lines follow two interwoven Fibonacci sequences. The order of the distances is a hint that there must be a connection of the substrate potential with the Penrose tiling. We already presented a way to produce decagon patches of the Penrose tiling called cartwheels[78]. The cartwheel tiling can also be recreated with the overlap rules of the Gummelt decagons[79]. Such a decagon overlap is shown for a second order cartwheel in the left panel of Fig. .1. In the right panel of Fig. .1 the kite and darts tiling of a combination of two second order cartwheels is shown. The two cartwheels are stacked above each other with the second cartwheel having been rotated by an angle of 180° . The resulting double cartwheel exhibits a perfect decagonal symmetry except for the inner most central part.

If we decorate the Gummelt decagon with a point pattern as shown in the middle panel of Fig. .2 the double cartwheel shows a point pattern which is displayed in the right panel of Fig. .2. In the left panel the corresponding patch of the substrate potential from Eq.(3.12) is shown. The substrate potential is filtered with a threshold of $V < -0.76$. Comparing the patterns of both patches reveals that all deep minima in the patch of the potential match positions of the points in the double cartwheel. The point pattern seems to be not complete for minima which are close to the threshold. We changed the threshold but there seemed to be no possibility to create a point pattern that perfectly matches the filtered substrate potential.

Therefore we change the general approach of using a point pattern as a decoration of the Gummelt decagon to a decagon which takes also the depth of the

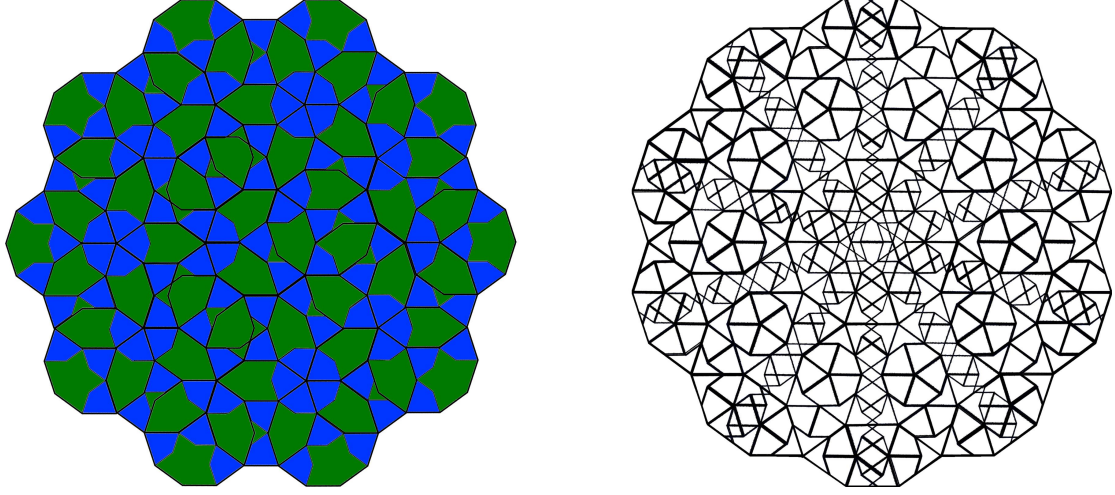


Figure .1: Left: Overlapping Gummelt decagons form a second order cartwheel tiling. Right : Kites and darts decoration of two second order cartwheels. The cartwheels are stacked on each other after a rotation of 180° building a almost 10-fold rotational symmetric double cartwheel.

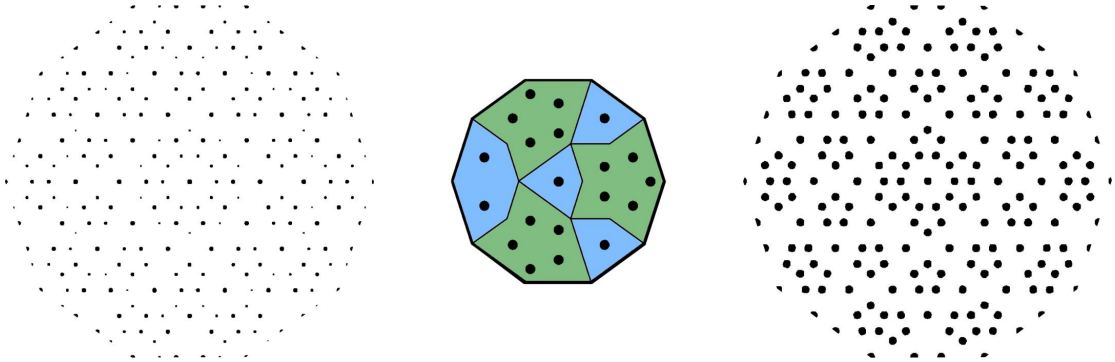


Figure .2: Left: All regions of the substrate potential with a potential strength of $V < -0.76$. Right: Distribution of points from a double cartwheel created from Gummelt decagons with a point decoration as shown in the middle panel.

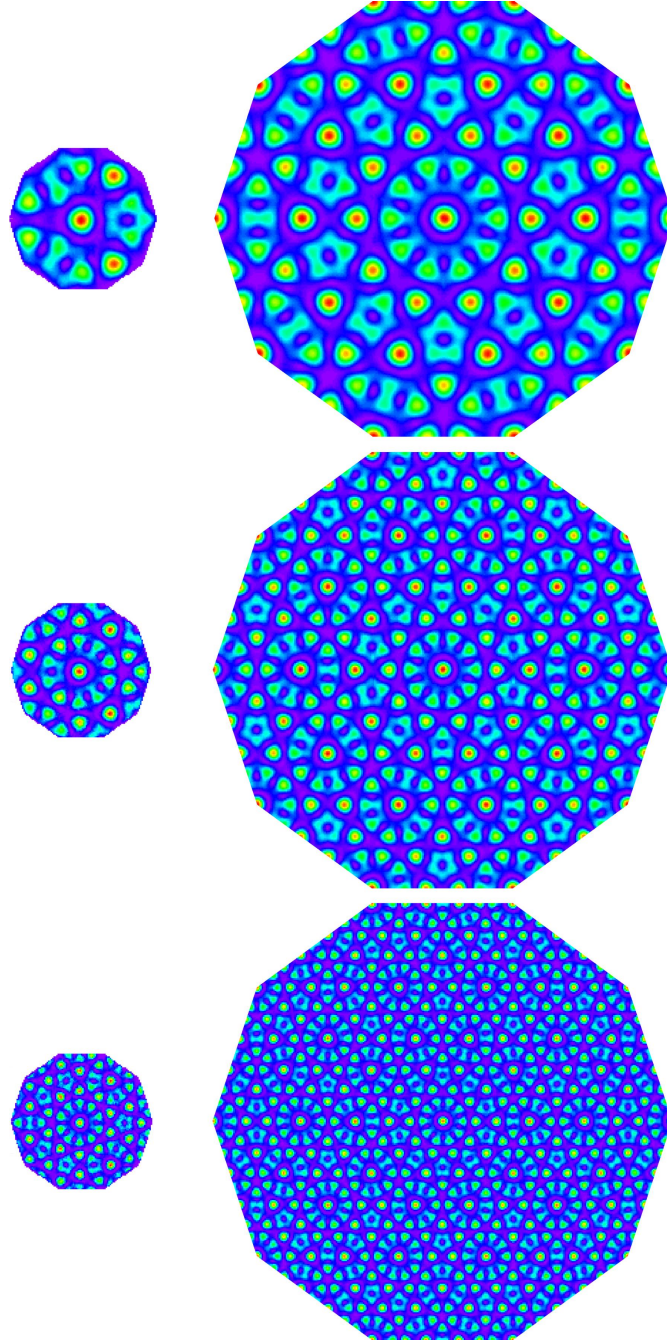


Figure .3: Left column: Simulation results for the decorations of Gummelt decagons of three sizes. The edge length of each decagon grows between two rows with a factor of the golden ratio τ starting from the top. Right column: the corresponding double cartwheel patches from the Gummelt decagons. Deviations from the real substrate potential are below 1%.

potential into account. We define a decagon shaped patch with a value assigned to every position inside the patch. We place the decagons in the same way like the Gummelt decagons with the point decoration to form a double cartwheel structure with a 10-fold rotational symmetry. The value at each position in the double cartwheel is derived by the sum of the values of each decagon contributing to this position divided by the number of overlapping decagons. The value field of the Gummelt decagon can not simply be guessed like the point decoration. Therefore, we derive the field decoration of the Gummelt decagon numerically. For this purpose the decagon is discretized into a two dimensional data field. The double cartwheel is also a discretized data field with values at each point derived from the Gummelt decagon overlaps. We define the energy E of the system by the sum of differences between the derived values in the double cartwheel and the exact values of substrate potential. We obtain a perfect match of the substrate potential with the double cartwheel if the energy is zero $E = 0$. Because of the overlap structure of decagons, a simple minimum search algorithm for the energy E could produce decagons in locked states with $E > 0$. Therefore, we apply a Monte Carlo simulation technique to create a Gummelt decagon which produces a pattern matching the substrate potential. In each Monte Carlo step the value of one randomly chosen point in the Gummelt decagon is altered by a random amount e_0 . Where e_0 is a number randomly chosen from the interval $[-e_{max}, e_{max}]$. Afterwards the double cartwheel is built from the new decagon following the given overlapping rules. Then the energy difference is calculated and the change of the decagon patch is accepted with the usual Monte Carlo criterion.

$$A = \min\{1, \exp(\frac{-\Delta E}{kT})\} \quad (.1)$$

The temperature of the system is lowered slowly to relax the decagon field to the absolute minimum difference to the substrate potential. While doing so, e_{max} is adjusted to keep an acceptance ratio of $a \approx 0.5$. The Monte Carlo scheme leads to a decagon decoration which produces a double cartwheel in a very good agreement with the substrate potential. We use two bigger Gummelt decagons where the lengths of the decagon edges are increased by a factor of τ and τ^2 respectively. With the bigger decagons we obtain bigger double cartwheels matching the corresponding substrate patches. The three Gummelt decagons and the resulting patches are shown in Fig. 3. As a test, we tried to produce similar decagon patches with a size of the decagon between the small and the medium sized patch.

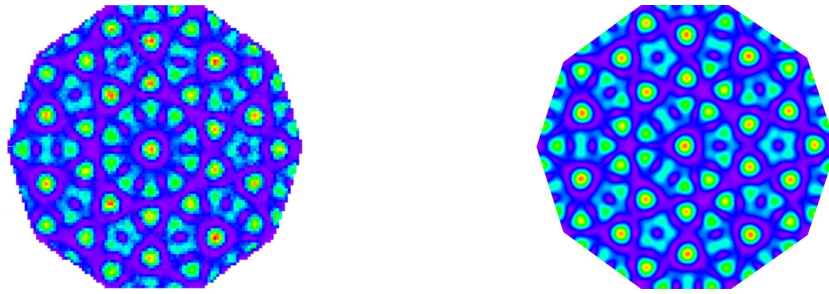


Figure .4: Left : The decoration of the biggest Gummelt decagon obtained by simulation. Right : The decoration of the biggest Gummelt decagon obtained from a second order cartwheel made from the smallest Gummelt decagon obtained by simulation.

The algorithm failed to produce a matching double cartwheel. In this way, we can be sure that we didn't find just a general way to produce an arbitrary patch of potential but a real decomposition of the potential using the basic properties of a quasicrystalline tiling.

The bigger decagons can be build from deflation rules also known for the Gummelt decagons. The deflation rules for decorated Gummelt decagons are much more complicated than for the Penrose tiling as shown by Jeong[98]. Two deflations of the Gummelt decagon are equivalent to one deflation of the Penrose tiling. Instead using the complicated deflation rules of the Gummelt decagon we take advantage of the properties of the cartwheel tilings. The Gummelt decagon corresponds to a first order cartwheel tiling. We know from Fig. .1 how to build a second order cartwheel from overlapping Gummelt decagons. The second order cartwheel stems from two successive deflations of the Penrose tiling or four deflations of the Gummelt decagon tiling. Starting with the Gummelt decagon decoration displayed in the first row in Fig. .3 and create a second order cartwheel, we end up with a double deflated decagon of the same size of the Gummelt decagon displayed at the last row of Fig. .3. In Fig. .4 the Gummelt decagon obtained by simulation and the Gummelt decagon derived from the deflation of the smallest Gummelt decagon are shown. The similarity of both patches is apparent. With the deflation rules one can produce in principle arbitrary huge patches of the substrate.

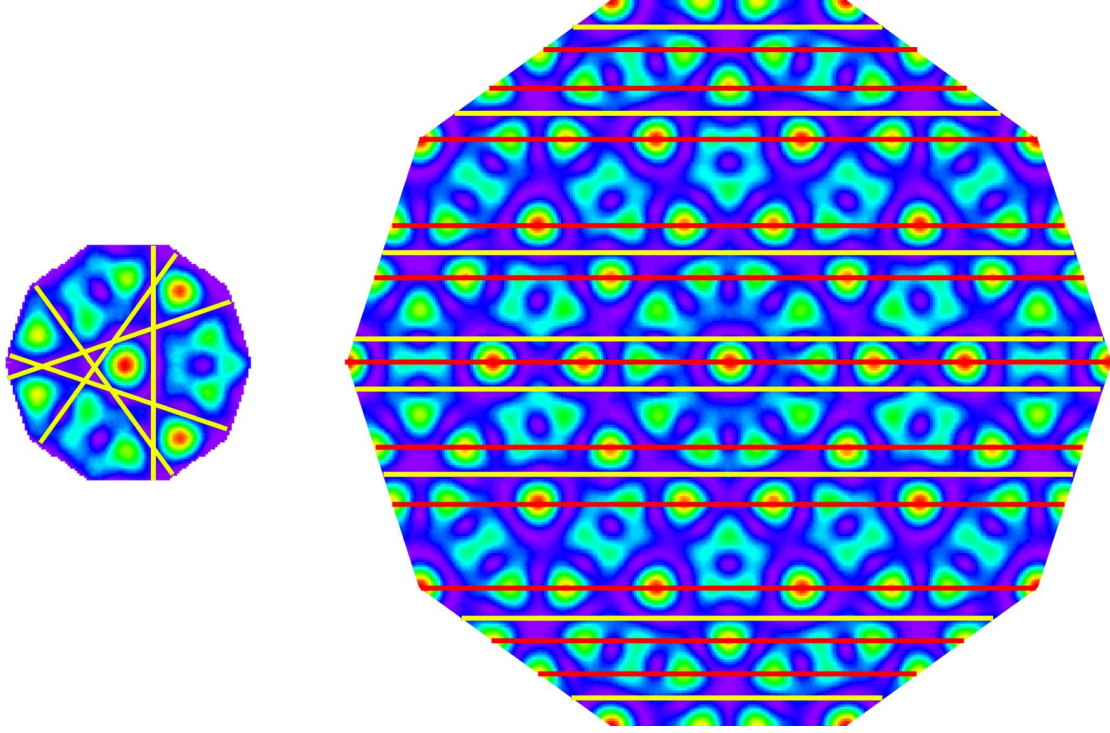


Figure .5: Left : The decoration of the smallest Gummelt decagon with Ammann bars from the middle-C sequence of the first order cartwheel. Right : The horizontal Ammann bars (yellow) and the corresponding shifted Ammann bars (red) from the double cartwheel.

The double Fibonacci sequence found in the substrate is a reminiscence of the double Penrose tiling as an underlying structure of the decagonal substrate. The Amman bar decoration of a cartwheel follows a Fibonacci sequence with the symmetry of the middle- C sequence[78]. In this tiling, the Ammann bars connecting the lines of the lowest potential strengths and not the positions of the minima. The bars connecting the strongest minima follow the Fibonacci sequence of the projection method. Both Fibonacci sequences are just shifted against each other by a short distance S what we can see in our substrate potential. On the left panel of Fig. .5 the Ammann bar decoration of the smallest Gummelt decagon is shown with yellow lines. On the right panel the double cartwheel with the Amman bar decoration is also displayed with yellow lines for clarity in the horizontal direction only. The red lines are the shifted Ammann bars which perfectly connect the minima positions.

List of publications

[A] Philipp Kählitz and Holger Stark. Phase ordering of hard needles on a quasicrystalline substrate. *J. Chem. Phys.*, **17**, 174705 (2012)

[B] Philipp Kählitz, Martin Schoen and Holger Stark. Clustering and mobility of hard rods in a quasicrystalline substrate potential. *J. Chem. Phys.*, accepted (2012).

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Bibliography

- [1] R Addou, A K Shukla, S Alarcon Villaseca, E Gaudry, Th Deniozou, M Heggen, M Feuerbacher, R Widmer, O Gröning, V Fournee, J-M Dubois, and J Ledieu. Lead adsorption on the Al₁₃Co₄(100) surface: heterogeneous nucleation and pseudomorphic growth. *New J. Phys.*, 13(10):103011, 2011. URL <http://stacks.iop.org/1367-2630/13/i=10/a=103011>. 7
- [2] R. Agra, F. van Wijland, and E. Trizac. Theory of Orientational Ordering in Colloidal Molecular Crystals. *Phys. Rev. Lett.*, 93:018304, Jul 2004. doi: 10.1103/PhysRevLett.93.018304. URL <http://link.aps.org/doi/10.1103/PhysRevLett.93.018304>. 10
- [3] B. J. Alder and T. E. Wainwright. Decay of the Velocity Autocorrelation Function. *Phys. Rev. A*, 1:18–21, Jan 1970. doi: 10.1103/PhysRevA.1.18. URL <http://link.aps.org/doi/10.1103/PhysRevA.1.18>. 8
- [4] van Blaaderen Alfons, Ruel Rene, and Wiltzius Pierre. Template-directed colloidal crystallization. *Nature*, 385(6614):321–324, jan 1997. doi: 10.1038/385321a0. 10.1038/385321a0. 9
- [5] Michael P. Allen. Molecular simulation and theory of the isotropic–nematic interface. *J. Chem. Phys.*, 112(12):5447–5453, 2000. doi: 10.1063/1.481112. URL <http://link.aip.org/link/?JCP/112/5447/1>. 31
- [6] P. Allen and D.J. Tildesley. *Computer Simulation of Liquids*. Oxford Science Publications. Oxford University Press, USA, 1989. ISBN 9780198556459. URL <http://books.google.de/books?id=032VXB9e5P4C>. 36
- [7] P. Allen and D.J. Tildesley. *Computer Simulation in Chemical Physics*. NATO ASI series: Mathematical and physical sciences. Kluwer Academic Publishers, 1993. ISBN 9780792322832. URL <http://books.google.de/books?id=VjZTL3yKwm4C>. 35

- [8] Robert Ammann, Branko Grünbaum, and G. Shephard. Aperiodic tiles. *Discrete & Computational Geometry*, 8:1–25, 1992. ISSN 0179-5376. URL <http://dx.doi.org/10.1007/BF02293033>. 10.1007/BF02293033. 20
- [9] A. Ashkin. Forces of a single-beam gradient laser trap on a dielectric sphere in the ray optics regime. *Biophys. J.*, 61(2):569–582, 1992. ISSN 0006-3495. doi: 10.1016/S0006-3495(92)81860-X. URL <http://www.sciencedirect.com/science/article/pii/S000634959281860X>. 9
- [10] Stefan Auer and Daan Frenkel. QUANTITATIVE PREDICTION OF CRYSTAL-NUCLEATION RATES FOR SPHERICAL COLLOIDS: A Computational Approach. *Annual Review of Physical Chemistry*, 55(1):333–361, 2004. doi: 10.1146/annurev.physchem.55.091602.094402. URL <http://www.annualreviews.org/doi/abs/10.1146/annurev.physchem.55.091602.094402>. PMID: 15117256. 8
- [11] Michael Baake. A guide to mathematical quasicrystals. *arXiv*, 1999. URL <http://arxiv.org/abs/math-ph/9901014>. 20
- [12] D. Babić, C. Schmitt, and C. Bechinger. Colloids as model systems for problems in statistical physics. *Chaos: An Interdisciplinary Journal of Nonlinear Science*, 15(2):026114, 2005. doi: 10.1063/1.1839311. URL <http://link.aip.org/link/?CHA/15/026114/1>. 8
- [13] Martin A. Bates and Daan Frenkel. Phase behavior of two-dimensional hard rod fluids. *J. Chem. Phys.*, 112(22):10034–10041, 2000. doi: 10.1063/1.481637. URL <http://link.aip.org/link/?JCP/112/10034/1>. 38
- [14] C. Bechinger, M. Brunner, and P. Leiderer. Phase Behavior of Two-Dimensional Colloidal Systems in the Presence of Periodic Light Fields. *Phys. Rev. Lett.*, 86:930–933, Jan 2001. doi: 10.1103/PhysRevLett.86.930. URL <http://link.aps.org/doi/10.1103/PhysRevLett.86.930>. 10
- [15] R. E. Belardinelli and V. D. Pereyra. Wang-Landau algorithm: A theoretical analysis of the saturation of the error. *J. Chem. Phys.*, 127(18):184105, 2007. doi: 10.1063/1.2803061. URL <http://link.aip.org/link/?JCP/127/184105/1>. 55

-
- [16] R. E. Belardinelli and V. D. Pereyra. Fast algorithm to calculate density of states. *Phys. Rev. E*, 75:046701, Apr 2007. doi: 10.1103/PhysRevE.75.046701. URL <http://link.aps.org/doi/10.1103/PhysRevE.75.046701>. 55
- [17] R. E. Belardinelli, S. Manzi, and V. D. Pereyra. Analysis of the convergence of the $1/t$ and Wang-Landau algorithms in the calculation of multidimensional integrals. *Phys. Rev. E*, 78:067701, Dec 2008. doi: 10.1103/PhysRevE.78.067701. URL <http://link.aps.org/doi/10.1103/PhysRevE.78.067701>. 55
- [18] B. Bilki, M. Erbudak, M. Mungan, and Y. Weisskopf. Structure formation of a layer of adatoms on a quasicrystalline substrate: Molecular dynamics study. *Phys. Rev. B*, 75(4):045437, 2007. 7
- [19] K. Binder and A. Baumgärtner. *Applications of the Monte Carlo method in statistical physics*. Topics in current physics. Springer-Verlag, 1987. ISBN 9780387176505. URL <http://books.google.de/books?id=EKjvAAAAMAAJ>. 46
- [20] K. Binder and D.W. Heermann. *Monte Carlo simulation in statistical physics*. Number 80 in Springer series in solid state sciences. Springer, Berlin, Heidelberg,D, 4., enl. edition, 2002. ISBN 3-540-43221-3. URL <http://www.bibsonomy.org/bibtex/2218df9e84a73895a2d4d26cf6a823cbd/lemming>. 35
- [21] Alexey Bobrovsky, Alexander Ryabchun, and Valery Shibaev. Liquid crystals photoalignment by films of side-chain azobenzene-containing polymers with different molecular structure. *J. Photochem. Photobio. A*, 218(1):137–142, 2011. ISSN 1010-6030. doi: 10.1016/j.jphotochem.2010.12.013. URL <http://www.sciencedirect.com/science/article/pii/S1010603010005186>. 31
- [22] J. P. Bramble, S. D. Evans, J. R. Henderson, C. Anquetil, D. J. Cleaver, and N. J. Smith. Nematic liquid crystal alignment on chemical patterns. *Liquid Crystals*, 34(9):1059–1069, 2007. doi: 10.1080/02678290701614665. URL <http://www.tandfonline.com/doi/abs/10.1080/02678290701614665>. 31

- [23] Matthias Brunner and Clemens Bechinger. Phase Behavior of Colloidal Molecular Crystals on Triangular Light Lattices. *Phys. Rev. Lett.*, 88:248302, May 2002. doi: 10.1103/PhysRevLett.88.248302. URL <http://link.aps.org/doi/10.1103/PhysRevLett.88.248302>. 10
- [24] Brunner M. and Bechinger C. *Colloidal systems in intense, two-dimensional laser fields Trends in Colloid and Interface Science XVI*, volume 123 of *Progress in Colloid and Polymer Science*, pages 156–159. Springer Berlin / Heidelberg, 2004. ISBN 978-3-540-00553-7. doi: 10.1007/978-3-540-36462-7_35. 10
- [25] P. Bruno. Absence of Spontaneous Magnetic Order at Nonzero Temperature in One- and Two-Dimensional Heisenberg and XY Systems with Long-Range Interactions. *Phys. Rev. Lett.*, 87:137203, Sep 2001. doi: 10.1103/PhysRevLett.87.137203. URL <http://link.aps.org/doi/10.1103/PhysRevLett.87.137203>. 32
- [26] Bryan-Brown G. P., Brown C. V., Sage I. C., and Hui V. C. Voltage-dependent anchoring of a nematic liquid crystal on a grating surface. *Nature*, 392(6674):365–367, mar 1998. ISSN 0028-0836. doi: 10.1038/32849. 10.1038/32849. 31
- [27] P. A. Buining and H. N. W. Lekkerkerker. Isotropic-nematic phase separation of a dispersion of organophilic boehmite rods. *J. Phys. Chem.*, 97(44): 11510–11516, 1993. doi: 10.1021/j100146a027. URL <http://pubs.acs.org/doi/abs/10.1021/j100146a027>. 31
- [28] Michael M. Burns, Jean-Marc Fournier, and Jene A. Golovchenko. Optical Matter: Crystallization and Binding in Intense Optical Fields. *Science*, 249(4970):749–754, 1990. doi: 10.1126/science.249.4970.749. URL <http://www.sciencemag.org/content/249/4970/749.abstract>. 9
- [29] Bawden F. C., Pirie N. W., Bernal J. D., and Fankuchen I. Liquid Crystalline Substances from Virus-infected Plants. *Nature*, 138:1051–1052, 1936. 31
- [30] J. Chakrabarti, H. R. Krishnamurthy, A. K. Sood, and S. Sengupta. Reentrant Melting in Laser Field Modulated Colloidal Suspensions. *Phys. Rev.*

- Lett.*, 75:2232–2235, Sep 1995. doi: 10.1103/PhysRevLett.75.2232. URL <http://link.aps.org/doi/10.1103/PhysRevLett.75.2232>. 10
- [31] Shuang Chen and Jing Ma. Substituent effects on packing entropy and film morphologies in the nucleation of functionalized pentacenes on SiO₂ substrate: Molecular dynamics simulations. *J. Chem. Phys.*, 137(7):074708, 2012. doi: 10.1063/1.4745899. URL <http://link.aip.org/link/?JCP/137/074708/1>. 31
- [32] David L. Cheung. Monte Carlo simulations of liquid crystals between microstructured substrates. *J. Chem. Phys.*, 128(19):194902, 2008. doi: 10.1063/1.2918737. URL <http://link.aip.org/link/?JCP/128/194902/1>. 31
- [33] Aslam Chowdhury, Bruce J. Ackerson, and Noel A. Clark. Laser-Induced Freezing. *Phys. Rev. Lett.*, 55:833–836, Aug 1985. doi: 10.1103/PhysRevLett.55.833. URL <http://link.aps.org/doi/10.1103/PhysRevLett.55.833>. 10
- [34] Eric Cockayne and Mike Widom. Structure and phason energetics of Al-Co decagonal phases. *Philosophical Magazine A*, 77(3):593–619, 1998. doi: 10.1080/01418619808224071. URL <http://www.tandfonline.com/doi/abs/10.1080/01418619808224071>. 21
- [35] W T Coffey, Yu P Kalmykov, and S V Titov. Langevin equation method for the rotational Brownian motion and orientational relaxation in liquids: II. Symmetrical top molecules. *Journal of Physics A: Mathematical and General*, 36(18):4947, 2003. URL <http://stacks.iop.org/0305-4470/36/i=18/a=301>. 50
- [36] I Commission on Aperiodic Crystals. Report of the Executive Committee for 1991. *Acta Cryst. A*, 48(6):922–946, Nov 1992. doi: 10.1107/S0108767392008328. URL <http://dx.doi.org/10.1107/S0108767392008328>. 6
- [37] Cronholm144. Creative Commons 3.0 by. *Wikimedia Commons*, 2007. 20, 109

- [38] Stefano Curtarolo, Wahyu Setyawan, Nicola Ferralis, Renee D. Diehl, and Milton W. Cole. Evolution of Topological Order in Xe Films on a Quasicrystal Surface. *Phys. Rev. Lett.*, 95:136104, Sep 2005. doi: 10.1103/PhysRevLett.95.136104. URL <http://link.aps.org/doi/10.1103/PhysRevLett.95.136104>. 7
- [39] Stefano Curtarolo, Wahyu Setyawan, and Renee D. Diehl. Gas-Surface Interactions on Quasicrystals. *Isr. J. Chem.*, 51(11-12):1304–1313, 2011. ISSN 1869-5868. doi: 10.1002/ijch.201100129. URL <http://dx.doi.org/10.1002/ijch.201100129>. 7, 99
- [40] N.G. de Bruijn. Algebraic theory of Penrose’s non-periodic tilings of the plane I and II. *Kon. Nederl. Akad. Wetensch. A*, 84:39–66, 1981. 22
- [41] E. Martin del Rio, M. M. Telo da Gama, E. de Miguel, and L. F. Rull. Wetting and interfacial order at nematic free surfaces. *EPL*, 35(3):189, 1996. URL <http://stacks.iop.org/0295-5075/35/i=3/a=189>. 30
- [42] Th. Deniozou, J. Ledieu, V. Fournée, D. M. Wu, T. A. Lograsso, H. I. Li, and R. D. Diehl. Aperiodic and modulated Pb thin films on fivefold icosahedral Al-Cu-Fe and Al(111): Tailoring the structure of Pb. *Phys. Rev. B*, 79:245405, Jun 2009. doi: 10.1103/PhysRevB.79.245405. URL <http://link.aps.org/doi/10.1103/PhysRevB.79.245405>. 7
- [43] N. Denkov, O. Veleev, P. Kralchevski, I. Ivanov, H. Yoshimura, and K. Nagayama. Mechanism of formation of two-dimensional crystals from latex particles on substrates. *Langmuir*, 8(12):3183–3190, 1992. doi: 10.1021/la00048a054. URL <http://pubs.acs.org/doi/abs/10.1021/la00048a054>. 9
- [44] J.K.G. Dhont. *An Introduction to Dynamics of Colloids*. Studies in Interface Science. Elsevier Science, 1996. ISBN 9780444820099. URL <http://books.google.de/books?id=mmArTF5SJ9oC>. 49
- [45] R D Diehl, J Ledieu, N Ferralis, A W Szmodis, and R McGrath. Low-energy electron diffraction from quasicrystal surfaces. *Journal of Physics: Condensed Matter*, 15(3):R63, 2003. URL <http://stacks.iop.org/0953-8984/15/i=3/a=201>. 6

-
- [46] R. D. Diehl, N. Ferralis, K. Pussi, M. W. Cole, W. Setyawan, and S. Curtarolo. The ordering of a Xe monolayer on quasicrystalline Al-Ni-Co. *Philos. Mag.*, 86(6-8):863–868, 2006. doi: 10.1080/14786430500227970. URL <http://www.tandfonline.com/doi/abs/10.1080/14786430500227970>. 7
- [47] R. D. Diehl, W. Setyawan, N. Ferralis, R. A. Trasca, M. W. Cole, and S. Curtarolo. Ordering of rare gas films on a decagonal Al-Ni-Co quasicrystal. *Philos. Mag.*, 87(18-21):2973–2980, 2007. doi: 10.1080/14786430701370843. URL <http://www.tandfonline.com/doi/abs/10.1080/14786430701370843>. 7
- [48] R D Diehl, W Setyawan, and S Curtarolo. Gas adsorption on quasicrystalline surfaces. *J. Phys.: Cond. Matt.*, 20(31):314007, 2008. URL <http://stacks.iop.org/0953-8984/20/i=31/a=314007>. 7
- [49] Marjolein Dijkstra, René van Roij, and Robert Evans. Wetting and capillary nematization of a hard-rod fluid: A simulation study. *Phys. Rev. E*, 63:051703, Apr 2001. doi: 10.1103/PhysRevE.63.051703. URL <http://link.aps.org/doi/10.1103/PhysRevE.63.051703>. 31
- [50] J. R. Dorfman and E. G. D. Cohen. Velocity-Correlation Functions in Two and Three Dimensions: Low Density. *Phys. Rev. A*, 6:776–790, Aug 1972. doi: 10.1103/PhysRevA.6.776. URL <http://link.aps.org/doi/10.1103/PhysRevA.6.776>. 8
- [51] Dubost B., Lang J-M., Tanaka M., Sainfort P., and Audier M. Large AlCuLi single quasicrystals with triacontahedral solidification morphology. *Nature*, 324(6092):48–50, nov 1986. doi: 10.1038/324048a0. 6
- [52] T Duguet, J Ledieu, J M Dubois, and V Fournee. Surface alloys as interfacial layers between quasicrystalline and periodic materials. *J. Phys.: Condensed Matter*, 20(31):314009, 2008. URL <http://stacks.iop.org/0953-8984/20/i=31/a=314009>. 1
- [53] Samir El Shawish, Jure Dobnikar, and Emmanuel Trizac. Ground states of colloidal molecular crystals on periodic substrates. *Soft Matt.*, 4:1491–1498, 2008. doi: 10.1039/B801907J. URL <http://dx.doi.org/10.1039/B801907J>. 10

- [54] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen. Asymptotic Time Behavior of Correlation Functions. I. Kinetic Terms. *Phys. Rev. A*, 4:2055–2065, Nov 1971. doi: 10.1103/PhysRevA.4.2055. URL <http://link.aps.org/doi/10.1103/PhysRevA.4.2055>. 8
- [55] N. Ferralis, R. D. Diehl, K. Pussi, M. Lindroos, I. Fisher, and C. J. Jenks. Low-energy electron diffraction study of Xe adsorption on the ten-fold decagonal Al-Ni-Co quasicrystal surface. *Phys. Rev. B*, 69:075410, Feb 2004. doi: 10.1103/PhysRevB.69.075410. URL <http://link.aps.org/doi/10.1103/PhysRevB.69.075410>. 7
- [56] N. Ferralis, K. Pussi, E. J. Cox, M. Gierer, J. Ledieu, I. R. Fisher, C. J. Jenks, M. Lindroos, R. McGrath, and R. D. Diehl. Structure of the tenfold *d*-Al-Ni-Co quasicrystal surface. *Phys. Rev. B*, 69:153404, Apr 2004. doi: 10.1103/PhysRevB.69.153404. URL <http://link.aps.org/doi/10.1103/PhysRevB.69.153404>. 1, 6
- [57] Aleksander E. Filippov, Andrea Vanossi, and Michael Urbakh. Origin of Friction Anisotropy on a Quasicrystal Surface. *Phys. Rev. Lett.*, 104:074302, Feb 2010. doi: 10.1103/PhysRevLett.104.074302. URL <http://link.aps.org/doi/10.1103/PhysRevLett.104.074302>. 1, 7
- [58] J. M. Fish and R. L. C. Vink. Isotropic-to-nematic transition in confined liquid crystals: An essentially nonuniversal phenomenon. *Phys. Rev. E*, 81:021705, Feb 2010. doi: 10.1103/PhysRevE.81.021705. URL <http://link.aps.org/doi/10.1103/PhysRevE.81.021705>. 32
- [59] V Fournée and P A Thiel. New phenomena in epitaxial growth: solid films on quasicrystalline substrates. *J. Phys. D: Appl. Phys.*, 38(6):R83, 2005. URL <http://stacks.iop.org/0022-3727/38/i=6/a=R01>. 7
- [60] V. Fournée, T. C. Cai, A. R. Ross, T. A. Lograsso, J. W. Evans, and P. A. Thiel. Nucleation and growth of Ag films on a quasicrystalline AlPdMn surface. *Phys. Rev. B*, 67:033406, Jan 2003. doi: 10.1103/PhysRevB.67.033406. URL <http://link.aps.org/doi/10.1103/PhysRevB.67.033406>. 1, 7

-
- [61] Seth Fraden, Georg Maret, D. L. D. Caspar, and Robert B. Meyer. Isotropic-nematic phase transition and angular correlations in isotropic suspensions of tobacco mosaic virus. *Phys. Rev. Lett.*, 63:2068–2071, Nov 1989. doi: 10.1103/PhysRevLett.63.2068. URL <http://link.aps.org/doi/10.1103/PhysRevLett.63.2068>. 31
- [62] K. J. Franke, H. R. Sharma, W. Theis, P. Gille, P. Ebert, and K. H. Rieder. Quasicrystalline Epitaxial Single Element Monolayers on Icosahedral Al-Pd-Mn and Decagonal Al-Ni-Co Quasicrystal Surfaces. *Phys. Rev. Lett.*, 89(15), 10 2002. 1
- [63] K. J. Franke, H. R. Sharma, W. Theis, P. Gille, Ph. Ebert, and K. H. Rieder. Quasicrystalline Epitaxial Single Element Monolayers on Icosahedral Al-Pd-Mn and Decagonal Al-Ni-Co Quasicrystal Surfaces. *Phys. Rev. Lett.*, 89:156104, Sep 2002. doi: 10.1103/PhysRevLett.89.156104. URL <http://link.aps.org/doi/10.1103/PhysRevLett.89.156104>. 7
- [64] K. J. Franke, P. Gille, K.-H. Rieder, and W. Theis. Achieving Epitaxy between Incommensurate Materials by Quasicrystalline Interlayers. *Phys. Rev. Lett.*, 99:036103, Jul 2007. doi: 10.1103/PhysRevLett.99.036103. URL <http://link.aps.org/doi/10.1103/PhysRevLett.99.036103>. 7
- [65] D. Frenkel and R. Eppenga. Evidence for algebraic orientational order in a two-dimensional hard-core nematic. *Phys. Rev. A*, 31:1776–1787, Mar 1985. doi: 10.1103/PhysRevA.31.1776. URL <http://link.aps.org/doi/10.1103/PhysRevA.31.1776>. 2, 37, 57, 61, 62, 64
- [66] Xiujun Fu, Zhilin Hou, and Youyan Liu. Relationship between Penrose vertices and decagonal covering configurations. *Solid State Communications*, 128(2-3):75–78, 2003. ISSN 0038-1098. doi: 10.1016/S0038-1098(03)00620-3. URL <http://www.sciencedirect.com/science/article/pii/S0038109803006203>. 27
- [67] J.-C. P. Gabriel and P. Davidson. New Trends in Colloidal Liquid Crystals Based on Mineral Moieties. *Adv. Mat.*, 12(1):9–20, 2000. ISSN 1521-4095. doi: 10.1002/(SICI)1521-4095(200001)12:1. URL [http://dx.doi.org/10.1002/\(SICI\)1521-4095\(200001\)12:1<9::AID-ADMA9>3.0.CO](http://dx.doi.org/10.1002/(SICI)1521-4095(200001)12:1<9::AID-ADMA9>3.0.CO). 31

- [68] F Gähler and J Rhyner. Equivalence of the generalised grid and projection methods for the construction of quasiperiodic tilings. *Journal of Physics A: Mathematical and General*, 19(2):267, 1986. URL <http://stacks.iop.org/0305-4470/19/i=2/a=020>. 21
- [69] Franz Gähler, Michael Baake, and Martin Schlottmann. Binary tiling quasicrystals and matching rules. *Phys. Rev. B*, 50:12458–12467, Nov 1994. doi: 10.1103/PhysRevB.50.12458. URL <http://link.aps.org/doi/10.1103/PhysRevB.50.12458>. 21
- [70] P.G. Gennes and J. Prost. *The physics of liquid crystals*. Clarendon press, 1993. 2, 29
- [71] Glotzer Sharon C. and Keys Aaron S. Materials science: A tale of two tilings. *Nature*, 454(7203):420–421, jul 2008. ISSN 0028-0836. doi: 10.1038/454420a. 10.1038/454420a. 2, 11
- [72] A. I. Goldman and R. F. Kelton. Quasicrystals and crystalline approximants. *Rev. Mod. Phys.*, 65:213–230, Jan 1993. doi: 10.1103/RevModPhys.65.213. URL <http://link.aps.org/doi/10.1103/RevModPhys.65.213>. 56
- [73] James P. Gordon. Radiation Forces and Momenta in Dielectric Media. *Phys. Rev. A*, 8:14–21, Jul 1973. doi: 10.1103/PhysRevA.8.14. URL <http://link.aps.org/doi/10.1103/PhysRevA.8.14>. 1, 9
- [74] H. Graf and H. Löwen. Phase diagram of tobacco mosaic virus solutions. *Phys. Rev. E*, 59(2), 2 1999. 31
- [75] C.G. Gray and K.E. Gubbins. *Theory of Molecular Fluids: I: Fundamentals*. International Series of Monographs on Chemistry. OUP Oxford, 1984. ISBN 9780198556022. URL <http://books.google.de/books?id=3mz2RcnnMGwC>. 46
- [76] Manuel Greschek and Martin Schoen. Orientational prewetting of planar solid substrates by a model liquid crystal. *J. Chem. Phys.*, 135(20):204702, 2011. doi: 10.1063/1.3660377. URL <http://link.aip.org/link/?JCP/135/204702/1>. 31

- [77] Grier David G. A revolution in optical manipulation. *Nature*, 424(6950): 810–816, aug 2003. ISSN 0028-0836. doi: 10.1038/nature01935. 10.1038/nature01935. 9
- [78] Branko Grünbaum and G.C. Shephard. *Tilings and patterns*. New York: W. H. Freeman and Company. IX, 700 p., 1987. 18, 22, 25, 101, 106
- [79] P. Gummelt. Penrose tilings as coverings of congruent decagons. *Geometriae Dedicata*, 62(1):1–17, 1996. 27, 101
- [80] P. Gummelt. Decagon covering model and equivalent HBS-tiling model. *Zeitschrift für Kristallographie*, 221(8):582–588, 2006. ISSN 2194-4946. doi: 10.1524/zkri.2006.221.8.582. doi: 10.1524/zkri.2006.221.8.582. 27
- [81] Vinay K. Gupta and Nicholas L. Abbott. Design of Surfaces for Patterned Alignment of Liquid Crystals on Planar and Curved Substrates. *Science*, 276(5318):1533–1536, 1997. doi: 10.1126/science.276.5318.1533. URL <http://www.sciencemag.org/content/276/5318/1533.abstract>. 31
- [82] B. I. Halperin and D. R. Nelson. Theory of Two-Dimensional Melting. *Phys. Rev. Lett.*, 41:121–124, 1978. 32
- [83] J. P. Hansen and I. McDonald. *Theory of Simple Liquids*. Academic Press Inc., London,UK, 1990. URL <http://www.bibsonomy.org/bibtex/2522326475ad9c92b639d9e4d350043b3/kaigrass>. 49, 56
- [84] E. Harriss, I. Suschko, and F. Gähler. Creative Commons : Attribution-NonCommercial-ShareAlike 2.0. *Tilings Encyclopedia*, 2005-2009. URL <http://tilings.math.uni-bielefeld.de>. 23, 109
- [85] Martin Hasenbusch. The two-dimensional XY model at the transition temperature: a high-precision Monte Carlo study. *J. Phys. A*, 38(26):5869, 2005. URL <http://stacks.iop.org/0305-4470/38/i=26/a=003>. 32
- [86] D.W. Heermann. *Computer Simulation Methods in Theoretical Physics*. Computer simulation methods. Springer, 1990. ISBN 9783540522102. URL <http://books.google.de/books?id=1xSqQgAACAAJ>. 49

- [87] M El Helou, E Lietke, J Helzel, W Heimbrodtt, and G Witte. Structural and optical properties of pentacene films grown on differently oriented ZnO surfaces. *Journal of Physics: Condensed Matter*, 24(44):445012, 2012. URL <http://stacks.iop.org/0953-8984/24/i=44/a=445012>. 99
- [88] R. Hentschke, L. Askadskaya, and J. P. Rabe. A simple model for dense phases of two-dimensional hard rods and its application to mono- and bidisperse alkanes physisorbed on graphite. *J. Chem. Phys.*, 97(9):6901–6909, 1992. doi: 10.1063/1.463643. URL <http://link.aip.org/link/?JCP/97/6901/1>. 31
- [89] D. M. Heyes and A. C. Branka. Monte Carlo as Brownian dynamics. *Molecular Physics*, 94(3):447–454, 1998. doi: 10.1080/002689798167953. URL <http://www.tandfonline.com/doi/abs/10.1080/002689798167953>. 52
- [90] D. M. Heyes and A. C. Branka. More efficient Brownian dynamics algorithms. *Molecular Physics*, 98(23):1949–1960, 2000. doi: 10.1080/00268970009483398. URL <http://www.tandfonline.com/doi/abs/10.1080/00268970009483398>. 52
- [91] Cyril Hilsum. Flat-panel electronic displays: a triumph of physics, chemistry and engineering. *Phil. Trans. R. Soc. A*, 368(1914):1027–1082, 2010. doi: 10.1098/rsta.2009.0247. URL <http://rsta.royalsocietypublishing.org/content/368/1914/1027.abstract>. 2, 30
- [92] J. P. Hoogenboom, A. K. van Langen-Suurling, J. Romijn, and A. van Blaaderen. Epitaxial growth of a colloidal hard-sphere hcp crystal and the effects of epitaxial mismatch on crystal structure. *Phys. Rev. E*, 69:051602, May 2004. doi: 10.1103/PhysRevE.69.051602. URL <http://link.aps.org/doi/10.1103/PhysRevE.69.051602>. 9
- [93] Paul S. Hubbard. Rotational Brownian Motion. *Phys. Rev. A*, 6:2421–2433, Dec 1972. doi: 10.1103/PhysRevA.6.2421. URL <http://link.aps.org/doi/10.1103/PhysRevA.6.2421>. 50
- [94] C. Janot. *Quasicrystals: A Primer*. Monographs on the Physics and Chemistry of Materials. Oxford University Press, USA, 1997. ISBN

9780198565512. URL <http://books.google.de/books?id=dpPePU-xs2oC>. 1, 6, 16, 22
- [95] M.V. Jaric. *Introduction to the mathematics of quasicrystals*. Aperiodicity and order. Academic Press, 1989. ISBN 9780120406029. 15
- [96] M C Jenkins and S U Egelhaaf. Colloidal suspensions in modulated light fields. *J. Phys.: Cond. Matt.*, 20(40):404220, 2008. URL <http://stacks.iop.org/0953-8984/20/i=40/a=404220>. 1, 9, 10
- [97] H.C. Jeong. Comparison of quasi-unit-cell models to Penrose-tile models for decagonal quasicrystals. *J. Alloy. Compd.*, 342(1-2):191–194, 2002. 27
- [98] Hyeong-Chai Jeong. Inflation rule for Gummelt coverings with decorated decagons and its implication for quasi-unit-cell models. *Acta Crystallographica Section A*, 59(4):361–366, Jul 2003. doi: 10.1107/S0108767303012030. URL <http://dx.doi.org/10.1107/S0108767303012030>. 105
- [99] B Jerome. Surface effects and anchoring in liquid crystals. *Rep. Prog. Phys.*, 54(3):391, 1991. URL <http://stacks.iop.org/0034-4885/54/i=3/a=002>. 30
- [100] B Jerome. Interfacial structural transitions in nematic liquid crystals. *Journal of Physics: Condensed Matter*, 6(23A):A269, 1994. URL <http://stacks.iop.org/0953-8984/6/i=23A/a=042>. 30
- [101] B. Jérôme, J. O’Brien, Y. Ouchi, C. Stanners, and Y. R. Shen. Bulk re-orientation driven by orientational transition in a liquid crystal monolayer. *Phys. Rev. Lett.*, 71:758–761, Aug 1993. doi: 10.1103/PhysRevLett.71.758. URL <http://link.aps.org/doi/10.1103/PhysRevLett.71.758>. 30
- [102] P. D. Kaplan, J. L. Rouke, A. G. Yodh, and D. J. Pine. Entropically Driven Surface Phase Separation in Binary Colloidal Mixtures. *Phys. Rev. Lett.*, 72: 582–585, Jan 1994. doi: 10.1103/PhysRevLett.72.582. URL <http://link.aps.org/doi/10.1103/PhysRevLett.72.582>. 8
- [103] K. Kikuchi, M. Yoshida, T. Maekawa, and H. Watanabe. Metropolis Monte Carlo method for Brownian dynamics simulation generalized to include hydrodynamic interactions. *Chem. Phys. Lett.*, 196(1-2):57–61, 1992.

- ISSN 0009-2614. doi: 10.1016/0009-2614(92)85928-4. URL <http://www.sciencedirect.com/science/article/pii/0009261492859284>. 49, 52
- [104] Jongwook Kim, Alexis de la Cotte, Rodolphe Deloncle, Samuel Archambeau, Claudine Biver, Jean-Paul Cano, Khalid Lahlil, Jean-Pierre Boilot, Eric Grelet, and Thierry Gacoin. LaPO₄ Mineral Liquid Crystalline Suspensions with Outstanding Colloidal Stability for Electro-Optical Applications. *Adv. Func. Mat.*, pages n/a–n/a, 2012. ISSN 1616-3028. doi: 10.1002/adfm.201200825. URL <http://dx.doi.org/10.1002/adfm.201200825>. 31
- [105] Kim Jong-Hyun, Yoneya Makoto, and Yokoyama Hiroshi. Tristable nematic liquid-crystal device using micropatterned surface alignment. *Nature*, 420(6912):159–162, nov 2002. ISSN 0028-0836. doi: 10.1038/nature01163. 10.1038/nature01163. 31
- [106] S. Kondrat, A. Poniewierski, and L. Harnau. Nematic liquid crystal in contact with periodically patterned surfaces. *Liquid Crystals*, 32(1):95–105, 2005. doi: 10.1080/02678290512331324039. URL <http://www.tandfonline.com/doi/abs/10.1080/02678290512331324039>. 31
- [107] V. E. Korepin, F. Gähler, and J. Rhyner. Quasiperiodic tilings: a generalized grid-projection method. *Acta Crystallographica Section A*, 44(5):667–672, Sep 1988. doi: 10.1107/S010876738800368X. URL <http://dx.doi.org/10.1107/S010876738800368X>. 21
- [108] A. Refik Kortan, Russell S. Becker, F. A. Thiel, and H. S. Chen. Real-space atomic structure of a two-dimensional decagonal quasicrystal. *Phys. Rev. Lett.*, 64:200–203, Jan 1990. doi: 10.1103/PhysRevLett.64.200. URL <http://link.aps.org/doi/10.1103/PhysRevLett.64.200>. 6
- [109] J M Kosterlitz. The critical properties of the two-dimensional xy model. *J. Phys. C*, 7(6):1046, 1974. URL <http://stacks.iop.org/0022-3719/7/i=6/a=005>. 32
- [110] J. M. Kosterlitz and D. J. Thoules. Ordering, metastability and phase transitions in two-dimensional systems. *J. Phys. C*, 6(7):1181, 1973. URL <http://stacks.iop.org/0022-3719/6/i=7/a=010>. 8, 32

-
- [111] Justus A. Kromer, Michael Schmiedeberg, Johannes Roth, and Holger Stark. What Phasons Look Like: Particle Trajectories in a Quasicrystalline Potential. *Phys. Rev. Lett.*, 108:218301, May 2012. doi: 10.1103/PhysRevLett.108.218301. URL <http://link.aps.org/doi/10.1103/PhysRevLett.108.218301>. 11, 100
- [112] Anke Kuijk, Alfons van Blaaderen, and Arnout Imhof. Synthesis of Monodisperse, Rodlike Silica Colloids with Tunable Aspect Ratio. *J. Am. Chem. Soc.*, 133(8):2346–2349, 2011. doi: 10.1021/ja109524h. URL <http://pubs.acs.org/doi/abs/10.1021/ja109524h>. 31
- [113] D.P. Landau and K. Binder. *A guide to Monte Carlo simulations in statistical physics*. Cambridge Univ Pr, 2005. 54
- [114] D.P. Landau and F. Wang. Determining the density of states for classical statistical models by a flat-histogram random walk. *Computer Physics Communications*, 147(1-2):674–677, 2002. ISSN 0010-4655. doi: 10.1016/S0010-4655(02)00374-0. URL <http://www.sciencedirect.com/science/article/pii/S0010465502003740>. 54
- [115] J. Ledieu, J. T. Hoeft, D. E. Reid, J. A. Smerdon, R. D. Diehl, T. A. Lograsso, A. R. Ross, and R. McGrath. Pseudomorphic Growth of a Single Element Quasiperiodic Ultrathin Film on a Quasicrystal Substrate. *Phys. Rev. Lett.*, 92:135507, Apr 2004. doi: 10.1103/PhysRevLett.92.135507. URL <http://link.aps.org/doi/10.1103/PhysRevLett.92.135507>. 7
- [116] Eun-Kyu Lee and Jong-Hyun Kim. Multistability of nematic liquid crystals realized on microscopic orientation patterns. *J. Appl. Phys.*, 102(3):036102, 2007. doi: 10.1063/1.2767851. URL <http://link.aip.org/link/?JAP/102/036102/1>. 2, 31
- [117] Eun-Kyu Lee and Jong-Hyun Kim. Alignment characteristic of nematic liquid crystals on orientational patterns realized by interfering laser light. *J. Phys. D*, 41(4):045407, 2008. URL <http://stacks.iop.org/0022-3727/41/i=4/a=045407>. 31
- [118] O. Lehmann. Über fließende Krystalle. *Z. Phys. Chem.*, 4:462, 1889. 29

- [119] D. Levine and P.J. Steinhardt. Quasicrystals. I. Definition and structure. *Phys. Rev. B*, 34(2):596, 1986. [15](#), [16](#), [21](#), [22](#)
- [120] L. S. Levitov. Local rules for quasicrystals. *Communications in Mathematical Physics*, 119:627–666, 1988. ISSN 0010-3616. URL <http://dx.doi.org/10.1007/BF01218348>. 10.1007/BF01218348. [20](#)
- [121] L.-S. Li and A.P. Alivisatos. Semiconductor Nanorod Liquid Crystals and Their Assembly on a Substrate. *Adv. Mat.*, 15(5):408–411, 2003. ISSN 1521-4095. doi: 10.1002/adma.200390093. URL <http://dx.doi.org/10.1002/adma.200390093>. [31](#)
- [122] Liang-shi Li, Joost Walda, Liberato Manna, and A. Paul Alivisatos. Semiconductor Nanorod Liquid Crystals. *Nano Let.*, 2(6):557–560, 2002. doi: 10.1021/nl0255146. URL <http://pubs.acs.org/doi/abs/10.1021/nl0255146>. [31](#)
- [123] S. Lim, M. Mihalkovic, and C.L. Henley. Penrose matching rules from realistic potentials in a model system. *Philosophical Magazine*, 88(13-15):1977–1984, 2008. doi: 10.1080/14786430802302026. URL <http://www.tandfonline.com/doi/abs/10.1080/14786430802302026>. [21](#)
- [124] K. Loudiyi and Bruce J. Ackerson. Direct observation of laser induced freezing. *Physica A: Stat. Mech. Appl.*, 184(1-2):1–25, 1992. ISSN 0378-4371. doi: 10.1016/0378-4371(92)90155-J. URL <http://www.sciencedirect.com/science/article/pii/037843719290155J>. [9](#), [10](#)
- [125] Hartmut Löwen. Brownian dynamics of hard spherocylinders. *Phys. Rev. E*, 50:1232–1242, Aug 1994. doi: 10.1103/PhysRevE.50.1232. URL <http://link.aps.org/doi/10.1103/PhysRevE.50.1232>. [50](#)
- [126] Peter J. Lu and Paul J. Steinhardt. Decagonal and Quasi-Crystalline Tilings in Medieval Islamic Architecture. *Science*, 315(5815):1106–1110, 2007. doi: 10.1126/science.1135491. URL <http://www.sciencemag.org/content/315/5815/1106.abstract>. [20](#), [109](#)
- [127] Xuemin Lu, Fuk Kay Lee, Ping Sheng, H. S. Kwok, V. Chigrinov, and Ophelia K. C. Tsui. Substrate patterning for liquid crystal alignment by

- optical interference. *Appl. Phys. Lett.*, 88(24):243508, 2006. doi: 10.1063/1.2209713. URL <http://link.aip.org/link/?APL/88/243508/1>. 31
- [128] Alan L. Mackay. Crystallography and the penrose pattern. *Physica A*, 114(1–3):609–613, 1982. ISSN 0378-4371. doi: 10.1016/0378-4371(82)90359-4. URL <http://www.sciencedirect.com/science/article/pii/0378437182903594>. 5
- [129] Hideatsu Maeda and Yoshiko Maeda. Atomic Force Microscopy Studies for Investigating the Smectic Structures of Colloidal Crystals of β -FeOOH. *Langmuir*, 12(6):1446–1452, 1996. doi: 10.1021/la950495j. URL <http://pubs.acs.org/doi/abs/10.1021/la950495j>. 31
- [130] A. Mauger, G. Zribi, D. L. Mills, and John Toner. Substrate-Induced Orientational Order in the Isotropic Phase of Liquid Crystals. *Phys. Rev. Lett.*, 53:2485–2488, Dec 1984. doi: 10.1103/PhysRevLett.53.2485. URL <http://link.aps.org/doi/10.1103/PhysRevLett.53.2485>. 30
- [131] R.M. Mazo. *Brownian Motion: Fluctuations, Dynamics, and Applications*. International Series of Monographs on Physics. Oxford University Press, USA, 2009. ISBN 9780199556441. URL <http://books.google.de/books?id=LbeN6U9UT3kC>. 49
- [132] R. McGrath, H. R. Sharma, J. A. Smerdon, and J. Ledieu. The memory of surfaces: epitaxial growth on quasi-crystals. *Phil. Trans. R. Soc. A*, 370(1969):2930–2948, 2012. doi: 10.1098/rsta.2011.0220. URL <http://rsta.royalsocietypublishing.org/content/370/1969/2930.abstract>. 1, 7
- [133] Ronan McGrath, Julian Ledieu, Erik J Cox, and Renee D Diehl. Quasicrystal surfaces: structure and potential as templates. *J. Phys.: Cond. Matt.*, 14(4):R119, 2002. URL <http://stacks.iop.org/0953-8984/14/i=4/a=201>. 7
- [134] N. D. Mermin and H. Wagner. Absence of Ferromagnetism or Antiferromagnetism in One- or Two-Dimensional Isotropic Heisenberg Models. *Phys. Rev. Lett.*, 17:1133–1136, Nov 1966. doi: 10.1103/PhysRevLett.17.1133. URL <http://link.aps.org/doi/10.1103/PhysRevLett.17.1133>. 32

- [135] N. David Mermin, David A. Rabson, Daniel S. Rokhsar, and David C. Wright. Stacking quasicrystallographic lattices. *Phys. Rev. B*, 41:10498–10502, May 1990. doi: 10.1103/PhysRevB.41.10498. URL <http://link.aps.org/doi/10.1103/PhysRevB.41.10498>. 27
- [136] Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth, Augusta H. Teller, and Edward Teller. Equation of State Calculations by Fast Computing Machines. *J. Chem. Phys.*, 21(6):1087–1092, 1953. doi: 10.1063/1.1699114. URL <http://link.aip.org/link/?JCP/21/1087/1.56>
- [137] Jules Mikhael, Michael Schmiedeberg, Sebastian Rausch, Johannes Roth, Holger Stark, and Clemens Bechinger. Proliferation of anomalous symmetries in colloidal monolayers subjected to quasiperiodic light fields. *PNAS*, 107(16):7214–7218, 2010. doi: 10.1073/pnas.0913051107. URL <http://www.pnas.org/content/107/16/7214.abstract>. 2, 11
- [138] Jules Mikhael, Gunter Gera, Thomas Bohlein, and Clemens Bechinger. Phase behavior of colloidal monolayers in quasiperiodic light fields. *Soft Matter*, 7:1352–1357, 2011. doi: 10.1039/C0SM00486C. URL <http://dx.doi.org/10.1039/C0SM00486C>. 2, 11, 99
- [139] Mikhael Jules, Roth Johannes, Helden Laurent, and Bechinger Clemens. Archimedean-like tiling on decagonal quasicrystalline surfaces. *Nature*, 454(7203):501–504, jul 2008. ISSN 0028-0836. doi: 10.1038/nature07074. URL http://www.nature.com/nature/journal/v454/n7203/supinfo/nature07074_S1.html. 10.1038/nature07074. 2, 11, 12, 99, 109
- [140] Muhittin Mungan, Yves Weisskopf, and Mehmet Erbudak. Deposition of atoms on a quasicrystalline substrate: Molecular dynamics study in three dimensions. *Phys. Rev. B*, 76:195443, Nov 2007. doi: 10.1103/PhysRevB.76.195443. URL <http://link.aps.org/doi/10.1103/PhysRevB.76.195443>. 7
- [141] David R. Nelson and B. I. Halperin. Dislocation-mediated melting in two dimensions. *Phys. Rev. B*, 19:2457–2484, Mar 1979. doi: 10.1103/PhysRevB.19.2457. URL <http://link.aps.org/doi/10.1103/PhysRevB.19.2457>. 8

-
- [142] M. E. J. Newman and G. T. Barkema. *Monte Carlo methods in statistical physics*. Oxford University Press, USA, 1999. URL <http://www.bibsonomy.org/bibtex/220609e1b7d724f464775785ae2986b1a/josephausterwei>. 35, 46
- [143] Lars Onsager. The effects of the shape on the interaction of colloidal particles. *Annals of the New York Academy of Sciences*, 51(4):627–659, 1949. ISSN 1749-6632. doi: 10.1111/j.1749-6632.1949.tb27296.x. URL <http://dx.doi.org/10.1111/j.1749-6632.1949.tb27296.x>. 32
- [144] Gerald Oster. Two-phase formation in solutions of tobacco mosaic virus and the problem of long-range forces. *J. Gen. Physiol.*, 33(5):445–473, 1950. doi: 10.1085/jgp.33.5.445. URL <http://jgp.rupress.org/content/33/5/445.abstract>. 31
- [145] V. Palermo, F. Biscarini, and C. Zannoni. Abrupt orientational changes for liquid crystals adsorbed on a graphite surface. *Phys. Rev. E*, 57:R2519–R2522, Mar 1998. doi: 10.1103/PhysRevE.57.R2519. URL <http://link.aps.org/doi/10.1103/PhysRevE.57.R2519>. 31
- [146] Jeong Young Park and P A Thiel. Atomic scale friction and adhesion properties of quasicrystal surfaces. *Journal of Physics: Condensed Matter*, 20(31):314012, 2008. URL <http://stacks.iop.org/0953-8984/20/i=31/a=314012>. 1, 7
- [147] Jeong Young Park, D. F. Ogletree, M. Salmeron, R. A. Ribeiro, P. C. Canfield, C. J. Jenks, and P. A. Thiel. High Frictional Anisotropy of Periodic and Aperiodic Directions on a Quasicrystal Surface. *Science*, 309(5739):1354–1356, 2005. doi: 10.1126/science.1113239. URL <http://www.sciencemag.org/content/309/5739/1354.abstract>. 1, 7
- [148] Alessandro Patti and Alejandro Cuetos. Brownian dynamics and dynamic Monte Carlo simulations of isotropic and liquid crystal phases of anisotropic colloidal particles: A comparative study. *Phys. Rev. E*, 86:011403, Jul 2012. doi: 10.1103/PhysRevE.86.011403. URL <http://link.aps.org/doi/10.1103/PhysRevE.86.011403>. 53

- [149] W. Paul and J. Baschnagel. *Stochastic Processes: From Physics to Finance*. Springer, 2000. ISBN 9783540665601. URL <http://books.google.de/books?id=jyWzPtawtP8C>. 49
- [150] Pauling Linus. Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals. *Nature*, 317(6037):512–514, oct 1985. doi: 10.1038/317512a0. 10.1038/317512a0. 6
- [151] R. Penrose. Pentaplexity A Class of Non-Periodic Tilings of the Plane. *The Mathematical Intelligencer*, 2:32–37, 1979. ISSN 0343-6993. URL <http://dx.doi.org/10.1007/BF03024384>. 10.1007/BF03024384. 20, 22
- [152] Pawel Pieranski, L. Strzelecki, and B. Pansu. Thin Colloidal Crystals. *Phys. Rev. Lett.*, 50:900–903, Mar 1983. doi: 10.1103/PhysRevLett.50.900. URL <http://link.aps.org/doi/10.1103/PhysRevLett.50.900>. 8
- [153] Pieranski, P., Strzelecki, L., and Friedel, J. Observation of edge dislocations in ordered polystyrene latexes. *J. Phys. France*, 40(9):853–859, 1979. doi: 10.1051/jphys:01979004009085300. URL <http://dx.doi.org/10.1051/jphys:01979004009085300>. 8
- [154] P. Poulain, F. Calvo, R. Antoine, M. Broyer, and Ph. Dugourd. Performances of Wang-Landau algorithms for continuous systems. *Phys. Rev. E*, 73:056704, May 2006. doi: 10.1103/PhysRevE.73.056704. URL <http://link.aps.org/doi/10.1103/PhysRevE.73.056704>. 54
- [155] K Pussi, M Gierer, and R D Diehl. The uniaxially aperiodic structure of a thin Cu film on fivefold i-AlPdMn. *J. Phys. : Cond. Matt.*, 21(47):474213, 2009. URL <http://stacks.iop.org/0953-8984/21/i=47/a=474213>. 7
- [156] Tie-Zheng Qian and Ping Sheng. Orientational states and phase transitions induced by microtextured substrates. *Phys. Rev. E*, 55:7111–7120, Jun 1997. doi: 10.1103/PhysRevE.55.7111. URL <http://link.aps.org/doi/10.1103/PhysRevE.55.7111>. 31
- [157] Michael Reichert and Franz Gähler. Cluster model of decagonal tilings. *Phys. Rev. B*, 68:214202, Dec 2003. doi: 10.1103/PhysRevB.68.214202. URL <http://link.aps.org/doi/10.1103/PhysRevB.68.214202>. 27

-
- [158] C. Reichhardt and C. J. Olson Reichhardt. Dynamical Ordering and Directional Locking for Particles Moving over Quasicrystalline Substrates. *Phys. Rev. Lett.*, 106:060603, Feb 2011. doi: 10.1103/PhysRevLett.106.060603. URL <http://link.aps.org/doi/10.1103/PhysRevLett.106.060603>. 11
- [159] C. Reichhardt and C. J. Olson Reichhardt. Ordering and melting in colloidal molecular crystal mixtures. *Phys. Rev. E*, 71:062403, Jun 2005. doi: 10.1103/PhysRevE.71.062403. URL <http://link.aps.org/doi/10.1103/PhysRevE.71.062403>. 10
- [160] Friedrich Reinitzer. Beiträge zur Kenntniss des Cholesterins. *Monatshefte für Chemie / Chemical Monthly*, 9:421–441, 1888. ISSN 0026-9247. URL <http://dx.doi.org/10.1007/BF01516710>. 10.1007/BF01516710. 29
- [161] Clifford A. Reiter. Atlas of quasicrystalline tilings. *Chaos, Solitons & Fractals*, 14(7):937–963, 2002. ISSN 0960-0779. doi: 10.1016/S0960-0779(02)00045-0. URL <http://www.sciencedirect.com/science/article/pii/S0960077902000450>. 20
- [162] Flavio Romano, Cristiano De Michele, Davide Marenduzzo, and Eduardo Sanz. Monte Carlo and event-driven dynamics of Brownian particles with orientational degrees of freedom. *J. Chem. Phys.*, 135(12):124106, 2011. doi: 10.1063/1.3629452. URL <http://link.aip.org/link/?JCP/135/124106/1>. 53
- [163] Jörg Rottler, Michael Greenwood, and Benedikt Ziebarth. Morphology of monolayer films on quasicrystalline surfaces from the phase field crystal model. *J. Phys.: Cond. Matt.*, 24(13):135002, 2012. URL <http://stacks.iop.org/0953-8984/24/i=13/a=135002>. 11
- [164] W.B. Russel, D.A. Saville, and W.R. Schowalter. *Colloidal Dispersions*. Cambridge Monographs on Mechanics & Applied Mathematics. Cambridge University Press, 1992. ISBN 9780521426008. URL <http://books.google.de/books?id=3shp8Kl6YoUC>. 1, 8
- [165] Panikkanvalappil Sajanalal, Theruvakkattil Sreeprasad, Akshaya Samal, and Thalappil Pradeep. Anisotropic nanomaterials: structure, growth, as-

- pembly, and functions.
- Nano Rev.*
- , 2(0):5883, 2011. URL
- <http://www.nano-reviews.net/index.php/nano/article/view/5883>
- . 1, 31
- [166] E. Sanz and D. Marenduzzo. Dynamic Monte Carlo versus Brownian dynamics: A comparison for self-diffusion and crystallization in colloidal fluids. *J. Chem. Phys.*, 132(19):194102, 2010. doi: 10.1063/1.3414827. URL <http://link.aip.org/link/?JCP/132/194102/1>. 53
- [167] M. Schmiedeberg. *Colloidal particles on quasicrystalline substrates*. PhD thesis, TU Berlin, 2008. 35, 56
- [168] M. Schmiedeberg, J. Roth, and H. Stark. Brownian particles in random and quasicrystalline potentials: How they approach the equilibrium. *Eur. Phys. J. E*, 24:367–377, 2007. ISSN 1292-8941. URL <http://dx.doi.org/10.1140/epje/i2007-10247-7>. 10.1140/epje/i2007-10247-7. 11
- [169] M. Schmiedeberg, J. Mikhael, S. Rausch, J. Roth, L. Helden, C. Bechinger, and H. Stark. Archimedean-like colloidal tilings on substrates with decagonal and tetradecagonal symmetry. *Eur. Phys. J. E*, 32:25–34, 2010. ISSN 1292-8941. URL <http://dx.doi.org/10.1140/epje/i2010-10587-1>. 10.1140/epje/i2010-10587-1. 2, 11, 99
- [170] Michael Schmiedeberg and Holger Stark. Colloidal Ordering on a 2D Quasicrystalline Substrate. *Phys. Rev. Lett.*, 101:218302, Nov 2008. doi: 10.1103/PhysRevLett.101.218302. URL <http://link.aps.org/doi/10.1103/PhysRevLett.101.218302>. 2, 11
- [171] Michael Schmiedeberg and Holger Stark. Comparing light-induced colloidal quasicrystals with different rotational symmetries. *Journal of Physics: Condensed Matter*, 24(28):284101, 2012. URL <http://stacks.iop.org/0953-8984/24/i=28/a=284101>. 1, 11
- [172] B. J. Schulz, K. Binder, M. Müller, and D. P. Landau. Avoiding boundary effects in Wang-Landau sampling. *Phys. Rev. E*, 67:067102, Jun 2003. doi: 10.1103/PhysRevE.67.067102. URL <http://link.aps.org/doi/10.1103/PhysRevE.67.067102>. 55
- [173] A. K. Sen and D. E. Sullivan. Landau de Gennes theory of wetting and orientational transitions at a nematic-liquid substrate interface. *Phys. Rev.*

- A, 35:1391–1403, Feb 1987. doi: 10.1103/PhysRevA.35.1391. URL <http://link.aps.org/doi/10.1103/PhysRevA.35.1391>. 30
- [174] W. Setyawan, N. Ferralis, R.D. Diehl, M.W. Cole, and S. Curtarolo. Xe films on a decagonal Al-Ni-Co quasicrystalline surface. *Phys. Rev. B*, 74(12):125425, 2006. 7
- [175] W. Setyawan, RD Diehl, N. Ferralis, MW Cole, and S. Curtarolo. Noble gas films on a decagonal AlNiCo quasicrystal. *J. Phys.: Condens. Mat.*, 19:016007, 2007. 7
- [176] Wahyu Setyawan. *Computational study of low friction quasicrystalline coatings via simulations of thin film growth of hydrocarbons and rare gases*. PhD thesis, Duke University, 2008. 99
- [177] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn. Metallic Phase with Long-Range Orientational Order and No Translational Symmetry. *Phys. Rev. Lett.*, 53:1951–1953, Nov 1984. doi: 10.1103/PhysRevLett.53.1951. URL <http://link.aps.org/doi/10.1103/PhysRevLett.53.1951>. 1, 6
- [178] M. Scott Shell, Pablo G. Debenedetti, and Athanassios Z. Panagiotopoulos. Generalization of the Wang-Landau method for off-lattice simulations. *Phys. Rev. E*, 66:056703, Nov 2002. doi: 10.1103/PhysRevE.66.056703. URL <http://link.aps.org/doi/10.1103/PhysRevE.66.056703>. 54
- [179] Ping Sheng. Boundary-layer phase transition in nematic liquid crystals. *Phys. Rev. A*, 26:1610–1617, Sep 1982. doi: 10.1103/PhysRevA.26.1610. URL <http://link.aps.org/doi/10.1103/PhysRevA.26.1610>. 30
- [180] Jonathan Richard Shewchuk. Triangle: Engineering a 2D Quality Mesh Generator and Delaunay Triangulator. In Ming C. Lin and Dinesh Manocha, editors, *Applied Computational Geometry: Towards Geometric Engineering*, volume 1148 of *Lecture Notes in Computer Science*, pages 203–222. Springer-Verlag, Berlin, Heidelberg, D, 1996. 35
- [181] M. Shimoda, T. J. Sato, A. P. Tsai, and J. Q. Guo. Epitaxial crystalline film with psuedo-tenfold symmetry formed by Au-deposition on a decagonal $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal. *Phys. Rev. B*, 62:11288–11291, Nov 2000. doi:

- 10.1103/PhysRevB.62.11288. URL <http://link.aps.org/doi/10.1103/PhysRevB.62.11288>. 7
- [182] T. J. Sluckin and A. Poniewierski. Novel surface phase transition in nematic liquid crystals: Wetting and the Kosterlitz-Thouless transition. *Phys. Rev. Lett.*, 55:2907–2910, Dec 1985. doi: 10.1103/PhysRevLett.55.2907. URL <http://link.aps.org/doi/10.1103/PhysRevLett.55.2907>. 30
- [183] J A Smerdon. The various modes of growth of metals on quasicrystals. *J. Phys. : Cond. Matt.*, 22(43):433002, 2010. URL <http://stacks.iop.org/0953-8984/22/i=43/a=433002>. 1, 7
- [184] J A Smerdon, H R Sharma, J Ledieu, and R McGrath. Nucleation and growth of pseudomorphic monolayers on quasicrystal surfaces. *J. Phys.: Cond. Matt.*, 20(31):314005, 2008. URL <http://stacks.iop.org/0953-8984/20/i=31/a=314005>. 7
- [185] J A Smerdon, J K Parle, L H Wearing, L Leung, T A Lograsso, A R Ross, and R McGrath. C 60 adsorption on an aperiodically modulated Cu surface. *J. Phys.: Conference Series*, 226(1):012006, 2010. URL <http://stacks.iop.org/1742-6596/226/i=1/a=012006>. 7
- [186] J. E. S. Socolar, T. C. Lubensky, and P. Steinhardt. Phonons , phasons and dislocations in quasicrystals. *Phys. Rev. B*, 34(5), 9 1986. 21
- [187] J.E.S. Socolar and P.J. Steinhardt. Quasicrystals. II. Unit-cell configurations. *Phys. Rev. B*, 34(2):617, 1986. 15, 16, 20, 21, 22
- [188] Joshua E. S. Socolar. Weak matching rules for quasicrystals. *Communications in Mathematical Physics*, 129:599–619, 1990. ISSN 0010-3616. URL <http://dx.doi.org/10.1007/BF02097107>. 10.1007/BF02097107. 20
- [189] Joshua E. S. Socolar, Paul J. Steinhardt, and Dov Levine. Quasicrystals with arbitrary orientational symmetry. *Phys. Rev. B*, 32:5547–5550, Oct 1985. doi: 10.1103/PhysRevB.32.5547. URL <http://link.aps.org/doi/10.1103/PhysRevB.32.5547>. 21
- [190] H.E. Stanley. *Introduction to phase transitions and critical phenomena*, Clarendon. Oxford University Press, 1971. 35

-
- [191] Holger Stark, Jun-ichi Fukuda, and Hiroshi Yokoyama. Nematic wetting layers in liquid crystal colloids. *J. Phys.: Cond. Matt.*, 16(19):S1911, 2004. URL <http://stacks.iop.org/0953-8984/16/i=19/a=004>. 30
- [192] Paul J Steinhardt. Penrose tilings, cluster models and the quasi-unit cell picture. *Mat. Sc. Eng. A*, 294-296(0):205–210, 2000. ISSN 0921-5093. doi: 10.1016/S0921-5093(00)01194-1. URL <http://www.sciencedirect.com/science/article/pii/S0921509300011941>. 27
- [193] J. Stelzer, P. Galatola, G. Barbero, and L. Longa. Molecular dynamics simulations of surface-induced ordering in a nematic liquid crystal. *Phys. Rev. E*, 55:477–480, Jan 1997. doi: 10.1103/PhysRevE.55.477. URL <http://link.aps.org/doi/10.1103/PhysRevE.55.477>. 30
- [194] Steurer Walter. Twenty years of structure research on quasicrystals. Part I. Pentagonal, octagonal, decagonal and dodecagonal quasicrystals. *Zeitschrift für Kristallographie*, 219(7-2004):391–446, 2004. ISSN 2194-4946. doi: 10.1524/zkri.219.7.391.35643. doi: 10.1524/zkri.219.7.391.35643. 27
- [195] Katherine J. Strandburg. Two-dimensional melting. *Rev. Mod. Phys.*, 60: 161–207, Jan 1988. doi: 10.1103/RevModPhys.60.161. URL <http://link.aps.org/doi/10.1103/RevModPhys.60.161>. 8
- [196] J.B. Suck and P. Häussler. *Quasicrystals: An Introduction to Structure, Physical Properties and Applications*. Springer Series in Materials Science. Springer, 2002. ISBN 9783540642244. 1, 6, 21
- [197] Y Tang, R M Malzbender, R C Mockler, W J O’Sullivan, and J A Beall. Programmed symmetry lowering in 2D colloids. *J. Phys. A*, 20(3):L189, 1987. URL <http://stacks.iop.org/0305-4470/20/i=3/a=013>. 9
- [198] Thiel Patricia A. Quasicrystal Surfaces*. *Ann. Rev. Phys. Chem.*, 59(1): 129–152, 2008. ISSN 0066-426X. doi: 10.1146/annurev.physchem.59.032607.093736. doi: 10.1146/annurev.physchem.59.032607.093736. 7
- [199] Tsvi Thusty, Amit Meller, and Roy Bar-Ziv. Optical Gradient Forces of Strongly Localized Fields. *Phys. Rev. Lett.*, 81:1738–1741, Aug 1998. doi: 10.1103/PhysRevLett.81.1738. URL <http://link.aps.org/doi/10.1103/PhysRevLett.81.1738>. 9

- [200] R.A. Trasca, N. Ferralis, R.D. Diehl, and M.W. Cole. The adsorption of Xe and Ar on quasicrystalline AlNiCo. *J. Phys.: Condens. Mat.*, 16:S2911–S2921, 2004. 7
- [201] M. Tuckerman. *Statistical Mechanics: Theory and Molecular Simulation*. Oxford Graduate Texts. OUP Oxford, 2010. ISBN 9780198525264. URL <http://books.google.de/books?id=Lo3Jqc0pgrcC>. 45
- [202] Baris Unal, C J Jenks, and P A Thiel. Adsorption sites on icosahedral quasicrystal surfaces: dark stars and white flowers. *J. Phys.: Cond. Matt.*, 21(5):055009, 2009. URL <http://stacks.iop.org/0953-8984/21/i=5/a=055009>. 7
- [203] Alfons van Blaaderen and Pierre Wiltzius. Growing large, well-oriented colloidal crystals. *Advanced Materials*, 9(10):833–835, 1997. ISSN 1521-4095. doi: 10.1002/adma.19970091015. URL <http://dx.doi.org/10.1002/adma.19970091015>. 9
- [204] M. P. B. van Bruggen and H. N. W. Lekkerkerker. Metastability and Multistability: Gelation and Liquid Crystal Formation in Suspensions of Colloidal Rods. *Langmuir*, 18(19):7141–7145, 2002. doi: 10.1021/la020161b. URL <http://pubs.acs.org/doi/abs/10.1021/la020161b>. 31
- [205] M. P. B. van Bruggen, H. N. W. Lekkerkerker, and J. K. G. Dhont. Long-time translational self-diffusion in isotropic dispersions of colloidal rods. *Phys. Rev. E*, 56:4394–4403, Oct 1997. doi: 10.1103/PhysRevE.56.4394. URL <http://link.aps.org/doi/10.1103/PhysRevE.56.4394>. 31
- [206] M. P. B. van Bruggen, H. N. W. Lekkerkerker, G. Maret, and J. K. G. Dhont. Long-time translational self-diffusion in isotropic and nematic dispersions of colloidal rods. *Phys. Rev. E*, 58:7668–7677, Dec 1998. doi: 10.1103/PhysRevE.58.7668. URL <http://link.aps.org/doi/10.1103/PhysRevE.58.7668>. 31
- [207] Martin A. van der Hoef, Daan Frenkel, and Anthony J. C. Ladd. Self-diffusion of colloidal particles in a two-dimensional suspension: Are deviations from Fick’s law experimentally observable? *Phys. Rev. Lett.*, 67:

- 3459–3462, Dec 1991. doi: 10.1103/PhysRevLett.67.3459. URL <http://link.aps.org/doi/10.1103/PhysRevLett.67.3459>. 8
- [208] R. van Roij, M. Dijkstra, and R. Evans. Orientational wetting and capillary nematization of hard-rod fluids. *EPL*, 49(3):350, 2000. URL <http://stacks.iop.org/0295-5075/49/i=3/a=350>. 31
- [209] R.L.C. Vink. The isotropic-to-nematic transition in a two-dimensional fluid of hard needles: a finite-size scaling study. *Eur. Phys. J. B-Condens. Mat. and Complex Systems*, 72(2):225–231, 2009. 37, 64
- [210] Fugao Wang and D. P. Landau. Determining the density of states for classical statistical models: A random walk algorithm to produce a flat histogram. *Phys. Rev. E*, 64:056101, Oct 2001. doi: 10.1103/PhysRevE.64.056101. URL <http://link.aps.org/doi/10.1103/PhysRevE.64.056101>. 54
- [211] Fugao Wang and D. P. Landau. Efficient, Multiple-Range Random Walk Algorithm to Calculate the Density of States. *Phys. Rev. Lett.*, 86:2050–2053, Mar 2001. doi: 10.1103/PhysRevLett.86.2050. URL <http://link.aps.org/doi/10.1103/PhysRevLett.86.2050>. 54
- [212] Q.-H. Wei, C. Bechinger, D. Rudhardt, and P. Leiderer. Experimental Study of Laser-Induced Melting in Two-Dimensional Colloids. *Phys. Rev. Lett.*, 81:2606–2609, Sep 1998. doi: 10.1103/PhysRevLett.81.2606. URL <http://link.aps.org/doi/10.1103/PhysRevLett.81.2606>. 10
- [213] Y. Weisskopf, R. Lüscher, and M. Erbudak. Structural modifications upon deposition of Fe on the icosahedral quasicrystal Al-Pd-Mn. *Surface Science*, 578(1-3):35–42, 2005. ISSN 0039-6028. doi: 10.1016/j.susc.2005.01.010. URL <http://www.sciencedirect.com/science/article/pii/S0039602805000361>. 7
- [214] Xin Wen, Robert B. Meyer, and D. L. D. Caspar. Observation of smectic- A ordering in a solution of rigid-rod-like particles. *Phys. Rev. Lett.*, 63:2760–2763, Dec 1989. doi: 10.1103/PhysRevLett.63.2760. URL <http://link.aps.org/doi/10.1103/PhysRevLett.63.2760>. 31
- [215] Anieke Wierenga, Albert P. Philipse, Henk N. W. Lekkerkerker, and David V. Boger. Aqueous Dispersions of Colloidal Boehmite: Structure,

- Dynamics, and Yield Stress of Rod Gels. *Langmuir*, 14(1):55–65, 1998. doi: 10.1021/la970376z. URL <http://pubs.acs.org/doi/abs/10.1021/la970376z>. 31
- [216] Thomas A. Witten. Insights from soft condensed matter. *Rev. Mod. Phys.*, 71:S367–S373, Mar 1999. doi: 10.1103/RevModPhys.71.S367. URL <http://link.aps.org/doi/10.1103/RevModPhys.71.S367>. 1, 8
- [217] Nuttawisit Yasarawan and Jeroen S. van Duijneveldt. Dichroism in Dye-Doped Colloidal Liquid Crystals. *Langmuir*, 24(14):7184–7192, 2008. doi: 10.1021/la800849y. URL <http://pubs.acs.org/doi/abs/10.1021/la800849y>. PMID: 18553987. 31
- [218] Anand Yethiraj. Tunable colloids: control of colloidal phase transitions with tunable interactions. *Soft Matter*, 3:1099–1115, 2007. doi: 10.1039/B704251P. URL <http://dx.doi.org/10.1039/B704251P>. 8
- [219] Youngwoo Yi, Giuseppe Lombardo, Neil Ashby, Riccardo Barberi, Joseph E. Maclennan, and Noel A. Clark. Topographic-pattern-induced homeotropic alignment of liquid crystals. *Phys. Rev. E*, 79:041701, Apr 2009. doi: 10.1103/PhysRevE.79.041701. URL <http://link.aps.org/doi/10.1103/PhysRevE.79.041701>. 31
- [220] A. P. Young. Melting and the vector Coulomb gas in two dimensions. *Phys. Rev. B*, 19:1855–1866, Feb 1979. doi: 10.1103/PhysRevB.19.1855. URL <http://link.aps.org/doi/10.1103/PhysRevB.19.1855>. 8, 32
- [221] K. Zahn, R. Lenke, and G. Maret. Two-Stage Melting of Paramagnetic Colloidal Crystals in Two Dimensions. *Phys. Rev. Lett.*, 82:2721–2724, Mar 1999. doi: 10.1103/PhysRevLett.82.2721. URL <http://link.aps.org/doi/10.1103/PhysRevLett.82.2721>. 8
- [222] Bruno Zappone and Emmanuelle Lacaze. Surface-frustrated periodic textures of smectic-*A* liquid crystals on crystalline surfaces. *Phys. Rev. E*, 78:061704, Dec 2008. doi: 10.1103/PhysRevE.78.061704. URL <http://link.aps.org/doi/10.1103/PhysRevE.78.061704>. 31
- [223] Z. X. Zhang and Jeroen S. van Duijneveldt. Isotropic-nematic phase transition of nonaqueous suspensions of natural clay rods. *J. Chem. Phys.*, 124

- (15):154910, 2006. doi: 10.1063/1.2185642. URL <http://link.aip.org/link/?JCP/124/154910/1>. 31
- [224] Chenggang Zhou and R. N. Bhatt. Understanding and improving the Wang-Landau algorithm. *Phys. Rev. E*, 72:025701, Aug 2005. doi: 10.1103/PhysRevE.72.025701. URL <http://link.aps.org/doi/10.1103/PhysRevE.72.025701>. 54
- [225] Chenggang Zhou and Jia Su. Optimal modification factor and convergence of the Wang-Landau algorithm. *Phys. Rev. E*, 78:046705, Oct 2008. doi: 10.1103/PhysRevE.78.046705. URL <http://link.aps.org/doi/10.1103/PhysRevE.78.046705>. 55
- [226] Chenggang Zhou, T. C. Schulthess, Stefan Torbrügge, and D. P. Landau. Wang-Landau Algorithm for Continuous Models and Joint Density of States. *Phys. Rev. Lett.*, 96:120201, Mar 2006. doi: 10.1103/PhysRevLett.96.120201. URL <http://link.aps.org/doi/10.1103/PhysRevLett.96.120201>. 54
- [227] H. Zocher. Über freiwillige Strukturbildung in Solen. (Eine neue Art anisotrop flüssiger Medien.). *Zeitschrift für anorganische und allgemeine Chemie*, 147(1):91–110, 1925. ISSN 1521-3749. doi: 10.1002/zaac.19251470111. URL <http://dx.doi.org/10.1002/zaac.19251470111>. 31

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