SELF-ASSEMBLY OF TWO-DIMENSIONAL NON-SPHERICAL PARTICLES:

A MONTE CARLO SIMULATION STUDY

A Dissertation in
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by
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Abstract

For applications in device fabrication, such as sensors or nanoelectronics, it is often desirable to utilize the self-assembly behavior of particles in two dimensions to produce the structures. However, using particle self assembly in achieving long-range or complex order can be difficult due to the inability to control or a lack in understanding of the various interparticle interactions. The work presented in this dissertation contributes to the understanding necessary to achieve self-assembled structures using non-spherical particles in two dimensions. Non-spherical particle geometries result in phases that symmetric particles, such as disks or spheres, do not exhibit. Rectangles, spherocylinders, ellipses, cubes, and squares have the ability to produce diverse structures depending on their aspect ratio, concentration, and subtle differences in their geometry. Using Monte Carlo (MC) simulations, this work studies the assembly of hard rectangles confined between two infinitely-long hard walls and establishes the orientational and structural characteristics imparted by the confining walls as compared to bulk rectangles. In all cases, the rectangles align with their long axis parallel to the confining wall. Systems of rectangles that are in the nematic phase in the bulk exhibit layering next to the wall.
when confined. The dependence of the depletion interaction between two squares on depletant shape (either rectangles or disks), size relative to the squares, and concentration is established. At short separations between the squares, the effect of the depletant is found to induce attraction between the squares. Further, the rectangles and disks are found to align the squares so that they approach via a preferred pathway. The depletion interaction is extended to ensembles of rectangles and disks, where the influence of the disks on the structure of the rectangles is studied. At sufficiently high concentrations of rectangles and disks, the two components microphase separate into alternating rectangle-rich and disk-rich layers. Based on unique structural features of the rectangles and disks, a phase diagram delineating three different phases is constructed. MC simulations are also used to understand recent experimental results on the self assembly of electrostatically stabilized gold nanowires on a surface. The simulations resolve the physical origin of the nanowires’ preference for the smectic phase and capture the experimentally observed trend of decreasing order as nanowire length increases.
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Chapter 1

Introduction

For applications in device fabrication, such as sensors or nanoelectronics, it is often desirable to utilize the self-assembly behavior of particles in two dimensions to produce the structures. Self-assembly is often hindered when non-specific forces (e.g., van der Waals, electrostatic, and in the case of larger particles, gravity) dominate the interparticle interaction. For example, van der Waals attraction often leads to uncontrolled particle aggregation. In studies aimed at understanding the interplay of various forces than can affect assembly, the knowledge necessary to bring about specific assemblies is gained.

Understanding the forces that control the self-assembly of micro- and nanoparticle will enable rational designs that incorporate the particles into higher-order devices. Most studies to date have examined the assembly of spherical particles. The structures formed by these particles have numerous uses including patterning masks for developing surface-enhanced Raman substrates [1], templates for photonic crystals used in electronic paper [2, 3], as well as in sensing and separation applications [4]. In addition to spherical particles, a variety of other nanoparticle shapes such as rods, cubes, and branched structures have been studied and assembled [5–24]. Nanowires present many material properties that spherical par-
articles can not easily offer, such as facile control of coatings, composition (multiple segments can be made of a diverse set of materials), and size (both length and diameter). Functionalized nanowires have already been incorporated into sensing devices such as field effect transistors [25] and cantilevers [26, 27], as well as other devices, such as complementary metal oxide semiconductor (CMOS) chips [28]. However, high-density, well-ordered assemblies of functional nanowires are challenging to achieve, and understanding and controlling their assembly could prove useful in technologies such as nanoelectronics [28–36] and sensors [37].

This work investigates both hard, non-spherical particles and non-spherical particles that possess energetic interactions. Fluids composed of hard, non-spherical particles, such as rectangles, spherocylinders, ellipses, and squares are interesting building blocks for assembly since they have the ability to produce diverse structures depending on their aspect ratio, concentration, and subtle differences in their geometry. These systems can produce intriguing phases without the aid of specific interactions, such as DNA functionalization, between particles. Since all interactions are hard at their core, it is interesting to explore this form of assembly. The addition of energetic interactions can either enhance or detract from these hard assemblies. This dissertation explores different approaches to influence the assembly of non-spherical particles and elucidates the physical origins responsible for the observed behavior.

1.1 Bulk Non-spherical Particles

From a fundamental perspective, the phase behavior of rod-like entities is surprisingly diverse and still not yet fully understood. Much work has been done to develop an understanding of the various phases exhibited by hard-rod fluids
Figure 1.1. Example illustrations of the (a) isotropic, (b) nematic, (c) smectic, (d) tetratic, and (e) lamellar phases.

In two [38–45] and three [46–52] dimensions, Onsager determined that when the density is increased in a system of three-dimensional hard rods, the rods transition from a low-density, isotropic phase, in which they have no preferred alignment, to a nematic phase, in which they are orientationally aligned [46]. Figure 1.1(a) illustrates the isotropic phase and Fig. 1.1(b) illustrates the nematic phase. The isotropic and nematic phases are observed for most rod-like entities in three-dimensions if the aspect ratio (the ratio of their length to width) is sufficiently high. However, other phases can be observed in rods with low aspect ratios. For example, studies of short cylinders [50] and cuboids [48] have explored the possibility of a cubatic phase [47, 48, 50], in which the particles have long-range orientational order with cubic symmetry, but lack positional order. In simulations of cuboids [48] and spherocylinders [52], as well as in experimental studies of fd virus particles [49], smectic phases have been observed. The smectic phase, shown in Fig. 1.1(c),
is characterized by rods that are orientationally aligned and have positional order to their centers of mass. For spherocylinders and cuboids, the existence of the smectic phase was shown to depend on the aspect ratio [48, 52]. In two dimensions, studies have probed the phase behavior of spherocylinders [38, 39], rectangles [38, 45], ellipses [40, 41], and needles [43, 44]. The isotropic-to-nematic transition has been observed with increasing density in theoretical studies of rectangles [38], spherocylinders [38], and ellipses [41], as well as in simulations of spherocylinders [39], ellipses [40], and needles [43, 44]. If the density is sufficiently high, a transition from the nematic to the solid (smectic) phase occurs for spherocylinders with aspect ratios \( \gtrsim 7 \) [39]. Two-dimensional simulation studies of low-aspect-ratio rectangles [38, 45] have explored the possibility of the tetratic phase in which small domains of rectangles align perpendicular to each other. An example illustration of the tetratic phase is shown in Fig. 1.1(d). In Chapters 2 and 4, the bulk phase behavior of hard rectangles is investigated. These results serve as a reference point for understanding the ways in which their structure can be altered by adding an external constraint (Chapter 2) or a second particle type to the system (Chapter 4).

1.2 Hard-wall Templated Assembly

To be able to exploit the ordering of rods for certain applications (e.g., nanoelectronic circuits), it is desirable to confine them in nanoscale geometries on surfaces. Such confinement can be achieved by patterning the surface, either physically [31] or chemically [32, 33]. Experiments with Langmuir-Blodgett troughs have been useful at probing rod ordering in quasi-two-dimensional confined systems [14, 22, 29, 53–55]. Simulation studies have explored the ordering and phase behavior of rods under confinement by hard walls in two [56] and three [57–61]
dimensions, as well as in quasi-two-dimensional slit-pore geometries [62–64]. A typical finding in such studies is that hard walls induce rods to align with their long axes parallel to the walls. For example, studies of spherocylinders in quasi-two-dimensional slits have demonstrated that the spherocylinders align with their long axes parallel to the slit walls and exhibit an isotropic to nematic transition with increasing density [62]. In studies involving spherocylinders near a single hard wall, Dijkstra et al. observed alignment in biaxial domains with rod axes parallel to the wall. They also observed that the distance over which rods maintain their parallel alignment with the wall increases with increasing density [58]. Martínez-Ratón explored the effect of confinement on short rectangles in two dimensions and reported extensive layering near the wall [56]. In Chapter 2, the extent to which hard walls influence rectangle alignment in two dimensions is explored. In particular, two-dimensional hard rectangles confined between hard walls that are infinitely long, but spaced a finite distance apart is studied. Although the system is strictly two dimensional, it is a similar geometry to the Langmuir-Blodgett trough.

Only a few theoretical studies have focused on understanding the sedimentation of rods against a hard wall [65–67]. Simulations and theoretical calculations on the phase coexistence of short, hard spherocylinders revealed that in a semi-infinite container, the spherocylinders always pack with the densest phase at the bottom of the container with the least dense phase at higher altitudes [65]. The presence of the smectic, nematic, and isotropic phases depended on the number of spherocylinders, as well as the gravitational strength.
1.3 Depletion Interactions

Large particles immersed in a sea of small particles experience a force known as the depletion interaction. As the large particles approach, a critical separation is reached where the small particles are unable to occupy the gap between the surfaces of the large particles and are expelled from the gap. This critical separation results in an imbalance of pressures which drives the large particles together. The evacuation of the small particles from the interparticle gap results in a gain of free volume accessible to the smaller particles and is entropically favorable.

Depletion interactions have been studied for a variety of systems, including binary hard spheres [68–73], ellipsoids and spheres [74], spheres and rods [71, 75–85], and spheres and disks [71, 86]. Studies have also looked at depletion interactions in two dimensions for binary hard disks [69, 75, 87] and disks and rods [87]. The first theoretical work to predict depletion attraction came from Asakura and Oosawa [70] who calculated the depletion interaction between large spheres in a sea of small spheres. They noted that in the dilute limit of the small spheres, the interaction between large spheres is always attractive and the range of the interaction is determined by the size of the small spheres. Studies on binary hard disks in two dimensions have predicted the depletion interaction between two large disks to be attractive with the observance of repulsive interactions at sufficiently high densities of the small disks [87]. These interactions are correlated over distances longer than the size of the small disk. Lin et al. experimentally measured the depletion interaction between two large spheres in a suspension of long, thin viruses [79]. They noted that this interaction was always attractive and the range was determined by the length of the virus. They also found that losses in rotational entropy of the virus between two spheres makes the virus a more
effective depletion agent than spheres.

Depletion interactions have also been calculated between non-spherical particles. An example is the depletion interaction between two oblate ellipsoids in a sea of hard spheres [74]. The authors found a strong relationship between the specific orientations of the ellipsoids and the shape and magnitude of the depletion interaction curve. Similar calculations between two spherocylinders in a sea of hard spheres also found the depletion interaction to depend strongly on the orientation of the spherocylinders [76]. The dependence of the depletion interaction on particle orientation and separation is an interesting result that could potentially be exploited for particle self-assembly purposes. However, these studies only considered specific orientations of the ellipsoids and spherocylinders. The work in this dissertation considers the depletion interaction between two squares where the orientations are not fixed in suspensions of rectangles and disks. Squares were chosen for this work since the non-spherical shape has interesting rotational effects associated with it. Also, motivated by work on solvent mediated alignment of nanoparticles [88], this dissertation determines the pathway by which the squares approach. Unique configurations of the squares are shown to exist that are a direct result of their non-spherical shape and the presence of the rectangles and disks.

Depletion interactions have also been studied with respect to particle-surface interactions and assembly [68, 69, 75, 78, 87, 89–96]. Calculations between a large sphere and curved surface in a sea of small spheres revealed a dependence of the depletion interaction on whether the surface is concave or convex. Lin et al. exploited depletion forces in the growth of crystalline multilayer assemblies of spheres on a substrate with an inverted pyramid pattern [89].
1.4 Rod and Sphere Systems

A discussion of depletion interactions between two particles is a natural precursor to the study of this interaction in ensembles of particles. Here, the focus is on the assembly of binary systems of elongated particles (rods) such as spherocylinders, viruses, and ellipses with spheres. In three dimensions, rod and sphere systems have been studied experimentally [97–99], theoretically [100–107], and through computer simulation [101, 103, 107–114]. Studies have focused on many different binary systems including needles and spheres [98–100], ellipses and spheres [110], spherocylinders and spheres [101, 102, 104, 106, 107, 109, 111–113], ellipses and disks [103], and spherocylinders and disks [114]. However, the phase behavior is relatively unexplored in two dimensions [115]. Using scaled particle theory, Martínez-Ratón et al. determined the phase diagram of several binary systems which included spherocylinders and disks in two dimensions [115]. The notable result of this system is the presence of isotropic (disk rich) and nematic (rod rich) phases at low pressures with a demixing region observed at sufficiently high pressures.

The phase behavior of the different three-dimensional binary systems has a strong dependence on the size difference between the particles as well as their concentrations. A system of short, hard ellipses with spheres showed a shift of the isotropic-to-nematic transition to higher total densities as the concentration of spheres increased [110]. The point at which the ellipses go from being in the isotropic phase to the nematic phase is referred to as the isotropic-to-nematic transition. Urakami et al. found that the addition of large spheres can induce an isotropic-to-nematic transition by increasing the sphere concentration at a fixed spherocylinder concentration [111]. They found that increasing the sphere
concentration first leads to phase separation of the spherocylinders and spheres where the spherocylinders remain isotropic. Further increases in the sphere concentration lead to the formation of the nematic phase. Schmidt and Dijkstra found for a system of spherocylinders whose length is equal to the sphere diameter that the isotropic-to-nematic transition is suppressed to lower spherocylinder densities as the sphere density is increased [112].

Experimental work on the assembly of non-interacting tobacco mosaic virus (rods) and polystyrene spheres found rich phase behavior of the particles as a function of their concentration [97]. At low concentrations, the rods and spheres are miscible and at higher concentrations can form lamellar, nematic, and smectic phases. The nematic and smectic phases are predominately observed at low sphere concentration and high rod concentration whereas the lamellar phase forms at both high rod and sphere concentrations. Although the lamellar phase is a three-dimensional phase, Fig. 1.1(e) illustrates the essential characteristics of this phase which is alternating layers of rods and spheres. Experiments with silica rods and spheres whose diameter is larger than the rod length exhibited phase separation where the spheres formed high density crystalline structures [98, 99].

The formation of the lamellar phase [105–107, 109] versus phase separation [102, 104, 105] is dependent on the size difference of the rods and spheres. Small spheres can fit between the smectic layers which enhances the formation of the lamellar phase, whereas large spheres cannot fit between the smectic layers as there is an insufficient free volume gain by undergoing a layering transition.

Inspired by the elaborate phase behavior observed for three dimensional systems, in Chapter 4, the phase behavior of systems of rectangles and disks in two dimensions which has received less attention is explored. The impact of the disks on the structure of the rectangles is examined and explained in terms of the
depletion force due to the disks. To study the phase behavior of the rectangles and disks, the area fraction of each component is systematically varied. The presence of microphase separation is found, in which rectangles exhibit both positional and orientational order.

1.5 Rods with Energetic Interactions

Studies of hard-particle systems provide insight into entropy-driven assembly, which is often used as a basis for understanding the assembly of rods with energetic interactions [116–128]. Avendano et al. showed that short, hard spherocylinders with short-range repulsive interactions create an effectively larger spherocylinder and excluded volume which shifts the nematic-to-smectic phase transition to lower densities [125]. A similar conclusion was obtained by Earl et al. for a system of soft repulsive spherocylinders [122]. A different behavior was found for soft repulsive spherocylinders at higher temperatures by Cuetos et al., where the nematic phase was found to be stabilized with respect to the smectic phase [123]. The stabilization of the nematic phase was attributed to better sampling of high energy configurations that reduced the importance of excluded volume effects responsible for the transition to the smectic phase. A central longitudinal point dipole placed in the center of hard spherocylinders was found to stabilize the smectic phase over the nematic phase [128], whereas spherocylinders with terminal longitudinal point dipoles were shown to destabilize the smectic phase in favor of the nematic phase [127]. In Chapter 5, simulations are employed to understand experimental results on the self-assembly of colloidal gold nanowires coated with a negatively-charged monolayer and adsorbed onto a glass substrate. The interactions between nanowires are not purely short-range repulsive as discussed above, but include
van der Waals attraction and electrostatic repulsion. The simulations resolve the physical origin of the nanowires’ preference for the smectic phase and capture the experimentally observed trend of decreasing order as nanowire length increases.
Two-dimensional hard rectangles: Confinement effects

This chapter explores the extent to which hard walls influence rod alignment in two dimensions. In particular, this chapter explores two-dimensional hard rectangles confined between hard walls that are infinitely long, but spaced a finite distance apart. Based on the results of previous studies [56–60, 62, 63], it was expected (and found) that rectangles near the walls orient their long axes parallel to the walls. The wall orientation effect occurs even for rods that exhibit tetratic tendencies in the bulk. The orientations of rods near the walls are surprisingly similar (but not completely identical) to those of rods near other rods in the bulk. This work demonstrates that the wall effect can be exploited to achieve confined nematics at densities for which the bulk phase is isotropic.

2.1 Models and Methods

The phase behavior of two-dimensional hard rods confined between hard walls and in bulk is studied. Figure 2.1 illustrates the essential elements of the confined
Figure 2.1. Example simulation box of (a) a confined system and (b) a bulk system. $L$ and $D$ are the length and width of the rectangles, respectively, while $H_{\text{box}}$ and $W_{\text{box}}$ are the height and width of the simulation box, respectively. The lightly shaded portions of the rods shown in (b) reflect the periodic boundary conditions used.

The rods are modeled as two-dimensional rectangles having a length $L$, a width $D$, and an aspect ratio of $\alpha = L/D$. In the confined systems, the distance between the walls is given by $W_{\text{box}}$. The distances between the walls studied were $W_{\text{box}} = L, 2L, 5L,$ and $10L$. The length parallel to the confining walls is given by $H_{\text{box}}$, which is set to be a minimum of $10L$ to avoid finite-size effects. Simulations verified that doubling the value of $H_{\text{box}}$ in the confined systems had no measurable effect on the results. Periodic boundary conditions were enforced parallel to the walls to give the effect of infinitely long, hard barriers. In the bulk systems, $H_{\text{box}} = W_{\text{box}}$, which ranges from $W_{\text{box}} = 10L$ to $W_{\text{box}} = 26L$, and periodic boundary conditions were applied in both dimensions. For low rod densities, these box sizes are larger than rod-rod correlation lengths. However, for the highest rod densities, where nematic phases are present, rod-rod correlation lengths exceed the box size. Rods with aspect ratios of $\alpha = 7.5, 13.3,$ and $20.0$ were studied. For each of these aspect ratios, fractional coverages of $A_{f,\text{rods}} = 0.4, 0.6,$ and $0.7$ were
probed, where the fractional coverage is defined as

\[ A_{f,rods} = \frac{N_{rods} LD}{A_{box}}, \tag{2.1} \]

where \( N_{rods} \) is the number of rods in the system and \( A_{box} \) is the area of the simulation box, \( A_{box} = H_{box} \times W_{box} \). The number of rods ranges from 80, for confined systems with \( W_{box} = L \), to 3,200 for bulk simulations.

To probe the phase behavior, orientational-bias Monte Carlo (MC) was used \cite{129}, which was found to be more efficient than conventional Metropolis MC. In orientational-bias MC, multiple trial angles of a rod are attempted for a given center-of-mass displacement. Here, a trial move consists of a random center-of-mass displacement with a maximum distance of \( D \). For a given center-of-mass displacement, ten trial angles, ranging between 0° and 179° are randomly attempted about the rod’s new and old center of mass. In both the new and old center-of-mass locations, the Rosenbluth factor \( W \) is calculated as

\[ W = \sum_{j=1}^{k} \exp[-\beta U^{or}(b_j)] . \tag{2.2} \]

Here \( k \) is the number of trial orientations, \( b_j \) is a specific trial orientation, \( U^{or} \) is the energy of the orientation, and \( \beta = (k_BT)^{-1} \). The energy \( U^{or} \) is given by a hard-core potential, \( i.e., U^{or} = \infty \), if two rods overlap and \( U^{or} = 0 \), otherwise. The rods also interact with the walls via a hard-core potential, \( i.e., U^{or} = \infty \), if a rod overlaps with a wall. Out of the \( k \) orientations in the new location with \( W_{new} \), a particular orientation \( b_n \) is selected with a probability given by

\[ P(b_n) = \frac{\exp[-\beta U^{or}(b_n)]}{W_{new}} . \tag{2.3} \]
The probability of accepting the move $P_{\text{old} \rightarrow \text{new}}$ is given by

$$P_{\text{old} \rightarrow \text{new}} = \min\left(1, \frac{W_{\text{new}}}{W_{\text{old}}}\right).$$  \hspace{1cm} (2.4)

A uniform random number $\text{ran}X$ is generated. If $\text{ran}X$ is less than $P_{\text{old} \rightarrow \text{new}}$ the move is accepted, otherwise the move is rejected. The average acceptance rate of trial moves is typically 20% but can vary from a minimum of 5%, for the simulations with high $A_{f,\text{rods}}$, to a maximum of 35% for low $A_{f,\text{rods}}$.

These simulations were performed on-lattice, so that the rods are represented by discrete points on a grid. It was shown by Panagiotopoulos for a system of interacting spheres that discretizing the spheres can lead to greater computational efficiency as compared to a real space simulation [130]. In the study by Panagiotopoulos, it was noted that a minimum of ten lattice sites was necessary to represent the sphere diameter in order to reproduce thermodynamic quantities consistent with real-space models. For the aspect ratios of rods studied here, it was determined that a rod width must be represented by a minimum of ten lattice sites to produce equivalent results from a real-space simulation. Thus, all the rods studied here have a width of 10 and the length is adjusted to achieve the desired aspect ratio. For example, the rods with $\alpha = 7.5$ have $D = 10$ and $L = 75$.

One method to accelerate the test for overlap (to obtain $U_{\text{or}}$) is to render the rods hollow, as it is only necessary to check for overlap with points along the rod perimeter.

A discrete number of possible rod orientations were also considered. Recently, Shundyak and van Roij [131] calculated the equation of state for hard rods ($L >> D$) for an increasing number of allowed orientations and compared their results to Onsager’s continuum result. They showed that when greater than 9
angles are allowed, the discrete solution begins to converge to the continuum solution and that the continuous Onsager result can be reproduced when greater than 50 angles are incorporated into the discrete model. They showed that as the density of rods is increased, an increasing number of rod orientations is required to reproduce the Onsager result. For $L > D$ (but not $>> D$), it is expected that fewer rod orientations are required. The work in Chapter 2 allows for 180 different possible rod orientations, ranging from $0^\circ$ to $179^\circ$, in one-degree increments. Thus, the results are expected to accurately reflect the continuum.

A simulation run consists of initialization, followed by equilibration and production runs. Most simulations were initialized by starting all rods with the same orientation but with random center-of-mass locations. For $A_{f,rods} = 0.7$, order was specified to the centers of mass, as randomly placed centers of mass led to long initialization times because of the difficulty in locating free space to place all the rods. Following initialization, equilibration times ranged between $5 \times 10^5$ MC steps (MCS) for the lowest area fractions to upwards of 10 million MCS for $A_{f,rods} = 0.7$. Here, a MCS is defined as an average of one attempted center-of-mass move per rod per step. To verify that the systems were adequately equilibrated, reproducibility of sampled quantities were checked by performing several short production runs. Also, the simulations were initialized with rods having various different starting angles and center-of-mass distributions and obtained reproducible sampled quantities. Production runs for the bulk systems consisted of $7 - 10$ runs ranging in length from $3.5 \times 10^5 - 7 \times 10^5$ MCS. In the confined systems, $6 - 17$ runs were conducted ranging in length from $5 \times 10^5 - 5 \times 10^6$ MCS. The results reported in this chapter were obtained as averages over all production runs.
2.2 Simulation Measures

Several different measures were employed to characterize the ordering and phase behavior of our systems. A useful measure of the strength of the angular correlations between rods are the orientational correlation functions, $g_2$ and $g_4$, which are given as ensemble averages $\langle \ldots \rangle$ by

$$g_2(r) = \langle \cos 2[\theta_i(0) - \theta_j(r)] \rangle,$$ \hspace{1cm} (2.5)

and

$$g_4(r) = \langle \cos 4[\theta_i(0) - \theta_j(r)] \rangle. \hspace{1cm} (2.6)$$

For bulk simulations, $\theta_i(0) - \theta_j(r)$ is the difference between the angles of rods $i$ and $j$ and $r$ is the distance between the centers of mass of the rods. In the confined systems, $\theta_i(0)$ is the angle of the confining walls, which is taken to be $90^\circ$, and $r$ is measured as the perpendicular distance from half a rod width behind the edge of the wall to the center of mass of the rod. Measuring $r$ from behind the wall edge facilitates comparisons between confined and bulk systems. A value of $g_2$ or $g_4 = 1$ indicates that the rod angles are strongly correlated, while a value of $g_2$ or $g_4 = 0$ indicates that the rod angles are uncorrelated. When rods align parallel to one another (or to the wall), they contribute positively to both $g_2$ and $g_4$, whereas rods aligned perpendicular to each other (or to the wall) only contribute positively to $g_4$. In the bulk, $g_2$ is thus a measure of nematic correlations, whereas $g_4$ is a measure of tetratic correlations.

Another useful measure is the angular distribution function $P(\theta)$, which is given by

$$P(\theta) = \frac{\langle N(\theta) \rangle}{N_{\text{rods}} \Delta \theta}. \hspace{1cm} (2.7)$$
\( P(\theta) \) is the probability of observing angle \( \theta \) and \( \langle N(\theta) \rangle \) is an ensemble average of the number of rods with an angle between \( \theta \) and \( \theta + \Delta \theta \). In the case of an isotropic phase, it is expected the rods adopt all possible orientations, resulting in a uniform distribution. In a nematic phase, where the orientational correlation lengths are larger than the box length, it is expected that at any instant all the rods will have a similar orientation; although in the thermodynamic limit, a uniform distribution for a nematic phase is also expected.

For the confined systems, the rod density profile \( \rho(r) \) indicates the influence of the walls on rod positioning. This measure is given by

\[
\rho(r) = \frac{\langle N(r) \rangle}{2H_{\text{box}} \Delta r},
\]

where \( \langle N(r) \rangle \) is an ensemble average of the number of rods that have their center of mass at a distance between \( r \) and \( r + \Delta r \) from the wall. As for \( g_2 \) and \( g_4 \), \( r \) is measured as the perpendicular distance from half a rod width behind the edge of the wall to the center of mass of the rod.

The nematic order parameter \( S \) is calculated from the order parameter tensor \( \mathbf{Q} \) using

\[
Q_{\alpha\beta} = \frac{1}{N_{\text{rods}}} \left\langle \sum_{i=1}^{N_{\text{rods}}} \left[ 2u_\alpha(i)u_\beta(i) - \delta_{\alpha\beta} \right] \right\rangle.
\]

Here, \( u_\alpha(i) \) and \( u_\beta(i) \) are the \( \alpha^{th} \) and \( \beta^{th} \) Cartesian coordinates of the unit vector specifying the orientation of rod \( i \), and \( \delta_{\alpha\beta} \) is the Kronecker delta [44]. The largest eigenvalue of this \( 2 \times 2 \) matrix is taken as the order parameter \( S \). In a system with a high level of orientational order, such as the nematic phase, the order parameter will have high values with an upper limit of 1 for a perfectly aligned system. A system with a low level of orientational order, such as the isotropic phase, or
systems in which high levels of orientational order persist over short distances, such as the tetratic phase, the order parameter with have a small value with a lower limit of zero.

2.3 Results

2.3.1 Bulk Systems

Results from simulations of bulk systems are first presented. These results serve as a reference for the confined systems. Further, there have been previous studies of two-dimensional hard rods that are relevant to our work. In particular, Martínez-Ratón et al. [38] used density-functional theory (DFT) based on scaled-particle theory to delineate a phase diagram for hard rectangles with various area fractions and aspect ratios. The authors noted two phases of rectangles that corresponded to our simulation conditions, the isotropic (I) and uniaxial nematic ($N_u$). Bates and Frenkel [39] used MC simulations to probe the phase diagram of hard discorectangles (DR) (the two-dimensional limit of spherocylinders) from the disc to needle limit. These results for $\alpha$ and $A_{f,rods}$ that overlap with the Chapter 2 conditions, along with values of the order parameter $S_{bulk}$ that were obtained using Eq. (2.9), are included in Table 2.1.

For the $\alpha = 13.3$ and 20.0 at all three area fractions and $\alpha = 7.5$ at $A_{f,rods} = 0.4$, our results are in good agreement with the DFT [38] and MC DR [39] results. The high value of the order parameter for $\alpha = 13.3$ and 20.0 indicates a strong preference for uniaxial alignment indicative of the nematic phase. The small value of the order parameter for $\alpha = 7.5$ at $A_{f,rods} = 0.4$ is consistent with the isotropic phase. As can be seen for $\alpha = 13.3$ and 20.0, increasing the area fraction in the
Table 2.1. Phases observed in DFT calculations of rectangles [38] and MC simulations of DR [39], as well as values of the order parameter obtained using Eq. (2.9) from our simulations of bulk ($S_{\text{bulk}}$) and confined ($S_{1L} - S_{10L}$) rectangles.

<table>
<thead>
<tr>
<th>$A_{f,\text{rods}}$</th>
<th>$\alpha$</th>
<th>DFT [38]</th>
<th>MC DR [39]</th>
<th>$S_{\text{bulk}}$</th>
<th>$S_{1L}$</th>
<th>$S_{2L}$</th>
<th>$S_{5L}$</th>
<th>$S_{10L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>7.5</td>
<td>I</td>
<td>I</td>
<td>0.03</td>
<td>0.81</td>
<td>0.49</td>
<td>0.19</td>
<td>0.09</td>
</tr>
<tr>
<td>0.4</td>
<td>13.3</td>
<td>$N_u$</td>
<td>$I/N_u$</td>
<td>0.59</td>
<td>0.91</td>
<td>0.84</td>
<td>0.75</td>
<td>0.69</td>
</tr>
<tr>
<td>0.6</td>
<td>20.0</td>
<td>$N_u$</td>
<td>$\ldots$</td>
<td>0.88</td>
<td>0.94</td>
<td>0.92</td>
<td>0.90</td>
<td>0.89</td>
</tr>
<tr>
<td>0.6</td>
<td>7.5</td>
<td>$N_u$</td>
<td>I</td>
<td>0.04</td>
<td>0.92</td>
<td>0.77</td>
<td>0.41</td>
<td>0.18</td>
</tr>
<tr>
<td>0.6</td>
<td>13.3</td>
<td>$N_u$</td>
<td>$N_u$</td>
<td>0.93</td>
<td>0.96</td>
<td>0.95</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>0.6</td>
<td>20.0</td>
<td>$N_u$</td>
<td>$\ldots$</td>
<td>0.96</td>
<td>0.97</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>0.7</td>
<td>7.5</td>
<td>$N_u$</td>
<td>$N_u$</td>
<td>0.05</td>
<td>0.94</td>
<td>0.76</td>
<td>0.33</td>
<td>0.22</td>
</tr>
<tr>
<td>0.7</td>
<td>13.3</td>
<td>$N_u$</td>
<td>$N_u$</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>0.7</td>
<td>20.0</td>
<td>$N_u$</td>
<td>$\ldots$</td>
<td>0.97</td>
<td>0.98</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
</tr>
</tbody>
</table>

The low value of the order parameter obtained for $\alpha = 7.5$ is in contrast with DFT results [38] for $A_{f,\text{rods}} = 0.6$ and 0.7 and contrasts MC DR results [39] for $A_{f,\text{rods}} = 0.7$. More insight into these bulk phases can be gained from the orientational correlation functions $g_2$ and $g_4$, which are shown in Fig. 2.2 for nematic and isotropic phases [Fig. 2.2(a)], as well as for $\alpha = 7.5$ and $A_{f,\text{rods}} = 0.6$ [Fig. 2.2(b)]. Similar results to those in Fig. 2.2(b) are seen for $\alpha = 7.5$ and $A_{f,\text{rods}} = 0.7$. As is seen for the nematic in Fig. 2.2(a), both $g_2$ and $g_4$ retain high values over the entire distance range probed. This slow decay and the fact that $g_2 > g_4$ both reflect the predominately parallel alignment of the rectangles. On the other hand, for the isotropic phase [cf., Fig. 2.2(a)], both $g_2$ and $g_4$ decay rapidly to zero. If we look at $g_2$ and $g_4$ for $\alpha = 7.5$ at $A_{f,\text{rods}} = 0.6$, [Fig. 2.2(b)], we can see that $g_4$, a measure of tetratic correlations, dominates over longer distances than $g_2$, a measure of nematic correlations. This analysis indicates the possibility that the system is in a tetratic phase.
Figure 2.2. $g_2(r)$, given by Eq. (2.5), and $g_4(r)$, given by Eq. (2.6), as a function of rod center-of-mass separation for bulk systems with (a) $\alpha = 13.3$ and $A_{f,rods} = 0.6$, a nematic, and $\alpha = 7.5$ and $A_{f,rods} = 0.4$, an isotropic; and (b) $\alpha = 7.5$ and $A_{f,rods} = 0.6$.

The possibility of a tetratic phase in two dimensions has been discussed in the literature. Although the DFT phase diagram in Ref. [38] does not predict the presence of the tetratic phase for $\alpha = 7.5$ at $A_{f,rods} = 0.6$ or 0.7, the authors note the presence of a metastable tetratic phase at shorter aspect ratios and higher area.
Figure 2.3. Characteristics of tetratic order for $\alpha = 7.5$ at $A_{f,rods} = 0.6$. (a) Snapshot from a bulk simulation. Here, the rectangles are represented by lines for clarity. (b) Angular distribution, given by Eq. (2.7).
fractions. They note that they could not rule out the possibility of a stable tetratic phase. Experimental work on the ordering of cylinders on a two-dimensional surface reveals strong fourfold correlations, indicative of the tetratic phase, for $\alpha = 5.2$ and $12.6$ at $A_{f,rods} = 0.87$ [42].

Figure 2.4. $g_2(r)$, given by Eq. (2.5), and $g_4(r)$, given by Eq. (2.6), as a function of (a) parallel and (b) perpendicular rod center-of-mass separation for $\alpha = 7.5$ at $A_{f,rods} = 0.6$. 
A qualitative indication of tetratic order for $\alpha = 7.5$ at $A_{f,\text{rods}} = 0.6$ can be obtained from a snapshot for this system, shown in Fig. 2.3(a). Here, a tendency for the system to organize into perpendicular bundles of rods is noted. The angular distribution of rods for this system, shown in Fig. 2.3(b), has peaks at $0^\circ$, $90^\circ$, and $180^\circ$, indicating tetratic tendencies. Finally, ensemble averages of $g_2$ and $g_4$ resolved in directions parallel and perpendicular to the long axis of a central rectangle were obtained. A similar method was used by Bates and Frenkel to study a system of spherocylinders with $\alpha = 5$ at a density of $\rho = 0.125 \ D^{-2}$, whose ordering was tetratic-like [39]. Figures 2.4(a) and (b) show $g_2$ and $g_4$ in the directions parallel and perpendicular to the long axis of a rectangle, respectively. In the parallel direction, Fig. 2.4(a), there is little structure to the rectangles, as can be seen from the nearly monotonic decay of $g_2$ and $g_4$. The peaks in the perpendicular direction [Fig. 2.4(b)] are spaced approximately one rod width apart, indicating small bundles of rods aligned with their long axes in parallel. It is interesting to note that in both the parallel and perpendicular directions the asymptotic value of $g_4$ is greater than $g_2$, as seen in Fig. 2.2(b). This is due to tetratic alignment of the rods. However, it is evident that this ordering is weak, as the overall magnitudes of $g_2$ and $g_4$ are small and the rod alignment persists only over small distances. Thus, it can be concluded that although the phases for $\alpha = 7.5$ with $A_{f,\text{rods}} = 0.6$ and 0.7 have characteristics of tetratic order, these are isotropic phases.

### 2.3.2 Confined Systems

The results for the confined systems will now be discussed. Here, an overall measure of order is given by the order parameter $S$, which is included in Table 2.1 for all
the wall separations studied. In Table 2.1, it is seen that for a given area fraction, the value of the order parameter increases as $W_{box}$ decreases. As for the bulk systems, qualitatively similar trends are seen for $\alpha = 13.3$ and 20.0 at all three area fractions. For these systems the rods align in a nematic phase in the bulk and under confinement. For $\alpha = 7.5$, the phase behavior of the rods depends on the wall separation and can differ from the bulk. The high values of $S$ for short wall spacings with $\alpha = 7.5$ are characteristic of the nematic phase, but the value of $S$ decreases toward the bulk (isotropic) value as $W_{box}$ increases. While the value of the order parameter provides an indication of the net order in the confined systems, other measures more clearly indicate the influence of the walls. Below, the measures for the two different types of confined systems are discussed.

2.3.2.1 Nematic in Bulk and Under Confinement: $\alpha = 13.3$ and 20.0

Confined systems that exhibit nematic ordering in both the bulk and under confinement are first discussed. As discussed above, rods with aspect ratios of 13.3 and 20.0 fall under this category for all area fractions. Representative snapshots of three systems, with $\alpha = 13.3$, $W_{box} = 5L$, and varying fractional coverage are shown in Fig. 2.5. These snapshots illustrate the trends that will be discussed below.

Figure 2.6 shows a plot of the orientational correlation function $g_2$ at conditions corresponding to the snapshots in Fig. 2.5. At distances near 0, i.e. near the wall, the rods orient themselves parallel to the wall. As the rod-wall separation approaches the center of the confined region (i.e. half the box width), the rod-wall correlations are still strong for $A_{f,rods} = 0.6$ and 0.7, while there is some decay for $A_{f,rods} = 0.4$. The slow decay in $g_2$ indicates that under confinement the rods basically adopt the wall angle throughout the confined region, that is,
the wall determines the nematic director. This is evident from the snapshots in Fig. 2.5 and stands in contrast to bulk nematics, for which the director is a random orientation that can change (slowly) with time.

Figure 2.7, which shows $g_2$ for all the confined and bulk systems having $\alpha = 13.3$ and $A_{f,rods} = 0.4$, indicates the influence of wall spacing on rod orientation. Figure 2.7 is representative of $g_2$ and $g_4$ for all area fractions. Here, rods with the greatest confinement (smallest wall spacing) have the highest angular correlation near the center of the confined region and, for the wall spacings studied, this angular correlation is greater than would be seen in the bulk. This reflects the fact that $W_{box}$ is significantly smaller than the nematic correlation length for these systems. Thus, the parallel rod orientation set by the wall is largely preserved throughout the entire confined region.
Figure 2.6. $g_2(r)$, given by Eq. (2.5), as a function of rod-wall separation distance. This plot shows the effect of increasing area fraction $A_{f,rods}$ in the confined region while holding constant the aspect ratio, $\alpha = 13.3$, and wall spacing, $W_{box} = 5L$.

Figure 2.7. $g_2(r)$, given by Eq. (2.5), as function of rod center-of-mass separation (bulk system) and rod-wall separation (confined systems with $W_{box} = 1L - 10L$) for rods with $\alpha = 13.3$ and $A_{f,rods} = 0.4$. 
Figure 2.8. $g_2(r)$, given by Eq. (2.5), as function of rod center-of-mass separation (bulk system) and rod-wall separation (confined systems with $W_{\text{box}} = 1L - 10L$) for rods with (a) $\alpha = 13.3$ and $A_{f,\text{rods}} = 0.4$ and (b) $\alpha = 20.0$ and $A_{f,\text{rods}} = 0.6$.

Looking to small distances on Fig. 2.7, it is interesting to see that $g_2$ appears to exhibit a universal curve, which follows the bulk curve for sufficiently short rod-rod distances. This seems to indicate that angular correlations between two, closely spaced rods in the bulk are the same as those between a rod and an infinite
Figure 2.9. Rod density profiles, given by Eq. (2.8), as a function of rod-wall separation for $\alpha = 13.3$ with (a) $A_{f,rods} = 0.4$ and $W_{box} = 1L$; and (b) $A_{f,rods} = 0.7$ with $W_{box} = 1L$ and $2L$.

To further investigate this trend, $g_2$ is shown for short rod-wall / rod-rod separations in Fig. 2.8. For $A_{f,rods} = 0.4$ [cf., Fig. 2.8(a)], it is seen that all the curves for the confined systems superimpose. However, the bulk curve lies perceptibly above the confined curves at short separations. At higher rod densities
(which are representative of \(A_{f,\text{rods}} = 0.6\) and 0.7 for \(\alpha = 13.3\) and 20.0), Fig. 2.8(b) shows that \(g_2\) exhibits oscillatory behavior for the confined systems, but not for the bulk. It should be noted that such oscillations fall below the resolution of a plot such as Fig. 2.6, which shows \(g_2\) for the entire confined region. These oscillations can lie above or below the bulk values and they reflect the layered structure that the walls impart to the rods. Thus, upon close inspection it is seen that \(g_2\) does not follow a universal curve at close rod-rod/rod-wall separations.

Differences between the confined and bulk systems can be understood to arise from a combination of two effects: the density effect and the distance-sampling effect. As is seen in Fig. 2.9(a), which shows the density profile for \(A_{f,\text{rods}} = 0.4\) with \(\alpha = 13.3\), the rod density exhibits a broad peak near the wall followed by a shallow minimum where the density is lower than the bulk value achieved near the center of the confined system. Over most of the distance range where \(g_2\) for the bulk is greater than that for the confined system [\(\text{cf.},\) Fig. 2.8(a)], the density is lower for the confined system. Rods in a lower density region have more orientational freedom and, thus, lower values of \(g_2\). The density effect is more pronounced for higher overall rod densities [Fig. 2.8(b)], where the oscillatory structure of \(g_2\) near the wall mirrors oscillations seen in the density profile. The density profile for \(\alpha = 20.0\) is shown in Fig. 2.9(b) for \(A_{f,\text{rods}} = 0.7\), where strong oscillatory behavior with 13 peaks is seen. The strong density oscillations reflect rod layering near the wall. For both \(\alpha = 13.3\) and 20.0 at \(A_{f,\text{rods}} = 0.6\), the rods form five layers of rods next to the wall. For \(\alpha = 13.3\) at \(A_{f,\text{rods}} = 0.7\), nine layers occur. Interestingly, for the separations studied here, the degree of confinement does not appear to influence the rod density profiles near a wall as each of the profiles superimpose. Thus, wall-induced layering and its associated density variations can influence the value of \(g_2\) close to a confining wall.
Although the above discussion has emphasized rod layering in the confined region, rod layering also occurs in the high-density, bulk nematic phases for $A_{f,\text{rods}} = 0.6$ and $0.7$. However, $g_2$ does not reflect this layering for the bulk systems [c.f., Fig. 2.8(b)]. This is due to the “distance sampling” effect. In the confined systems, separations are measured as the perpendicular distance between a rod’s center of mass and the wall, while in the bulk, separations are measured as the radial distance between the centers of mass of two rods. Thus, for a given rod-wall separation, there is only one possible configuration for a rod to have parallel alignment with the wall. In the bulk, however, the value of $g_2(r)$ reflects rods with perpendicular separations that can be less than $r$ (when two rods have staggered ends) and, thus, it is not sensitive to local variations in density. Despite these differences, the differences between $g_2$ for the bulk and confined curves are small. For practical (engineering) purposes it is possible to predict the degree of rod alignment near a wall by inspection of bulk behavior.

With regard to rod layering, the results found here differ from those observed in three-dimensional simulations of low-density spherocylinders in a slit-pore geometry [57]. In the study by Mao and colleagues [57], it was observed that rods with shorter aspect ratios had more pronounced layering in the vicinity of the wall than those with longer aspect ratios. This was attributed to the loss of rotational entropy near the wall being more significant in low density phases for longer rods. For the systems in this section, the layering is more extensive for the larger aspect-ratio rods and is due to the nematic nature of the bulk phases at the area fractions studied. Thus, the difference between the two-dimensional results in this section and the three-dimensional results of Mao and colleagues seems to be due to differences in density, rather than differences in dimensionality.
2.3.2.2 Rod Phase Depends on Confinement: $\alpha = 7.5$

In this section, results are discussed from simulations of confined rods with $\alpha = 7.5$ at all three area fractions. Table 2.1 shows that the bulk phases are isotropic for this aspect ratio. For $A_{f,rods} = 0.4$, the bulk rods have no preference to align in any particular direction. As discussed above, rods with $A_{f,rods} = 0.6$ and 0.7 have a tetratic-like alignment, but do not possess the orientational and positional order of a tetratic phase. Table 2.1 shows that decreasing the wall separation for $\alpha = 7.5$ results in an increasing value of the order parameter, indicating the rods are aligning in a uniaxial manner. The influence of the confining walls on rod ordering and how these bulk isotropic rods differ from the bulk nematics discussed above is discussed below.

Figure 2.10(a) shows the angular distribution function for $\alpha = 7.5$ at $A_{f,rods} = 0.4$ and Fig. 2.10(b) shows the angular distribution function for $A_{f,rods} = 0.6$, which is similar to that for $A_{f,rods} = 0.7$. In Fig. 2.10(a), the bulk phase shows a flat line, which indicates the rods have no preference to align in any direction. As the separation between the walls is decreased to $W_{box} = 10L$ a small peak arises that is centered around $\theta = 90^\circ$. This peak continues to sharpen as the spacing is further decreased, indicating the rods are collectively aligned parallel to the confining walls. Figure 2.10(b), shows that at a higher density, rods in the bulk phase exhibit a preference to align in perpendicular directions, which is demonstrated by the peaks at $0^\circ$, $90^\circ$, and $180^\circ$. When these rods are confined to $W_{box} = 10L$, their tetratic-like order persists but, compared to the bulk, a stronger peak occurs around $\theta = 90^\circ$. As the confinement of the rods increases, the peak at $\theta = 90^\circ$ increases, while the peaks at $\theta = 0^\circ$ and $180^\circ$ decrease. For $W_{box} = 1L$, there is no indication of tetratic order and the rods exhibit a single peak centered
Figure 2.10. Angular distribution functions, given by Eq. (2.7), for $\alpha = 7.5$ (a) $A_{f,rods} = 0.4$ for bulk and $W_{box} = 1L - 10L$ and (b) $A_{f,rods} = 0.6$ for bulk and $W_{box} = 1L - 10L$.

around the angle of the confining wall. Thus, with increasing confinement, the bulk behavior of the rods is suppressed in favor of uniaxial alignment parallel to the wall. However, a tendency is observed for the rods to be perpendicular to the wall. The remaining question to answer is where (relative to the wall) it can be expected to find parallel and perpendicular rods.
Figure 2.11. Rod density profiles, given by Eq. (2.8), as a function of rod-wall separation for $\alpha = 7.5$ at $W_{\text{box}} = 10L$.

Figure 2.11 shows the density profiles for $\alpha = 7.5$. The density profiles for $W_{\text{box}} = 10L$ are shown, truncated at $r/L = 2.5$, and it is noted that the density profiles at the shorter wall separations are nearly identical. The density profile for $A_{f,\text{rods}} = 0.4$ in Fig. 2.11 exhibits two peaks. Although two peaks are seen at $A_{f,\text{rods}} = 0.4$ for rods with higher aspect ratios [cf., Fig. 2.9(a)], a significant difference occurs in the location of the peaks. While the rods with higher aspect ratios [Fig. 2.9(a)] align in two layers that are parallel to the wall (a layer that is $\sim$ half a rod width away from the wall followed by a second layer that occurs $\sim$ one rod width further), the rods with the lower aspect ratio (Fig. 2.11) exhibit a peak at approximately one rod width, indicating a parallel layer, followed by a small, second peak at half a rod length; the distance where you would expect to find a peak if rods were perpendicular to the wall. Upon increasing the density in the confined region [cf., Fig. 2.11], the peak at $r/L = 0.5$ disappears and the density
profiles for $A_{f,rods} = 0.6$ and 0.7 reflect several parallel layers of rods immediately adjacent to the confining walls. A similar shift in the location of the peaks in the density profile has also been observed for spherocylinders in three dimensions in the presence of a single hard wall [58], where the authors found that as the density of rods was increased, the location of the peak in the density profile shifted closer to the confining wall.

Figure 2.12. $g_2(r)$, given by Eq. (2.5), as function of rod center-of-mass separation (bulk system) and rod-wall separation (confined systems with $W_{box} = 1L - 10L$) for rods with $\alpha = 7.5$ and $A_{f,rods} = 0.4$.

The orientational correlation functions shed more light onto the organization of rods near the confining walls. Figure 2.12 is a plot of $g_2$ for $\alpha = 7.5$ at $A_{f,rods} = 0.4$. A similar plot is obtained for $g_4$ but with smaller values, indicating that nematic correlations are more important than the tetratic correlations. With the exception of $W_{box} = 1L$, all the plots for the confined systems show a slight peak near $r/L = 0.5$, which is the distance where the second peak in the density profile
is observed [Fig. 2.11]. Because $g_2$ measures nematic correlations and this peak has higher values for $g_2$ than for $g_4$, it is concluded that the rods at $A_{f,rods} = 0.4$ have a greater tendency to be parallel to wall at this distance. The absence of peaks at $0^\circ$ and $180^\circ$ in the angular distribution in Fig. 2.10(a) confirms that there is no pronounced tendency for rods to be perpendicular to the walls. Thus, the relatively large spacing between the first and second peaks in the density profile in Fig. 2.11 reflects the weak organization of the rods as they move away from the wall.

**Figure 2.13.** $g_2(r)$, given by Eq. (2.5), and $g_4(r)$, given by Eq. (2.6), as function of rod-wall separation with $W_{box} = 5L$ for rods with $\alpha = 7.5$ and $A_{f,rods} = 0.6$.

Progressing to higher densities, Fig. 2.13 is plot of $g_2$ at $A_{f,rods} = 0.6$ and $W_{box} = 5L$. From this plot, it is seen that close to the wall, $g_2$ is greater than $g_4$. Also, oscillations are observed in $g_2$ and $g_4$ that are spaced approximately one rod width apart, indicating parallel alignment of the rods with the wall. Moving away from the wall, a crossover occurs to a region where the rods assume bulk-
like orientations \[ c.f., \text{Fig. 2.2(b)} \] and \( g_4 > g_2 \). The cross-over of \( g_2 \) and \( g_4 \) occurs for \( A_{f,\text{rods}} = 0.6 \) and \( 0.7 \) at \( W_{\text{box}} = 2L, 5L \) and \( 10L \). Only under the highest confinement \[ c.f., \text{Fig. 2.14} \] do nematic correlations dominate over the entire box width. The wall spacing for which a confined nematic is observed \( (W_{\text{box}} = 1L) \) corresponds to approximately twice the correlation length for \( g_2 \) for the bulk system, shown in Fig. 2.2(b). For \( W_{\text{box}} = 1L \), the center of the confined region is beyond the bulk correlation length from the wall and, thus, bulk-like ordering is observed there. Thus, taken together with the density profiles \[ c.f., \text{Fig. 2.11} \], Figs. 2.13 and 2.14 emphasize that near the walls, the rods align parallel to the walls, while the rods near the center of the confined region assume a bulk-like configuration. As the extent of the confined region decreases beyond twice the bulk correlation length for \( g_2 \), the tendency of the rods to align parallel to the walls increases. Different behavior was noted for spherocylinders in contact with a single hard wall and between two parallel hard walls in three dimensions. In these systems the confining wall induced a preference for the spherocylinders to have a biaxial alignment with the wall under certain conditions \[ 58 \]. Although the biaxial phase observed in these three-dimensional studies cannot occur in two dimensions, it is nevertheless interesting that in both three dimensions and in our two-dimensional simulations, hard walls induce rod orientations that do not occur in the associated bulk. Biaxial alignment was observed where the bulk is, depending on density, either isotropic or nematic in three dimensions, and nematic alignment is observed here where a bulk tetratic-like phase occurs in two dimensions.
Figure 2.14. $g_2(r)$, given by Eq. (2.5), and $g_4(r)$, given by Eq. (2.6), as function of rod-wall separation with $W_{box} = L$ for rods with $\alpha = 7.5$ and $A_{f,rods} = 0.7$.

### 2.4 Summary

In summary, these studies demonstrate several effects of confinement for hard rectangles in two dimensions. For all of the rod aspect ratios and area fractions studied, it was found that confinement induces the rods to align their long axes parallel to the walls. This increases the degree of nematic ordering over the bulk (indicated by the value of the nematic order parameter) to an extent that increases as the separation between the confining walls decreases. If the aspect ratio of the rectangles is sufficiently large (in this study, two aspect ratios, $\alpha = 13.3$ and 20.0, fall under this category), they exhibit nematic ordering in both the bulk and under confinement. Orientational correlations between these confined and bulk nematics are surprisingly similar for sufficiently close rod-wall or rod-rod separations. However, the hard, confining walls induce a subtle rod layering that
is not observed in analogous bulk nematics. Rods with a small aspect ratio ($\alpha = 7.5$) are isotropic in the bulk. For sufficiently high densities ($A_{f,\text{rods}} = 0.6$ and $0.7$), these bulk rods exhibit weak tetratic-like ordering, but are still deemed to be isotropic. Under confinement, low-aspect-ratio rods become nematic, in the sense that their order parameters take on sufficiently large values. From studies of density profiles, angular distributions, and orientational correlation functions, it is apparent that the rods align their long axes parallel to the wall in the near-wall region, where layering occurs for the higher rod densities. However, the confined rods still exhibit weak tetratic (isotropic) tendencies near the center of the confined region for all but the smallest wall separations ($W_{\text{box}} = 1L$). Although these studies probe the ordering of hard rectangles, the entropic tendencies observed here will still be present for rods with energetic interactions, such as those functionalized by DNA [132–135] and polymer linkers [136, 137]. Thus, these studies serve as a general starting point for understanding and controlling the assembly of rods in confining geometries.
In this chapter, the depletion interaction between two-dimensional hard squares immersed in hard rods and disks is explored. Squares were chosen since their non-spherical shape has interesting rotational effects associated with it. The interplay between the rotational entropy of the squares, as well as the role that rod and disk size and concentration have on the interactions between the squares is probed. Also, motivated by work on solvent mediated alignment of nanoparticles [88], the pathway by which the squares approach is determined since unique configurations of the squares may exist because of their non-spherical shape. Determining the pathway by which squares approach also aids in the interpretation of the depletion interaction between the squares.
3.1 Models and Methods

The two-dimensional depletion interaction between two hard squares in a sea of either hard rods or hard disks is studied. The squares have a side length of $s$, the rods are rectangles having a length of $L$ and a width of $D$, and the disks have a radius of $a$. Figure 3.1 illustrates the relative sizes of the particles used in this study. Disks were probed with sizes of $a/s = 0.12$, 0.18, and 0.24 and disk fractional coverages of $A_{f,\text{disks}} = 0.1, 0.2, 0.3,$ and 0.4, where the fractional coverage of disks is defined as

$$A_{f,\text{disks}} = \frac{N_{\text{disks}} \pi a^2}{A_{\text{box}}}. \quad (3.1)$$

Here, $N_{\text{disks}}$ is the number of disks in the simulation box. For the systems with rods, rod lengths of $L/s=0.55$ ($\alpha=8.2$) and $L/s=0.88$ ($\alpha=13$) were evaluated, at fractional coverages of 0.05, 0.1, and 0.2. The fractional coverage of rods is given by Eq. (2.1). For all aspect ratios of rods $\alpha$ and area fractions $A_{f,\text{rods}}$, the rods are in the isotropic phase. In the systems with disks, the simulation box size is $A_{\text{box}} = H_{\text{box}} \times W_{\text{box}} = 8s \times 8s$ and for systems with rods is $A_{\text{box}} = 10s \times 10s$. The
simulation box is prepared with periodic boundary conditions in both dimensions.

To understand the depletion interaction between two squares, simulations were performed in the absence and presence of the rods and disks. In both cases, the squares, rods, and disks were free to translate and rotate throughout the simulation box. For $A_{f,\text{rods}}=0.2$ and 0.3 and $A_{f,\text{disks}}=0.3$ and 0.4 additional simulations were performed in which the squares were allowed to freely rotate but had fixed centers of mass. The disks were allowed to freely translate and the rods were allowed to freely translate and rotate. These simulations allowed us to probe the relative orientations of the squares as a function of their separation. The center-of-mass separation between the squares was varied from near contact between the squares to a distance where the depletant had no measurable effect on the square’s orientation.

Metropolis MC simulations were used to calculate depletion interactions and approach pathways. The particles interact via a hard-core potential of the form $U = \infty$ if particles overlap and $U = 0$ if they do not, where $U$ is the potential energy. The probability of accepting a trial move is given by

$$P_{\text{move}} = \min\left(1, \exp\left[-\frac{\Delta U}{k_B T}\right]\right)$$

where $k_B$ is Boltzmann’s constant, $T$ is temperature, and $\Delta U$ is the difference in potential energy between the initial and trial configurations. If particles overlap the move is rejected. All trial moves that do not result in overlap between particles are accepted. The center-of-mass displacement of a square is uniformly distributed with a maximum of $a$ when disks are used as depletant and $D$ when rods are used. The displacement for disks and rods is uniformly distributed with a maximum of $a$ and $D$, respectively. The squares and rods are free to rotate and can randomly have any angle between $0^\circ$ and $179^\circ$ in $1^\circ$ increments.
A simulation is initialized by placing all particles at random locations in the simulation box. The rods were placed in the simulation box with the same orientation but randomly located centers of mass. Because of the low area fractions studied, equilibration required $5 \times 10^5$ MCS. Data production runs consisted of 8 to 20 simulations ranging in length from $2 \times 10^6$ to $10 \times 10^6$ MCS where the output of one simulation was used as the input to the next. The results reported here are an average of all production runs. At high area fractions of depletant, the acceptance rate of trial moves is typically 50% for disks, 20% for rods, and 5% for squares. At low area fractions of depletant, the acceptance rate is typically 80% for disks, 70% for rods, and 70% for squares.

These simulations were performed on-lattice, so that the squares, rods, and disks are represented by discrete points on a grid. We have previously used this method for simulating hard rectangles in two dimensions [138]. For the aspect ratios of rods studied here, it was determined that a rod width must be represented by a minimum of ten lattice sites to produce equivalent results from a real-space simulation. All the rods studied here have a width of ten sites and the length is adjusted to achieve the desired aspect ratio. The representation of the rods on the lattice determined the minimum resolution for the squares and disks.

### 3.2 Simulation Measures

In simulations where the squares are free to translate and rotate, the radial distribution function $g(r)$ between squares is measured. The square-square radial distribution function is given by

$$g(r) = \frac{\langle N(r, r + \delta r) \rangle}{2\pi r \delta r \rho_{\text{bulk}}}, \quad (3.3)$$
where $N$ is the number of squares found at a center-of-mass separation between $r$ and $r + \delta r$ and $\rho_{\text{bulk}}$ is the number density of squares. From the radial distribution function in Eq. (3.3), the potential of mean force [139] is calculated according to

$$w(r) = -k_B T \ln[g(r)] .$$

(3.4)

The potential of mean force is an indication of whether the squares possess attractive or repulsive interactions due to the depletant surrounding them. Negative values of $w$ indicate attraction and positive values indicate repulsion.

For the simulations where the squares are held fixed with respect to their centers of mass, the square-square angular probability ratio is calculated as

$$P(\theta_1, \theta_2) = \frac{\langle f(\theta_1, \theta_2) \rangle_{\text{depletant}}}{\langle f(\theta_1, \theta_2) \rangle_{\text{vacuum}}}$$

(3.5)

Here, $\theta_1$ and $\theta_2$ are the angles of the squares given between $0 \leq \theta_1, \theta_2 \leq 89^\circ$ and $\langle f(\theta_1, \theta_2) \rangle$ is the ensemble average of the frequency of observing each pair of angles. Symmetry of square orientations allows angles $90^\circ$ to $179^\circ$ to be averaged with $0^\circ$ to $89^\circ$ for statistical improvement of $P$. The ratio is calculated between the frequency of each pair of angles in the presence of depletant and that in vacuum (i.e., no depletant present). Values of the probability ratio greater than one indicate that the angles of the squares are more frequently observed when depletant is present and values less than one indicate that angles of the squares are less likely to be observed when depletant is present. From this measurement, the preferred configurations of the squares are identified at each center-of-mass separation.
3.3 Results

There are two competing effects in these systems, the rotational entropy of the squares and the depletion forces due to the rods and disks. A simulation with two squares in the absence of rods or disks isolates the rotational effects due to the squares and serves as a basis for later understanding the role of the rods and disks. Figure 3.2 contains the potential of mean force of two squares in the absence of depletant (vacuum). Center-of-mass separations between the squares of $r/s < 1$ are not allowed because of hard-core particle overlap which results in infinite repulsion between squares. For $1 < r/s < \sqrt{2}s$, the squares are close enough that one square can contact the other for certain square orientations. For $r/s < \sqrt{2}s$ the squares exhibit positive values of the potential of the mean force which indicates repulsive interactions. The repulsion results from the hindrance in rotation the squares experience as they approach at short center-of-mass separations. For $r/s > \sqrt{2}s$, the potential of mean force has a value of zero which indicates that the squares have no interaction at these distances.

3.3.1 Squares and Disks

Figure 3.2 also shows the potential of mean force between two squares for different sizes of disks. Figure 3.2(a) shows the results for the smallest disks studied, $a/s=0.12$. Differences in the potential of mean force for the different area fractions of disks are apparent for $r/s <1.3$, where the short-range repulsion observed for two squares in vacuum is still present but reduced in value. The reduction in short-range repulsion is related to the disk area fraction where higher values produce a stronger effect. For $r/s >1.5$, in Fig. 3.2(a) the disks have no effect on the potential of mean force, which has a value of zero at all area fractions of disks.
Figure 3.2. Potential of mean force, given by Eq. (3.4), for two squares in a sea of disks at different area fractions with a size of (a) $a/s=0.12$ and (b) $a/s=0.24$. $\beta$ is defined as $\beta=(k_B T)^{-1}$.

Figure 3.2(b) shows the potential of mean force for disks of size $a/s=0.24$ at different disk area fractions. The results shown for this disk size are representative for the results of disks with a size of $a/s=0.18$. Figure 3.2(b) has center-of-mass separations between the squares where the potential of mean force has negative values, indicating a depletion attraction between the squares. For
$A_{f,\text{disks}} \leq 0.3$ only one minimum ($r/s = 1.25$) is observed and for $A_{f,\text{disks}} = 0.4$, two minima ($r/s = 1.25$ and 1.8) are observed in the potential of mean force which are separated by a repulsive barrier. For $A_{f,\text{disks}} = 0.4$ the depth of the deepest minimum is $\sim 0.30k_B T$ at $r/s = 1.25$. The depth of the minimum increases as the area fraction of disk increases. At $A_{f,\text{disks}} = 0.2$, 0.3, and 0.4 a region of positive values near $r/s = 1.4 - 1.7$ indicates that the squares are being repelled. The height of the repulsive barrier increases in value with increasing disk area fraction. At sufficiently large center-of-mass separations between the squares, the potential of mean force is zero. Similar to the smaller disks [Fig. 3.2(a)], the larger disks also reduce the short-range repulsion between squares.

The oscillatory behavior of the depletion interaction has also been observed in two-dimensional systems of binary hard disks [87]. The authors studied the depletion interaction between two large disks in a sea of small disks and found that the amplitude of the oscillations (between repulsion and attraction) grew as the small disk concentration increased. The repulsion was attributed to spatial correlations that arise between the small disks which impedes the approach of the large disks.

Figure 3.3(a) compares the potential of mean force between two squares for different disk sizes at the same $A_{f,\text{disks}} = 0.3$. This graph shows that the depth of the minimum around $r/s = 1.25$ is proportional to the disk size. The short range repulsion, $r/s < 1.12$, is inversely proportional to disk size and is less than the repulsion experienced for two squares in vacuum. The contribution of the disks to the total potential of mean force can be isolated by subtracting the potential of mean force for two squares in vacuum from that in the presence of the disks. Figure 3.3(b) shows the effect of the disks isolated from the total potential of mean force graph at $A_{f,\text{disks}} = 0.3$ for all three sizes of disks. The disks influence
the interactions between the squares over a distance that is proportional to the disk radius. At short center-of-mass separations between the squares, $r/s \approx 1$, the smallest disks have the strongest affect on the potential of mean force, i.e. have the most negative value of the disk contribution. This result is consistent with the depletion interaction in the two-dimensional binary hard disk system where it was shown that reducing the small disk size while maintaining the same area fraction...
fraction produces a stronger attraction at distances near contact between the two large disks [87]. Isolating the role disks have in the total potential of mean force confirms that the repulsive barrier is due to the disks.

Although the smallest disks, \( a/s = 0.12 \), produce the strongest depletion attraction at short center-of-mass separations between squares in Fig. 3.3(b), a pronounced minimum in the total potential of mean force [Fig. 3.2(a)] was not observed. This is due to the short range over which the small disks have an effect on the interactions between the squares. At distances where the small depletant size has an effect, the square-square repulsion is a greater contribution to the total potential of mean force than the disks. A minimum in the total potential of mean force is observed for the two larger disk sizes because at longer separations between squares, where the square-square repulsion is weaker, the larger disks contribute more significantly to the total potential of mean force and subsequently an attractive minimum is formed.

![Figure 3.4](image)

**Figure 3.4.** Comparison of disk size on \( P \), given by Eq. 3.5, for (a) \( a/s = 0.18 \) (b) \( a/s = 0.24 \). Both (a) and (b) are at \( r/s = 1.3 \) and \( A_{f,disks} = 0.3 \).

Examining the probability ratio for different center-of-mass separations between the squares provides insight into the shape of the potential-of-mean-force
curves in Fig. 3.2. Figure 3.4 shows the effect of disk size on the square-square angular probability ratio for two squares at the same center-of-mass separation, \( r/s = 1.3 \), and disk area fraction, \( A_{f,\text{disks}} = 0.3 \). This center-of-mass separation between squares lies within the attractive minimum for both sizes of disks. These plots show that the squares prefer orientations around \( \theta_1 = \theta_2 = 40^\circ \) with greater frequency in the presence of disks than in vacuum (i.e. \( P > 1 \)). At these angles and center-of-mass separation the squares are in staggered vertex-to-vertex alignment where the sides of the squares are in contact. This alignment results in a free area gain for the disks since the disks are able to occupy additional positions around the squares. For squares angles \( \theta_1 = \theta_2 = 0^\circ \) the probability ratio is less than one indicating that this alignment of the squares is less likely to observed in the presence of disks than in vacuum. At these angles the squares are in face-to-face alignment. This alignment excludes the disks from occupying the gap between the squares and consequently no free area is gained by the disks. The white region in the center of the plots reflects angles of the squares that are not allowed because they result in overlap of the squares. The preference for staggered vertex-to-vertex alignment at this separation results in attraction between the squares since the disks cannot occupy positions between the faces of the squares. The deficit of disks in the gap results in more disks pushing the squares together.

Figure 3.4 also shows that the smaller disks induce a stronger configurational preference of the squares. The center region of the contour plot, which shows the preference for staggered vertex-to-vertex alignment, is observed with \( \sim 15\% \) greater frequency for the smaller disks [Fig. 3.4(a)] than for the larger disks [Fig. 3.4(b)]. The smaller disks induce a stronger alignment because the squares must adopt configurations with a smaller gap region with a higher frequency to create a favorable free area gain for the disks.
Figure 3.5. Comparing the effect of $A_{f, \text{disks}}$ on $P$, given by Eq. 3.5, for disks of size $a/s = 0.12$ at $r/s = 1.2$ for (a) $A_{f, \text{disks}} = 0.3$ and (b) $A_{f, \text{disks}} = 0.4$.

Figure 3.5 illustrates the effect of disk area fraction on square alignment for the same disk size. Both of these plots show that angles of the squares around $\theta_1 = \theta_2 = 35^\circ$ are exhibited with a probability ratio greater than one. These angles reflect staggered vertex-to-vertex alignment of the squares. Angles of the squares with $\theta_1 = \theta_2 = 0^\circ$ are exhibited less frequently in the presence of disks as compared to in vacuum. These angles reflect face-to-face alignment of the squares. At $A_{f, \text{disks}} = 0.4$, Fig. 3.5(b), the preference for particular square configurations is stronger than for $A_{f, \text{disks}} = 0.3$, Fig. 3.5(a). The increase in $P$ as $A_{f, \text{disks}}$ increases originates from the close spatial relationship between the disks at high area fractions. When there are few disks in the simulation box, the squares’ rotation is less hindered by the disks. As the area fraction of disks increases, squares are less free to rotate and consequently spend more time in configurations that are favorable for the translation of the disks. The effects shown in Figs. 3.4 and 3.5 are representative for all disk sizes and fractional coverages.

By calculating the probability ratio for several center-of-mass separations between squares, the preferred approach pathway can be determined. This
preferred approach pathway is determined relative to the pathway of two squares in vacuum. Two squares in vacuum approach (not shown) in a manner such that the squares reduce the probability of affecting the orientation of the other to maintain the rotational freedom of the pair. The range of influence of one square on another is limited to $\sqrt{2}s$. Beyond this distance, all configurations of the squares are equally probable in vacuum. Figure 3.6 summarizes the preferred configurations of squares placed on the potential-of-mean-force curve for disks of size $a/s=0.24$ at $A_{f,disks}=0.3$. For $r/s > 1.8$, the configurations of the squares are the same as those in vacuum. As the center-of-mass separation between the squares is reduced, the squares adopt face-to-face and face-to-vertex configurations. These configurations are present at separations where two squares in vacuum had no effect on one another. Between $r/s > 1.1$ and $r/s < 1.6$, the squares prefer vertex-to-vertex and
staggered vertex-to-vertex configurations. When the squares are far enough apart \((r/s > \sqrt{2}s)\) they are aligned in the vertex-to-vertex configuration. If the squares are close enough \((r/s < \sqrt{2}s)\) they are aligned in the staggered vertex-to-vertex configuration. The preference for two squares to be in staggered vertex-to-vertex alignment was never observed for two squares in vacuum at any center-of-mass separation. The squares also show a weaker preference for face-to-face alignment within the repulsive barrier because a disk can fit between the faces of the squares without significantly impacting the rotation of the squares. The repulsion between squares is created by the removal of disks from the interparticle gap in the face-to-face alignment. At the shortest center-of-mass separation studied, \(r/s=1.04\), the squares prefer a face-to-face configuration.

The results shown in Fig. 3.6 are similar for all disk sizes and area fractions with the differences being the distance over which the disks induce alignment of the squares. Comparing the approach pathway for the different size disks reveals that disks impart a configurational change to the squares over a distance that is consistent with their diameter. This is similar to the behavior observed with the potential-of-mean-force curves in Fig. 3.2.

### 3.3.2 Squares and Rods

Figures 3.7(a) \((L/s=0.55)\) and 3.7(b) \((L/s=0.88)\) show the potential of mean force between two squares for the two sizes of rods at different rod area fractions. Both lengths of rods show an attractive minimum that becomes more negative as the area fraction of rods increases. In Fig. 3.7(a), the depth of the deepest minimum is \(~0.3k_B T\) and in Fig. 3.7(b) it is \(~0.4k_B T\) both for \(A_{f,rods}=0.2\) at \(r/s=1.25\). Both lengths of rods show that increasing \(A_{f,rods}\) mitigates the short-range repulsion.
Figure 3.7. Potential of mean force, given by Eq. (3.4), for two squares in a sea of rods at different area fractions with a size of (a) $L/s=0.55$ ($\alpha=8$) and (b) $L/s=0.88$ ($\alpha=13$).

between the squares in vacuum. At sufficiently large center-of-mass separations between the squares, the rods have no effect on the potential of mean force, which has a value of zero.

A comparison of the potential of mean force between the different length rods at the same area fraction yields curves with similar shapes and values. The range of
the depletion interaction is greater and depth of the attractive minimum is more negative for the longer rods. The attractive minimum is deeper for the longer rods due to greater losses in rotational entropy of the rods that results from the constrained environment in the gap between two squares.

Figure 3.8. Comparing the effect of $A_{f,\text{rods}}$ on $P$, given by Eq. 3.5, for rods of size $L/s = 0.88$ at $r/s = 1.2$ for (a) $A_{f,\text{rods}} = 0.2$ and (b) $A_{f,\text{rods}} = 0.3$.

Figure 3.8 shows the dependence of the square configurations on the area fraction of rods for $L/s = 0.88$ at $A_{f,\text{rods}} = 0.2$ [Fig. 3.8(a)] and $A_{f,\text{rods}} = 0.3$ [Fig. 3.8(b)]. These plots reflect the orientations of the squares near the attractive minimum, $r/s = 1.2$, of the potential of mean force in Fig. 3.7(b). In both of these plots the alignment of the squares with $\theta_1 = \theta_2 = 90^\circ$ is the most preferred configuration. At these angles the squares are in face-to-face alignment which is similar to the result found for two squares in the absence of depletant. Two squares in vacuum prefer to align with as little angular constraint between themselves as possible which at this center-of-mass separation is satisfied with face-to-face alignment. It is unfavorable for the rods to occupy positions around the squares at a distance of less than $0.5L$ due to losses in rotational freedom of the rods. Consequently, the rods are not as sensitive to local changes in free area between the squares.
as are the disks which can occupy closer positions around the squares without a
hindrance to their free translation. Staggered vertex-to-vertex alignment of the
squares results in a constrained environment near the region where the two square
sides are in contact. The constrained region makes it difficult for the rods to ap-
proach the squares at this location of contact between the squares. The staggered
vertex-to-vertex alignment is also unfavorable for the rotational freedom of the
squares and without the close influence of depletant particles, the squares will not
stay in the staggered vertex-to-vertex alignment. The small gap region between
the squares is unfavorable for the rods to occupy since the rods would experience
significant losses in rotational freedom. This leads to a deficit of rods in the gap
and consequently the attractive minimum in the potential of mean force.

Similar to the results shown in Fig. 3.5 for disks, the squares also rotate
to similar configurations with a higher probability ratio at higher rod area
fractions. The maximum probability ratio at $A_{f,rods}=0.3$ is $\sim 2.3$ times higher
than for $A_{f,rods}=0.2$. The area fractions of rods used in this study are below
the isotropic to nematic transition but the increase in spatial and orientational
correlations between the rods drives the increase in preference for particular square
configurations.

Figure 3.9 summarizes the approach pathway between two squares for the two
rod lengths. In Fig. 3.9(a) and 3.9(b), it is shown that at $r/L=1.04$ that the
squares prefer a face-to-face configuration. In Fig. 3.9(a), for $1.1 < r/s \leq 1.3$,
the squares strongly prefer face-to-face alignment with a weaker preference for
staggered vertex-to-vertex alignment. For $r/s > 1.3$, the rods were not determined
to have a measurable effect on the alignment of the squares. Figure 3.9(b) shows
the approach pathway of squares in the presence of rods of length $L/s=0.88$ at
$A_{f,rods}=0.2$. This figure shows that the squares prefer face-to-face alignment at
all separations where the rods had a measurable effect on the alignment. A weak preference for face-to-vertex alignment was observed around $r/s=1.6$. For $r/s > 1.6$, the rods were not determined to have a measurable effect on the alignment of the squares. The distance over which the rods align the squares has a weak dependence on $A_{f,rods}$. For rods of length $L/s=0.55$, the rods influenced
the alignment of the squares up to a distance of $r/s=1.5$ and for $L/s=0.88$ up to a distance of $r/s=1.8$.

### 3.3.3 Comparing Rods and Disks

**Figure 3.10.** Comparison between the rods and disks contribution to the potential of mean force, given by Eq. 3.4. The rods are at $A_{f,rods}=0.2$ and $L/s=0.88$ and the disks are at $A_{f,disks}=0.4$ and $a/s=0.24$.

Figure 3.10 compares the effects of rods versus disks on the potential of mean force. The result with disks show both short-range attraction and a repulsive barrier that only forms at sufficiently high disk area fractions and sizes. The rods' contribution to the total potential of mean force is purely attractive and in this plot has comparable values as the disks for $r/s < 1.25$. The rods and disks produce similar values of attraction but the rods do so at an area fraction half the disk area fraction, $A_{f,rods}=0.2$ versus $A_{f,disks}=0.4$. This trend has also been discussed in three-dimensional systems where the depletion attraction induced by rods can be orders of magnitude larger than that induced by spheres [79]. Rods produce a stronger attraction, because in addition to losing translational freedom...
between two squares, they lose rotational freedom. Although separations between the squares occur where the total potential of mean force has negative values, the square-square repulsion still dominates at distances near contact.

Both rods and disks induce face-to-face alignment of the squares at $r_s = 1.04$ for all of the area fractions studied. The significant difference in the approach pathway of rods versus disks is that disks predominately induce vertex-to-vertex alignment between squares whereas rods induce face-to-face alignment. The shorter rods exhibit a combination of the approach pathway observed for disks and for the longer rods. Shorter rods exhibit both alignments because the losses in rotational entropy are less than those for the longer rods but the rods are not so short that they have no rotational component like disks.

3.4 Summary

In summary, The interplay between the rotational entropy of squares and the role depletant shape, size, and area fraction has on the depletion interaction was studied. It was also established that the approach pathway of two squares is dependent on characteristics of the depletant particles. For all of the depletant shapes, sizes, and area fractions studied, our results show a depletion attraction at short center-of-mass separations between the squares. Under certain conditions, when disks are used as depletant, a repulsive barrier forms. The repulsion is attributed to the high densities of disks that impede the approach of the squares. Under certain conditions, the rods are more effective as a depletant than the disks. This effect is attributed to losses in rotational entropy that the rods experience when confined between two approaching squares. The rotational entropy of the squares dominates the total potential of mean force at short center-of-mass
separations, even when depletant is included.

The approach pathway of squares depends on the type of depletant. Unlike previous studies that explored the depletion interaction between non-spherical particles of fixed orientation [74, 76], this work allowed the squares to freely rotate. Studying select particle orientations may result in the exclusion of important configurations that may not be anticipated. Collectively, the disks induce vertex-to-vertex or staggered vertex-to-vertex alignment the occurrence of which depends on the disk size and area fraction. Using rods as depletant, the squares prefer both staggered vertex-to-vertex and face-to-face alignment for the shorter rods and face-to-face alignment for the longer rods. Our results shed light onto the behavior of two-dimensional, non-spherical hard particles. The interactions and approach pathways of squares may be exploited in achieving self-assembled structures. The entropic tendencies observed here will still be present for systems with energetic interactions and therefore serve as a starting point for further understanding of the assembly of squares.
Chapter 4

Disk templated assembly of hard-rod fluids

In this chapter, the hard-disk templated assembly of hard-rod fluids in two dimensions is studied. These types of systems have been extensively studied in three dimensions and exhibit a rich and diverse phase behavior, but contributions in two dimensions are lacking. The phase behavior is examined and it is demonstrated that a number of interesting and potentially beneficial phases occur as the species concentrations are varied. The structure of the rods is examined as it relates to understanding depletion interactions in ensembles of particles. Chapter 4 demonstrates that rectangles, which are only observed to exhibit the isotropic and nematic phases in the absence of disks, can obtain significant positional order by microphase separating at sufficiently high area fractions of disks.

4.1 Simulation Method

The two-dimensional phase behavior in systems of disks and rectangles is studied. The rectangles, referred to as rods, have a length of $L$, a width of $D$, and an aspect
ratio $\alpha = L/D$, while the disks have a radius of $a$. The rods have $\alpha = 20$ and the disk diameter is equal to the width of the rod $2a = D$. These particles sizes were chosen because bulk phase separation is not often readily observed in three-dimensional systems when the disk diameter is comparable to the rod width for low to moderate particle concentrations. Also, a previous simulation study explored the formation of the lamellar phase in three dimensions using spherocylinders and disks of the same size [107]. The phase behavior of the rod and disk system is studied by varying the fractional coverages of both the rods and disks. The area fraction of rods is given by Eq. (2.1) and the area fraction of disks is given by Eq. (3.1). $A_{f,\text{disks}}$ was varied from a minimum of zero (rod only simulation) to a maximum of 0.065. $A_{f,\text{rods}}$ was varied from a minimum of 0.10 to a maximum of 0.70. The simulation box size was maintained at $A_{\text{box}} = 10L \times 10L$ and periodic boundary conditions were applied in both dimensions. The number of rods and disks vary depending on the fractional coverage.

MC simulations are used to determine the phase behavior of the hard rod and disk systems. Trial moves of rods are performed according to the orientational-bias MC algorithm outlined in Section 2.1. The particles interact via a hard-core potential of the form $U = \infty$ if particles overlap and $U = 0$ if they do not, where $U$ is the potential energy. For each trial move, the center-of-mass displacement of a rod was a maximum of $D$. The rods are free to rotate and can randomly have any angle between $0^\circ$ and $179^\circ$, in $1^\circ$ increments. The trial moves of disks are performed using the Metropolis MC algorithm outlined in Section 3.1. For $A_{f,\text{rods}} < 0.50$, the maximum displacement of a disk is $a$ and, at higher $A_{f,\text{rods}}$, the maximum displacement of a disk is $1.5L$. The large displacement of the disks is necessary as center-of-mass alignment of the rods can lead to slow sampling of the simulation box by the disks.
For $A_{f,\text{rods}} \leq 0.50$, a simulation was initialized by placing the rods and disks at random positions within the simulation box. The rods were placed with the same orientation to increase the probability of successfully initializing the box with a random center-of-mass distribution. For $A_{f,\text{rods}} > 0.50$ it was necessary to specify order to the rod and disk positions as the high area fractions could lead to prohibitively long random initializations. Different center-of-mass distributions were tested to ensure that the final configuration of particles was independent of the initial configuration. At low $A_{f,\text{rods}}$ and $A_{f,\text{disks}}$, equilibration required $5 \times 10^5$ MCS. At high $A_{f,\text{rods}}$ and $A_{f,\text{disks}}$, equilibration was done for a maximum of $15 \times 10^6$ MCS. Equilibration was tested by monitoring sampled quantities. Data production runs consisted of 3 to 12 simulations of $5 \times 10^5$ to $10^6$ MCS where the output of one simulation was used as the input to the next. The results reported here are an average over all data production runs. The acceptance rate of trial moves varies from a minimum of 20% for disks and 2% for rods at high area fractions to a maximum of 90% for disks and 70% for rods at low area fractions.

4.2 Simulation Measures

The nematic order parameter is calculated according to the order parameter tensor, given by Eq. (2.9), introduced in Section 2.2. The order parameter measures the orientational order of the rods and does not account for the positions of either the rods or disks.

The orientational correlation function $g_2$, given by Eq. (2.5) introduced in Section 2.2, measures the strength of parallel alignment of the rods. This measure accounts for both the alignment and position of the rods but does not include information about the disks.
The radial distribution function is a measure of the positional order of the rods. The rod-rod radial distribution function is given by

\[
g_{RR} = \frac{\langle N_{\text{rods}}(r, r + \delta r) \rangle}{2\pi r \delta r \rho_{\text{bulk}}},
\]

(4.1)

where \(N_{\text{rods}}\) is the number of rods found at a center-of-mass separation between \(r\) and \(r + \delta r\), and \(\rho_{\text{bulk}}\) is the bulk density of rods.

4.3 Results

4.3.1 Rods Only

A basis for understanding the disk-templated assembly of rods is the behavior of a system of rods with no disks present. In Fig. 4.1(a), the nematic order parameter \(S\) is plotted as a function of the area fraction of rods. Low values of \(S\) indicate the isotropic phase, a lack of positional and orientational order, whereas high values indicate the nematic phase with strong orientational order but a lack of positional order. For low area fractions of rods, the nematic order parameter has low values indicating that there is little orientational order between the rods. The lack of positional and orientational order is confirmed by the simulation snapshot taken at \(A_{f,\text{rods}}=0.10\) shown in Fig. 4.1(b). As the area fraction of rods increases, the nematic order parameter abruptly increases in value around \(A_{f,\text{rods}}=0.23\). For \(A_{f,\text{rods}} > 0.25\), the high value of the order parameter, \(S > 0.5\), indicates strong orientational order to the rods. The value of the order parameter at \(A_{f,\text{rods}}=0.35\) is \(S=0.83\) which is indicative of orientational order consistent with the nematic phase. The simulation snapshot shown in Fig. 4.1(c) illustrates the nematic phase which clearly exhibits strong orientational order but a lack of positional order. The
Figure 4.1. The nematic order parameter, given by Eq. (2.9), for a system of rods as a function of the area fraction of rods is shown in (a). A representative snapshot of the rods in the isotropic phase $A_{f,rods}=0.10$ is shown in (b) and the nematic phase $A_{f,rods}=0.35$ is shown in (c).

value of the area fraction of rods necessary to transition from the isotropic phase to the nematic phase is $A_{f,rods}=0.23$. This value was determined as the intersection of a line drawn through the isotropic-to-nematic transition region, the region of rapid increase in $S$, with the $x$-axis. This value is similar to DFT calculations of the phase transition of hard rectangles with $\alpha=20$ which was found to be $A_{f,rods}=0.22$ [38].

The nematic order parameter addresses the collective alignment of the rods throughout the simulation box. The orientational correlation function introduces
a spatial relationship between the orientation and position of the rods. Figure 4.2 shows the orientational correlation function $g_2$ for several values of the rod area fraction. All values of $g_2$ at $r/L$ near zero have a value of one for all area fractions of rods. The rods must align in parallel at this distance to avoid overlapping with one another. For $A_{f,rods}=0.2$, which is below the isotropic-to-nematic transition, $g_2$ quickly decays from a value of one at $r/L$ near zero to a value near zero for $r/L >3$. As the area fraction of rods increases, $g_2$ has higher values at longer distances. The increasing values of $g_2$ indicate that the orientational correlation between rods is increasing. At $A_{f,rods}=0.60$, the orientational correlation between rods is slow to decay which indicates strong alignment throughout the simulation box.

Information on the positional order of the rods is gained through the rod-rod radial distribution function shown in Fig. 4.3 for several rod area fractions. For low fractional coverages of rods, $A_{f,rods}=0.20$ and 0.40, $g_{RR}$ shows values less than one
Rod-Rod radial distribution function, given by Eq. (4.1), for various area fractions of rods.

For $r/L < 0.5$. These less-than-bulk values result from the rods maintaining their rotational freedom, which is achieved by maximizing the distance between the rod centers of mass. As the fractional coverage of rods increases, the higher levels of orientational order result in short-range peaks. The first peak for $A_{f,wires} = 0.70$ is located at $1.5D$ which is beyond the distance of closest approach between the rods. A small peak also develops at $r/L = 1$ in the nematic phase which reflects adjoining rods aligned near contact at their ends along their long axis. For $A_{f,rods} \leq 0.60$, $g_{RR}$ attains a bulk value of one for $r/L > 1.2$. For $A_{f,rods} = 0.65$ and 0.70, a weak decaying oscillatory shape is observed in $g_{RR}$. As the orientational order increases, the rods begin to weakly align in columns along the nematic director. The columns of rods give rise to the long-range oscillations observed in Fig. 4.3 for $A_{f,rods} = 0.70$. The presence of the oscillations is not a reflection of smectic-like ordering. Smectic-like ordering has been observed for two-dimensional spherocylinders [39]. For sufficiently long spherocylinders, the isotropic, nematic, and solid (smectic) phases
were observed. Semi-circular caps at each end of the spherocylinders drives the transition from the nematic to the smectic phase. Such a cap is absent in the rectangles studied here and it is also noted that the study by Martínez-Ratón et al. on the phase behavior of two-dimensional rectangles did not uncover the smectic phase [38]. For rectangles of aspect ratio $\alpha=20$, the isotropic and nematic phases were the only observed phases in their study.

4.3.2 Rods and Disks

As discussed in Section 1.4, spheres in three dimensions have been shown to have a profound influence on the structure of hard-rod fluids. In this section, the systematic variation of the area fraction of disks is explored with respect to the structure of the rods. The effect of the disks on the positional order of the rods is shown with the radial distribution function in Fig. 4.4. Figure 4.4(a) shows the effect of increasing $A_{f,\text{disks}}$ for a constant $A_{f,\text{rods}}$. The area fraction of rods shown in this figure is $A_{f,\text{rods}}=0.35$ which is above the isotropic-to-nematic transition. The role of disks on $g_{RR}$ is apparent for $r/L < 0.3$. At these distances, the peaks in $g_{RR}$ increase in height as $A_{f,\text{disks}}$ increases. These peaks indicate that the disks are pushing the rods closer together, increasing the amount of short-range order. This action is due to the depletion force of the disks which is a short-range interaction that occurs over distances on the scale of the disk diameter. The disks are forcing the rods’ centers of mass to align, which leads to a loss of rotational freedom of the rods, but creates a free-area gain that is favorable for the disks. Studies on the depletion interaction between two spherocylinders in a sea of small spheres found the depletion interaction to be highly dependent on the orientation and separation of the spherocylinders [76]. For the configurations of spherocylinders they studied,
the minimum energy of the depletion interaction favors the spherocylinders to have their centers of mass separated by a distance of their diameter $D$. Similar results have been found in ensembles of spherocylinders and spheres [111, 113, 109], where the alignment is also attributed to the depletion interaction induced by the spheres.

The shape and values of $g_{RR}$ for all $A_{f,disks}$ are similar for $r/L > 0.3$, which
indicates that disks only induce short-range order. At low area fractions of rods, it is favorable for the rods to maintain their rotational freedom, since the free area accessible to the disks is already high and consequently the disks have a weak effect on the alignment of the rods. The results shown in Fig. 4.4(a) are representative of the effect of disks on the structure of the rods for $A_{f,rods} < 0.50$ and all $A_{f,disks}$.

Figure 4.4(b) compares the result where the disks affected the short-range order of the rods, at $A_{f,rods}=0.45$, to the result where the disks affected the short and long-range order of the rods, at $A_{f,rods}=0.65$. For $A_{f,rods}=0.45$, $g_{RR}$ exhibits a small peak at $r/L=1$ after which the curve attains a value of unity indicating bulk conditions. For $A_{f,rods}=0.65$, $g_{RR}$ does not exhibit the weak peak at $r/L=1$ but rather an oscillatory behavior is noted. The period of the oscillations is indicative of layering of the rods in the direction of their long axis. The location of the peak around $r/L=1.2$ indicates that the rods are spaced further apart in the direction of their long axis as compared to bulk rods. For $A_{f,rods} \geq 0.50$, the curve shown for $A_{f,rods}=0.45$ in Fig. 4.4(b) is representative of low $A_{f,disks}$ and the curve shown for $A_{f,rods}=0.65$ is representative of high $A_{f,disks}$.

Figure 4.5 shows the orientational correlation function $g_2$ for different values of $A_{f,disks}$ at the same $A_{f,rods}$. The results shown in the figure are representative of $0.35 \leq A_{f,rods} \leq 0.60$. For $r/L < 0.3$, the values of $g_2$ are slightly higher at higher $A_{f,disks}$. This is due to the short-range order induced by the disks (cf., Fig. 4.4) that causes the rods to align with similar orientations. For $r/L > 0.3$, increasing $A_{f,disks}$ leads to increasingly lower values of $g_2$ for all distances which indicates weaker angular correlation between rods. The increase in short-range order between the rods effectively creates bundles of rods. These bundles are better aligned locally as compared to a bulk system of rods at the same area fraction. Figure 4.6 compares two simulation snapshots that illustrate the role disks have
Figure 4.5. Orientational correlation function $g_2$, given by Eq. (2.5), for $A_{f,rods}=0.50$ and different $A_{f,disks}$.

in inducing short-range order between the rods. Figure 4.6(a) shows a simulation snapshot of rods at $A_{f,rods}=0.45$ where the rods have clear orientational order. Figure 4.6(b) shows a simulation snapshot of rods and disks at $A_{f,rods}=0.45$ and $A_{f,disks}=0.065$ where the rods are better aligned locally and retain strong overall orientational order. The disks are shown in light gray in Fig. 4.6(b) to better illustrate the ordering of the rods. The average order parameter for the rods shown in Fig. 4.6(a) is $S=0.918$ and in Fig. 4.6(b) is $S=0.86$. The short-range alignment causes the loss of rotational freedom of an individual rod, but allows for rotational freedom of the bundle of rods. The increased rotational freedom of the bundles causes the decrease in the values of the orientational correlation function at the longer distances.

The reduction in orientational correlations at long distances between the rods, due to bundle formation, suggests a decrease in the total orientational order of the system. A plot of the nematic order parameter versus disk area fraction in Fig. 4.7
Figure 4.6. Simulation snapshots at (a) $A_{f,rods}=0.45$ and $A_{f,disks}=0.0$ and (b) $A_{f,rods}=0.45$ and $A_{f,disks}=0.065$. The disks are shown in light gray in (b).

shows that the overall alignment of the rods decreases with increasing disk area fraction due to the increase in short-range order between rods. The error bars in this plot are determined as the standard error of the order parameter values from each of the data production runs. This plot shows that the system with no disks present produced the highest value of the nematic order parameter. The maximum value of the order parameter is $S=0.936$ at $A_{f,disks}=0.0$ and continually decreases until the minimum value at $A_{f,disks}=0.065$ of $S=0.875$. The values of $S$ demonstrate strong orientational order for all $A_{f,disks}$ and that the decrease in overall order is not significant enough to render the system isotropic at the highest
Figure 4.7. Nematic order parameter, given by Eq. (2.9), for $A_{f,rods}=0.50$ as a function $A_{f,disks}$.

$A_{f,disks}$ studied. The trend of decreasing nematic order parameter with increasing $A_{f,disks}$ is found for $0.35 \leq A_{f,rods} \leq 0.60$. For $A_{f,rods} < 0.35$ and $> 0.60$, the value of the nematic order parameter is similar for all area fractions of disks at the same area fraction of rods.

For $A_{f,rods} \geq 0.50$, there are two effects of the disks on the structure of the rods. For lower values of $A_{f,disks}$, the rods have strong orientational order and the disks induce short-range order as was shown in Fig. 4.6(b). For sufficiently high $A_{f,disks}$ and certain $A_{f,rods}$, the rods and disks microphase separate. Figure 4.8 compares two simulation snapshots that illustrate the role disks have in inducing microphase separation of the rods and disks. Figure 4.8(a) shows a simulation snapshot of rods at $A_{f,rods}=0.65$ where the rods have orientational order but a lack of positional order. Figure 4.8(b) shows a simulation snapshot of rods and disks at $A_{f,rods}=0.65$ and $A_{f,disks}=0.055$ that have microphase separated. The disks are largely contained in the gap between well-aligned rows of rods. The average order
Figure 4.8. Simulation snapshots at (a) $A_{f,rods}=0.65$ and $A_{f,disks}=0.0$ and (b) $A_{f,rods}=0.65$ and $A_{f,disks}=0.055$. The disks are shown in light gray in (b).

parameter is similar for the rods shown in Fig. 4.8(a), $S=0.965$, and in Fig. 4.8(b), $S=0.974$. Microphase separation is reflected in $g_{RR}$ shown in Fig. 4.4(b) and also in $g_2$ at $A_{f,disks}=0.065$ in Fig. 4.5(b). Both of these results exhibit an oscillatory behavior of a microphase separated structure. Microphase separation has also been observed for systems of viruses (rods) and spheres [97] and spherocylinders and spheres [105–107, 109]. Microphase separation is favorable in these systems over bulk demixing because the spheres experience a sufficient gain in free volume by fitting into the gap between layers of rods.
4.4 Rectangle and Disk Phase Diagram

The above analyses of the structure and behavior of hard rectangles and disks are used to produce a phase diagram. Three phases of rods and disks were identified that possessed unique structural features that enabled them to be differentiated from one another. The conditions under which these phases are observed, i.e. the specific $A_{f,\text{disks}}$ and $A_{f,\text{rods}}$, determine the phase boundaries on the diagram. The three phases of rods and disks are the isotropic, nematic, and layered phases. The isotropic phase is characterized by a lack of positional order of the rods and disks as well as a lack of orientational order to the rods. The structural characteristics of this phase are low values of the order parameter ($S < 0.5$), decay of $g_2$ to zero within half the simulation box length, and a lack of microphase separation between the rods and disks. Microphase separation is denoted by $g_{RR}$ with characteristics similar to those of $A_{f,\text{rods}}=0.65$ shown in Fig. 4.4(b). An example snapshot of the isotropic phase is shown in Fig. 4.9(a). The nematic phase is characterized by a lack of positional order to the rods and disks and strong orientational order of the rods. The structural characteristics of this phase are high values of the order parameter ($S > 0.5$), non-zero value of $g_2$ for all distances, and a lack of microphase separation to the rods and disks. An example snapshot of the nematic phase is shown in Fig. 4.9(b). The layered phase is characterized by strong positional order to the rods and disks as well as strong orientational order to the rods. The structural characteristics of this phase are high values of the order parameter ($S > 0.88$), non-zero value of $g_2$ for all distances, and microphase separation between the rods and disks. An example snapshot of the layered phase is shown in Fig. 4.9(c).

Figure 4.10 contains the phase diagram summarizing the three phases of rods and disks identified in this study. The individual points in the phase diagram
Figure 4.9. Example simulation snapshots of the three phases of rods and disks (a) isotropic phase at $A_{f,\text{disks}}=0.045$ and $A_{f,\text{rods}}=0.20$ (b) nematic phase at $A_{f,\text{disks}}=0.015$ and $A_{f,\text{rods}}=0.60$ and (c) layered phase at $A_{f,\text{disks}}=0.065$ and $A_{f,\text{rods}}=0.70$. 
represent the simulation data points. The lines in the phase diagram delineate simulation data points that exhibited similar structural characteristics. The isotropic-to-nematic transition was found to be independent of $A_{f,\text{disks}}$ and all points below this line are regarded as being in the isotropic phase. Around the isotropic-to-nematic transition, the disks remain evenly distributed throughout the system such that the area fraction of rods at the transition is not altered. The rods prefer to maintain rotational freedom by remaining separated and the depletion force due to the disks is not strong enough to significantly alter the rod ordering at this transition. Lago et al. found that a system of spherocylinders with $\alpha=5$ with spheres of equal diameter to the rods showed a weak dependence of the isotropic-to-nematic transition on the volume fraction of spheres [109]. They studied low volume fractions of spheres such that the spheres remained evenly distributed throughout the simulation box. For systems where the sphere diameter is comparable to the length of the rods, a different behavior is noted which is related to the phase separation of the rods and spheres. Urakami et al. found that the addition of large spheres can induce an isotropic-to-nematic transition by increasing the sphere concentration at a fixed rod concentration [111]. They found that increasing the sphere concentration first leads to phase separation of the rods and spheres where the rods remain isotropic. Further increases in the sphere concentration lead to the formation of the nematic phase. In their system, the spheres occupy nearly half of the available volume.

The nematic phase is the only phase observed for $A_{f,\text{disks}} < 0.025$ above the isotropic-to-nematic transition. This phase is also observed for higher disk area fractions but with decreasing $A_{f,\text{rods}}$ as $A_{f,\text{disks}}$ increases. In this phase, the disks are evenly distributed throughout the simulation box. The layered phase is only observed at elevated $A_{f,\text{rods}}$ and $A_{f,\text{disks}}$. There is little difference between the
rotational freedom of the rods below and above the nematic-to-layered transition. It is favorable for the rods and disks to microphase separate for the configurational entropy gain of the rods and disks. Instead of the disks remaining distributed throughout the system, occupying positions at the ends of the rods, forming layers, creates a free area gain that is entropically favorable for the disks. The work by Dogic et al. explored the formation of the lamellar phase, alternating layers of rods and spheres, in a system of spherocylinders with $\alpha=20$ and spheres with diameter equal to the spherocylinder diameter [107]. These are the same sizes of particles as used in the present study. Their study was performed in three dimensions but has a notable similarity to the results presented here. They found that as the volume fraction of spheres increased, the lamellar phase formed at lower total volume fractions.

Figure 4.10. Phase diagram of rods and disks. The three phase are labeled as isotropic (I), nematic (N), and layered (L). The individual points represent the simulation data points.
4.5 Summary

In summary, the influence of hard disks on the structure of hard rods in two dimensions, which has received little attention to date was determined. The depletion force of the disks causes increased short-range order between the rods forming bundles. The bundles have increased rotational freedom which causes a decrease in total orientational order under certain conditions but is insufficient to alter the rod area fraction of the isotropic-to-nematic transition. At sufficiently high rod and disk area fractions it is favorable for the rods and disks to microphase separate. Microphase separation in rectangles and disks is an interesting result since bulk rectangles by themselves are not shown to exhibit any phase with a periodic density distribution [cf., Fig. 1.1(c)]. As discussed in Section 4.3.1, rectangles are only observed to exhibit the isotropic and nematic phases for $\alpha=20$.

Based on the structural characteristics of the rod and disks systems, a phase diagram was constructed that contained three phases of rods and disks. The three phases are the isotropic, nematic, and layered phases. The isotropic phase is characterized by a lack of positional and orientational order to the rods and the nematic phase is characterized by orientational order to the rods but a lack of positional order. The disks are evenly distributed throughout the system in both the isotropic and nematic phases. The isotropic-to-nematic transition is independent of the area fraction of disks used in this study as the depletion force due to disks is not strong enough to significantly alter the rod ordering. The layered phase is characterized by microphase separated rods and disks where the rods have strong positional and orientational order and the disks largely occupy the gap between the rods. The nematic and layered phases have similar orientational order to the rods, and it is the result of including sufficiently high area fractions.
of disks that drives the transition between phases. The rods and disks microphase separate because occupying positions at the ends of the rods, forming layers, results in a free area gain that is entropically favorable for the disks. The layered phase of rods and disks may be a beneficial phase for self-assembly purposes since the rods possess significant positional and orientational order.
Chapter 5

Assembly of gold nanowires by sedimentation from solution

In this chapter, simulations are employed to understand experimental results on the self-assembly of colloidal gold nanowires derivatized with a negatively-charged monolayer and adsorbed onto a glass substrate. These nanowires exhibit smectic ordering, the extent of which depends on nanowire length. Using MC simulations, the origins of the phase behavior seen experimentally are resolved.

5.1 Experimental Assembly of Au Nanowires

Experimental materials and methods are detailed in Appendix A. Nanowires were synthesized to be approximately 2, 4, and 7 µm in length and 300 nm in cross-sectional diameter. Measured dimensions were 1.8 ± 0.2, 4.3 ± 0.3, and 7.0 ± 0.5 µm, respectively for the three lengths, and 318 ± 45 nm diameter for all lengths. The nanowires are coated with 2-mercaptoethanesulfonic acid (MESA) to provide electrostatic stabilization to prevent aggregation. The self-assembly experiments were performed by allowing the nanowires to settle from suspension onto a glass
Figure 5.1. Representative experimental microscope images of self-assembled Au nanowires with lengths of 2 (a), 4 (c), and 7 µm (e). The corresponding Fourier transforms (b, d, and f) are included to the right of the corresponding microscope image. The Fourier transforms were cropped to magnify the features in the center.

slide. The bottom layer of nanowires is visualized with optical microscopy. The nanowires nearly always deposit on the slide as single nanowires, not higher order aggregates. Final configurations of nanowires were achieved approximately 30 min after initial deposition. Figures 5.1(a) (2 µm), (c) (4 µm), and (e) (7 µm) show representative experimental images of nanowire assemblies on a glass substrate. Figures 5.1(b), (d), and (f) are the corresponding Fourier transforms of the experimental images. A visual comparison of the microscope images in
Figs. 5.1(a), (c), and (e) reveals that as the length of the nanowire increases, the amount of order decreases. In Fig. 5.1(a), the 2 \( \mu \)m nanowires form well-defined rows with well-aligned ends. This high degree of orientational and positional order is consistent with the smectic phase. The 4 \( \mu \)m nanowires shown in Fig. 5.1(c) have many of the same features as the 2 \( \mu \)m nanowires, notably the distinct rows of nanowires, except that there is more disorder between the ends of the nanowires within a row. The 7 \( \mu \)m nanowires shown in Fig. 5.1(e) exhibit a marked decrease in order. The rows persist over only short distances and the ends of the nanowires are disordered and penetrate into the gap between rows.

The Fourier transforms (FTs) of sample images were obtained using the Image-Pro Plus software package. This software performs a fast Fourier transform of the images and the resulting transformation is plotted as the spectral form on a logarithmic scale. To enhance the features of the transformed images for analysis the brightness and contrast was uniformly enhanced. The FTs of the microscope images in Fig. 5.1 provide information on the characteristic distances in the assemblies and confirm our qualitative visual assessment of nanowire ordering. Each of the experimental FT images shows concentric rings, which reflect the multidomain smectic alignment of the nanowires. The FT image of the 2 \( \mu \)m nanowires [Fig. 5.1(b)] shows two distinctly separate rings, the 4 \( \mu \)m nanowires show three rings [Fig. 5.1(d)], and the 7 \( \mu \)m nanowires have a single, vaguely visible ring [Fig. 5.1(f)]. The 2 and 4 \( \mu \)m nanowires exhibit equally spaced rings, with radii that are integer multiples of one another. The distance from the origin to the middle of the first ring is 2.1 \( \mu \)m for the 2 \( \mu \)m nanowires, 4.4 \( \mu \)m for the 4 \( \mu \)m nanowires, and 7.9 \( \mu \)m for the 7 \( \mu \)m nanowires. These distances represent the nanowire length plus the inter-row spacing. The width of the rings represents the nonuniformity of nanowires within a row. For the 2 and 4 \( \mu \)m nanowires, each
of the rings within the respective FT image has a similar width. For the 2 \( \mu m \) nanowires, the width of the rings is 0.6 \( \mu m \) and for the 4 \( \mu m \) nanowires it is 1.8 \( \mu m \). The width of the ring is 4.0 \( \mu m \) for the 7 \( \mu m \) nanowires. In the case of the 2 \( \mu m \) nanowires, the shortest distance represented by the innermost ring \( \text{[i.e., the middle-of-the-ring distance (2.1 \( \mu m \)) minus one-half the ring width (0.3 \( \mu m \))] is equal to the nanowire length. The longest distance is the middle-of-the-ring distance plus one-half the ring width, which is equal to the nanowire length plus inter-row spacing. This indicates that the 2 \( \mu m \) nanowires have highly uniform rows. For the 4 and 7 \( \mu m \) nanowires, the minimum distances represented by the innermost ring are 3.5 and 5.9 \( \mu m \), respectively, which are less than the nanowire lengths, indicating interdigitation between rows of nanowires. Polydispersity of the nanowires can also contribute to broadening of the rings.

Unlike the shorter nanowires, the 7 \( \mu m \) nanowires exhibit only a single, vaguely visible ring about the center of the image. If disordering and interdigitation of the nanowire rows is significant, then the nanowires might be considered to be in the nematic phase. Our Fourier transform analysis of assembly pictures indicates that this is not the case and that ordering of the 7 \( \mu m \) nanowires can be considered to be smectic. Figure 5.2(a) shows a snapshot from a simulation where the nanowires are in a nematic phase [138]. The nanowires shown in Fig. 5.2(a) have an aspect ratio of \( L/D=13 \), similar to the experimental nanowires’ value of 12, with a similar density, \( A_{f,wires} = 0.6 \), to that in the experiments. The nanowire density is calculated as the fractional surface coverage according to Eq. (2.1). Unlike the experiments, the nanowires in Fig. 5.2(a) exist in a single domain, so the FT of this snapshot [Fig. 5.2(b)] does not exhibit a ring - instead the FT exhibits diffuse clouds perpendicular to the director (the dominant direction of alignment of the nanowires’ long axis), that results from the collective alignment of the nanowires.
While the length scale in the experimental FT in Fig. 5.1(f) represents the nanowire length plus inter-row spacing, the length scale associated with the blurry regions in Fig. 5.2(b) is consistent with the nanowire diameter plus intra-row spacing. Thus, ordering of the 7 µm nanowires can be considered to be smectic.

There is a large, circular, diffuse cloud that envelops the concentric rings in the FT in Fig. 5.1. The location of the edge of the cloud is related to the nanowire diameter plus intra-row spacing. The intra-row spacing is approximately 70 nm for the 2 µm nanowires, 80 nm for the 4 µm nanowires, and 100 nm for the 7 µm nanowires. The vertical and horizontal lines that intersect the middle of the FT images result from edge effects of the original microscope image [140].

![Figure 5.2](image)

**Figure 5.2.** A nematic phase of nanowires is shown in (a) with the corresponding FT in (b).

### 5.2 Model System

In an effort to understand nanowire ordering in the experiments, a model of the experimental systems was created. This model incorporates the three major interactions in the experimental system: gravity, van der Waals attraction, and electrostatic repulsion. Gravity is responsible for settling the nanowires from
the aqueous solution onto the glass substrate and holding them there. van der Waals attraction would give rise to nanowire aggregation in the absence of the stabilizing MESA layer; however, the electrostatic interactions due to the MESA coating are repulsive and keep the nanowires from aggregating. As is discussed below, the roughness of the nanowire ends creates additional electrostatic repulsion. Therefore, the balance of van der Waals and electrostatic interactions leads to the self-assembly of the nanowires on the surface.

In the simulations, the nanowires are represented as rigid chains consisting of spherical segments. This model has been used previously to simulate systems of rods [116–120]. The approximation of a rigid chain of spherical segments underestimates the van der Waals attraction as compared to two parallel aligned cylinders by approximately 30% [141]. The nanowire length is adjusted by varying the number of segments in the chain. Each of the segments is modeled as a core-shell sphere with a gold core and a MESA shell. The diameter and lengths of the nanowires in the simulations were selected to match the nominal dimensions for experimental nanowires, i.e., 2, 4, and 7 µm lengths and 300 nm diameter. The simulated diameter of the nanowires is 302 nm, which represents a 300-nanometer-diameter gold core with a one-nanometer-thick MESA layer. Thus, a total diameter of 302 nm is adopted for the spherical segments in the model. Monodisperse nanowires containing seven, 13, and 23 segments were simulated, which resulted in nanowire lengths of 2.1, 3.9, and 6.9 µm. In the discussion below, the nanowires are referred to as 2, 4, and 7 µm nanowires. As we will elaborate below, we simulated point charges on the end segments of each nanowire to represent the increase in electrostatic repulsion due to surface roughness at the nanowire ends.

Figures 5.3(a) and (b) illustrate the essential elements of the model nanowires.

To model a layer of nanowires on the glass substrate, a two-dimensional system
Figure 5.3. Characteristics of the model nanowires. The core-shell configuration of the spherical segments is shown in (a) and an example nanowire composed of seven spherical segments with point charges on the terminal segments is shown in (b). A cartoon of the simulation box is shown in (c).

was considered. Because of their high densities in the experiments, it is expected that the nanowires could exhibit either nematic ordering, in which nanowires adopt similar orientations, but have disordered center-of-mass positions, or smectic ordering, where the nanowires exhibit order in both their orientation and centers of mass. Since orientational ordering occurs in both cases, the nanowire orientations are fixed and only displacement of the nanowire centers of mass are considered. As shown in Fig. 5.3(c), the simulation box has dimensions of $H_{box}$ and $W_{box}$ and is periodic in both directions.

The total energy of the system $U_{total}$ is given by

$$U_{total} = \sum_{i,j \neq i} U_{vdW}(r_{ij}) + \sum_{i,j \neq i} U_{seg-seg}(r_{ij}) + \sum_{i,k} U_{seg-end}(r_{ik}) + \sum_{k,l \neq k} U_{end-end}(r_{kl})$$

(5.1)

where $U_{vdW}$ and $U_{seg-seg}$ are the van der Waals attraction and electrostatic repulsion, respectively, between segments $i$ and $j$ separated by a distance of $r_{ij}$, $U_{seg-end}$ is the electrostatic repulsion between segment $i$ and end-point charge $k$ separated by $r_{ik}$, and $U_{end-end}$ is the electrostatic repulsion between end-point charges $k$ and $l$ separated by $r_{kl}$. In all the sums in Eq. (5.2), the interactions are
pair-wise additive and intra-nanowire interactions are excluded. It should also be noted that overlap is prohibited between segments of different nanowires.

The core-shell van der Waals interaction $U_{vdW}$ is modeled using the potential developed by Vold [142], which is given by

$$U_{vdW}(r) = -\frac{1}{12} \left(A^\frac{1}{2}_{Au} - A^\frac{1}{2}_m\right)^2 H\left(\frac{r-D-2\delta}{D+2\delta}; 1\right) + \left(A^\frac{1}{2}_m - A^\frac{1}{2}_w\right)^2 H\left(\frac{r-D}{D}; 1\right) + 2 \left(A^\frac{1}{2}_w - A^\frac{1}{2}_m\right) \left(A^\frac{1}{2}_m - A^\frac{1}{2}_Au\right) H\left(\frac{r-D-\delta}{D}; D+\delta\right),$$  

(5.2)

with

$$H(x; y) = \frac{y}{x^2 + 2xy + x} + \frac{y}{x^2 + 2xy + x+y} + 2 \ln \left(\frac{x^2 + 2xy + x}{x^2 + 2xy + x+y}\right),$$  

(5.3)

Here, $A_w$, $A_m$, and $A_Au$ are the Hamaker constants for water, MESA, and gold, respectively; $r$ is the center-of-mass separation between segments; $\delta$ is the thickness of the MESA layer; and $D$ is the Au core-particle diameter. The following values of the Hamaker constants were used: $A_{Au}=40 \times 10^{-20}$ J, $A_w=3.73 \times 10^{-20}$ J, and $A_m=5.0 \times 10^{-20}$ J [143, 144]. In Eq. (5.2), the attraction between the gold segment cores is the dominant contribution because of the large value of the Hamaker constant of gold relative to MESA or water.

The segment-segment electrostatic interaction $U_{seg-seg}$ is modeled using the potential developed by Sader et al. [145], which has the form

$$U_{seg-seg}(r) = \epsilon \left(\frac{k_BT}{\epsilon_0}\right)^2 Y^2(r) \frac{q^2}{r} \ln \left[1 + e^{-\kappa(r-D-2\delta)}\right],$$  

(5.4)
with

\[
Y(r) = 4e^{-\kappa(r-D-2\delta)} \tanh^{-1}\left[ e^{-\kappa(r-D-2\delta)} \tanh\left( \frac{y_s}{4} \right) \right],
\]

(5.5)

Here, \(\epsilon\) is the permittivity of water, \(e_0\) is the charge of a proton, \(a\) is the segment radius, \(\kappa\) is the Debye screening parameter, and \(y_s\) is the reduced surface potential, which is determined from the zeta potential of the nanowires. This form for the electrostatic potential was chosen because it is valid for moderate to high surface potentials (25-100 mV), over a large range of particle separations \([\kappa(r-d-2\delta)>0.2]\), and for modest values of \(\kappa a\) (\(\kappa a >3\)), making it the most appropriate choice for the systems in this study. The experimental inverse Debye screening length is \(\kappa^{-1}=100\) nm, which is based on 10 \(\mu\)M ionic strength. In the paper by Dougherty et al., the zeta potential of gold nanowires coated with MESA was determined to be \(\xi_{Au}=55\) mV [146]. The zeta potential is related to the reduced surface potential in Eq. (5.5) by \(y_s = \frac{\xi_{Au}e_0}{k_B T}\).

Scanning electron microscope (SEM) images of nanowires that were synthesized with the technique employed here reveal that the sides of the nanowires are relatively smooth compared to the ends [147]. Structural irregularities can occur as protrusions or concavity of the nanowire ends. In previous work, it was found that such roughness can lead to an increase in electrostatic repulsion [148–152]. Kostoglou and Karabelas discussed that electrostatic repulsion of two interacting surfaces can be up to three times stronger on a rough surface than on a smooth one [148]. To address increased electrostatic repulsion associated with the rough ends of the nanowires, a point charge was placed at the terminal segments of the nanowires. A similar technique has been used by Suresh and Walz to describe a rough spherical particle interacting with a flat, smooth surface [150]. They modeled roughness as a uniform distribution of small hemispherical asperities on a larger
spherical particle surface and calculated the increase in electrostatic repulsion as a sum of pairwise interactions between the asperities and the flat smooth surface. Here, the ends of the experimental nanowires are not uniform and it would be difficult to characterize and model the different ends. Thus, the point charge represents the effect of increased electrostatic repulsion in a general way.

A screened Coulomb potential was used to describe the interaction between segments and end charges \( U_{\text{seg-end}} \) and between two end charges \( U_{\text{end-end}} \). A screened Coulomb potential been used previously to simulate colloids with adsorbed polyelectrolyte [153], where it was shown to successfully capture charge non-uniformity. The screened Coulomb potentials have the forms

\[
U_{\text{seg-end}}(r) = \frac{\exp(\kappa a)}{1 + \kappa a} \left( \frac{z_i z_{\text{seg}}}{4 \pi \varepsilon} \right) \left[ \frac{\exp(-\kappa r)}{r} \right], \quad (5.6)
\]

and

\[
U_{\text{end-end}}(r) = \left( \frac{z_i^2}{4 \pi \varepsilon} \right) \left[ \frac{\exp(-\kappa r)}{r} \right]. \quad (5.7)
\]

Here, \( z_i \) and \( z_{\text{seg}} \) are the number of elementary charges at the ends and segments, respectively. Based on the zeta potential of the nanowires, \( z_{\text{seg}} = 1282e_0 \). The value of the end-point charge was set to \( z_i = 50e_0 \), which results in less than a 4% increase in the total charge of an end segment. It should be noted that \( z_i \) is the only adjustable parameter in our model.

Metropolis MC simulations were used to determine the equilibrium configurations of nanowire assemblies. The simulations were performed in the canonical ensemble, where the number of nanowires \( N_{\text{wires}} \), area of the substrate \( A_{\text{box}} \), and temperature \( T = 293\text{K} \) are constant. In all simulations of 4 and 7 \( \mu \text{m} \) nanowires, \( N_{\text{wires}} = 1070 \), and for systems with 2 \( \mu \text{m} \) nanowires, \( N_{\text{wires}} = 1177 \). Results for 2, 4,
and 7 \( \mu m \) nanowires simulated at densities of \( A_{f,wires} = 0.69, 0.70, \) and 0.65, respectively, will be discussed below. These values are similar to the average experimental fractional coverage of \( A_{f,wires} = 0.7 \pm 0.2 \), which is the same for all wire lengths. The simulation box size \( (A_{box} = H_{box} \times W_{box}) \) varied from a minimum of \( (37.9 \times 24.9) \) \( \mu m^2 \) to a maximum of \( (46.7 \times 72.8) \) \( \mu m^2 \) to achieve the desired surface coverage. To determine the influence of density on nanowire ordering, a variety of additional surface coverages for each length were studied. For values within the experimental uncertainty, the influence of density was found to be negligible.

In the MC simulations, a trial move is performed by randomly displacing the center of mass of a nanowire in the \( x \) or \( y \) direction. The displacements are uniformly distributed with a maximum value of 0.1\( D \). The difference between the value of \( U_{total} \) for the initial and trial configuration \( U \) is obtained and the trial move is accepted with a probability given by Eq. (3.2). The acceptance rate of the trial moves varied from a minimum of 35\% to a maximum of 43\% for the various systems probed. Each simulation was equilibrated for a minimum of 50,000 MCS. By monitoring the convergence of the total energy, as well as sampled structural quantities, to a constant value, it was confirmed that the simulated systems were successfully equilibrated. Different initial nanowire configurations were employed to verify that the final configuration of nanowires was independent of the starting configuration. Data production runs consisted of 50,000 MCS. The results are an average over a minimum of ten production runs for each length of nanowire, where the output of one production run was used as the input to the next one.

The pair-longitudinal distribution function \( g_{||} \) was used to quantify the smectic ordering of the nanowires. This quantity yields the probability of finding a pair of nanowires whose center of mass is separated by a distance \( y_{||} \) in the direction
parallel to the long axis of the nanowire. It is defined by

\[
g_{\parallel}(y_{\parallel}) = \frac{\langle N(y_{\parallel}, y_{\parallel} + \Delta y_{\parallel}) \rangle}{W_{\text{box}} \Delta y_{\parallel} \rho_{\text{bulk}}},
\]

where \( \langle N(y_{\parallel}, y_{\parallel} + \Delta y_{\parallel}) \rangle \) is an ensemble average of the number of nanowires that have their center of mass at a distance between \( y_{\parallel} \) and \( y_{\parallel} + \Delta y_{\parallel} \) and \( \rho_{\text{bulk}} \) \((N_{\text{wires}}/A_{\text{box}})\) is the bulk density of nanowires. A smectic phase will exhibit peaks in \( g_{\parallel} \) indicating layers of nanowires. The nematic phase, due to a lack of positional order to the nanowires, will not exhibit peaks but rather has a value of unity.

Additionally, FTs are obtained from snapshots of the simulated nanowire assemblies using the same Image-Pro Plus software package that is used to analyze the experimental images. The snapshots are replicated along the periodic \( y \) direction to provide a large enough image so to obtain sufficient resolution with the FT to identify structural details.

### 5.3 Simulation Results

As discussed above, for the experimental and simulated nanowires, either nematic or smectic ordering could occur. To understand the preference for the smectic phase, it was contrasted to a rectangular columnar phase, shown in Fig. 5.4, in terms of how various energies contribute to the total energy in Eq. (5.1). In the rectangular columnar phase, maximum interdigitation occurs between the nanowires so, in this sense, it is the opposite of the smectic phase. For the test calculations, nanowires are fixed and have uniform inter-nanowire spacings at the densities discussed above. van der Waals attraction \( U_{\text{vdW}} \) favors aggregation of the nanowires, since this interaction is minimized at contact. Experimentally, there is
no contact between rows of nanowires or between nanowires in the same row. To minimize the van der Waals energy in an assembly without aggregation, nanowires tend to align within a row. For the 4 µm nanowires, the van der Waals energy is 5% (0.3 $k_B T$/nanowire) lower in the smectic phase than in the rectangular columnar phase. On the other hand, the segment-segment electrostatic repulsion $U_{seg-seg}$ is greatest when the nanowires are in the smectic phase. This repulsion is mitigated in the rectangular columnar phase. For the 4 µm nanowires, the segment-segment electrostatic repulsion is 3% (4.6 $k_B T$/nanowire) higher in the smectic phase than in the rectangular columnar phase.

Figure 5.4. The smectic phase is shown in (a) and the rectangular columnar phase is shown in (b).

Considering only van der Waals attraction and segment-segment repulsion (i.e., no end charges), it is expected that the dominant interaction would dictate the resulting phase. For all three lengths of nanowires, the van der Waals attraction accounts for approximately 3% of the total energy when only considering $U_{vdW}$ and $U_{seg-seg}$. Since the segment-segment repulsion is much greater than the van der Waals attraction in these systems, a disordered phase is expected. This is
observed in the MC simulation snapshot shown in Fig. 5.5(b), where the nanowires exhibit significant positional disorder when charges at the ends of the nanowires are neglected. The significant positional disorder results in the low peak values of $g_\parallel$ in Fig. 5.5(a).

Figure 5.5. The pair-longitudinal distribution function, given by Eq. (5.8), is shown in (a) for 4 $\mu$m nanowires with various end charges. Simulation snapshots are shown for $z_i=0$ (b), $z_i=25e_0$ (c), and $z_i=50e_0$ (d).

Adding a point charge to the terminal segments of the nanowires improves smectic ordering. To investigate this effect, MC simulations were performed with $z_i$ equal to $1e_0$, $5e_0$, $25e_0$, $50e_0$, and $100e_0$. Figures 5.5(c) and (d) show simulation snapshots of 4 $\mu$m nanowires with $z_i=25e_0$ (c) and $z_i=50e_0$ (d). The snapshot in Fig. 5.5(c) shows similar order to that for no end charge [Fig. 5.5(b)] and $g_\parallel$ is nearly identical for the two cases [Fig. 5.5(a)]. By increasing the end charge to
$z_i=50e_0$, it is evident in Fig. 5.5(d) that there is an increase in smectic ordering. This increase is also evident in $g_{||}$ in Fig. 5.5(a), which exhibits well defined peaks indicative of smectic layers. Thus, from the simulations, it is found that $z_i=50e_0$ is the lowest value of the end-point charge to induce a smectic phase for all lengths of nanowires and this value is adopted in the simulations and analysis below. The additional repulsion created by the end-point charge is within the range of values reported in the literature [148, 150].

 Returning to the analysis of the smectic and rectangular columnar structures in Fig. 5.4, assuming an end charge of $z_i=50e_0$, helps to understand how the end-point charge influences smectic ordering. The electrostatic repulsion between end-point charges $U_{\text{end-end}}$ favors the rectangular columnar phase over the smectic phase because end-end contact is minimized in this configuration. $U_{\text{end-end}}$ is 14\% (0.2 $k_B T$/nanowire) lower when the nanowires are in the rectangular columnar phase than in the smectic phase for 4 $\mu$m nanowires. On the other hand, the electrostatic repulsion due to segments and end-point charges $U_{\text{seg-end}}$ is minimized in the smectic phase, where contact between ends and non-terminal segments is minimized. For the 4 $\mu$m nanowires, $U_{\text{seg-end}}$ is 20\% (3.4 $k_B T$/nanowire) lower in the smectic phase than in the rectangular columnar phase.

 From the different contributions to $U_{\text{total}}$, two interactions favor the smectic phase ($U_{\text{vdW}}$ and $U_{\text{seg-end}}$) and two favor the rectangular columnar phase ($U_{\text{seg-seg}}$ and $U_{\text{end-end}}$). The two most significant contributions to the total energy are $U_{\text{seg-end}}$ and $U_{\text{seg-seg}}$. $U_{\text{seg-seg}}$ and $U_{\text{vdW}}$ are proportional to the length of the nanowire. In contrast, the localized repulsion due to roughness at the end of the nanowires, $U_{\text{seg-end}}$ and $U_{\text{end-end}}$, is independent of nanowire length. Thus, $U_{\text{seg-end}}$ and $U_{\text{end-end}}$ contribute less significantly to the total energy as the nanowire length increases and end roughness impacts ordering the most for the
2 µm nanowires and the least for the 7 µm nanowires. $U_{\text{seg-end}}$ and $U_{\text{end-end}}$ contribute $\sim 25\%$ of the total electrostatic repulsion for the 2 µm nanowires, $\sim 7\%$ for the 4 µm nanowires, and $\sim 2\%$ for the 7 µm nanowires.

In addition to energetic factors, entropic factors also govern nanowire ordering. The effects of entropy can be inferred from related studies of hard rectangles\[38, 45, 138\] and hard spherocylinders \[38, 39\]. For the area fractions and aspect ratios of nanowires in this study hard rectangles exhibit only the nematic phase \[38\]. The area fractions and aspect ratios of nanowires in this work are too low for the formation of the solid (smectic) phase in spherocylinders \[39\]. Thus, based on these studies, for the aspect ratios and area fractions of nanowires in this study, the nematic phase is favored by entropy.

Through an analysis of the different interactions, an understanding has been gained of why the smectic phase is energetically preferred in the adsorption of charged-stabilized, aqueous metallic nanowires. The MC simulations reflect these energetic tendencies. Upon inspection of representative simulation snapshots for the 2 [Fig. 5.6(a)], 4 [Fig. 5.6(c)], and 7 µm [Fig. 5.6(e)] nanowires, it is seen that as the length of the nanowire increases, the degree of smectic ordering decreases. The 2 µm nanowires [Fig. 5.6(a)] are well aligned and the space between rows of nanowires is mostly free of nanowire ends. Figure 5.6(c) shows that the ends of the 4 µm nanowires interdigitate between the rows to a greater extent than the 2 µm nanowires and Fig. 5.6(e) shows that the 7 µm nanowires exhibit greater interdigitation than the 4 µm nanowires. The simulation snapshots are qualitatively consistent with the experimental images in Fig. 5.1.

The visual observation of order is supported by the pair-longitudinal distribution function $g_{||}$ shown in Fig. 5.7. Figure 5.7(a) shows the entire function and Fig. 5.7(b) highlights the features of a single peak. The 2 µm nanowires exhibit
Figure 5.6. Simulation snapshots for the 2 (a), 4 (c), and 7 µm long nanowires (e). Corresponding FT images are shown to the right of each snapshot in (b), (d), and (f). FTs were cropped to enhance the features in the center.

The best ordered rows and have the highest peak value of $g_{||}$, as well as a zero value of $g_{\perp}$ between the peaks. The zero value of $g_{||}$ indicates that the rows of nanowires do not interdigitate. The 4 µm nanowires show a lower peak value than the 2 µm nanowires, which means the rows of nanowires are not as well aligned, as noted in the simulation snapshots of Fig. 5.6(c). The 7 µm nanowires have the lowest peak value, indicating the least amount of smectic order. This is supported by the simulation snapshot in Fig. 5.6(e).
Figure 5.7. Pair-longitudinal distribution function, given by Eq. 5.8, for the different lengths of nanowires. The entire function is shown in (a) and a single peak centered around $y_{||}/L=3$ is highlighted in (b). The features present in (b) are characteristic of all peaks.

Figures 5.6(b), (d), and (f) contain the FTs of the 2, 4, and 7 µm nanowires. Unlike the experiments (cf., Fig. 5.1), the FTs of the simulation snapshots do not show rings because the nanowires are aligned in a single direction and do not exhibit multiple ordered domains. The vertical dots in the center of the FT images are equally spaced and represent the same structure as the rings in the experimental FT images. The distances represented by the vertical dots is 2.2 µm for the 2 µm nanowires, 3.8 µm for the 4 µm nanowires, and 6.7 µm for the 7 µm nanowires. For the 2 µm nanowires [Fig. 5.6(b)], the vertical dots represent the nanowire length plus inter-row spacing because the ends of the nanowires within a row are well ordered and the rows are clearly separated. For the 4 and 7 µm nanowires [Figs. 5.6(d) and (f)], the vertical dots represent a distance that is less than the nanowire length because rows of nanowires are interdigitated. The distances extracted from the locations of the vertical dots in the center of the FTs
in Fig. 5.6 are consistent with the structure noted in $g_{||}$ in Fig. 5.7. For the 4 and 7 µm nanowires, $g_{||}$ exhibits side peaks to the left and right that flank the center of each main peak [cf., Fig. 5.7(b)], which represent the disorder of the nanowire ends between rows. The distance between the side peaks represents the deviation from perfectly aligned rows of nanowires, where a broader width indicates that the nanowires are more disordered. The distances between the vertical dots in the FTs in Fig. 5.6 are equal to the nanowire length plus inter-row spacing minus the distance between side peaks. The spacings between vertical dots in the simulation FTs and the rings in the experimental FTs are in good agreement.

The horizontal features in the simulation FTs in Fig. 5.6 provide a measure of the nanowire diameter plus intra-row spacing. These features represent the same structure as the edge of the large cloud in the experiments. The intra-row spacing is 100 nm and is equivalent for all three nanowire lengths in the simulations. This value is comparable to the experimental values which range from 70 nm for the 2 µm nanowires up to 100 nm for the 7 µm nanowires.

### 5.4 Summary

Smectic ordering was observed and quantified in charge-stabilized, colloidal Au nanowires that settle onto a glass substrate due to gravity. The MC simulations indicate that these assemblies are brought about by a balance of electrostatic and van der Waals interactions and that a small degree of end charging, associated with roughness of the nanowire ends, can lead to well-aligned nanowire rows. Smectic ordering has been observed in previous experimental studies involving self-assembled nanowires on solid substrates [8, 13–16, 21, 22]. However, these studies involved liquid-vapor interfaces or drying of the nanowires, so that capillary forces
were deemed significant. This work demonstrates that the balance of non-specific forces can lead to well-ordered nanowire arrays. This knowledge may be useful in the selective fabrication of devices.
Conclusions and recommendations for future studies

The research in this dissertation studied the self-assembly of non-spherical particles under the influence of hard barriers, depletion interactions, and van der Waals and electrostatic interactions. Each of the different influences was demonstrated to have a significant effect on the behavior of the non-spherical particles. The studies demonstrate several effects of confinement for hard rectangles in two dimensions. For all of the rod aspect ratios and area fractions studied, it was found that confinement induces the rods to align their long axes parallel to the walls. This increases the degree of nematic ordering over the bulk to an extent that increases as the separation between the confining walls decreases. Orientational correlations between confined and bulk nematics are surprisingly similar for sufficiently close rod-wall or rod-rod separations. However, the hard, confining walls induce a subtle rod layering that is not observed in analogous bulk nematics. Rods with a small aspect ratio are isotropic in the bulk. For sufficiently high densities, these bulk rods exhibit weak tetratic-like ordering, but are still deemed to be isotropic. Under confinement, low-aspect-ratio rods become nematic, in the sense that their
order parameters take on sufficiently large values. From studies of density profiles, angular distributions, and orientational correlation functions, it is apparent that the rods align their long axes parallel to the wall in the near-wall region, where layering occurs for the higher rod densities. However, the confined rods still exhibit weak tetratic (isotropic) tendencies near the center of the confined region for all but the smallest wall separations.

The interplay between the rotational entropy of squares and the role depletant shape, size, and area fraction has on the depletion interaction was studied. For all of the depletant shapes, sizes, and area fractions studied, the results show a depletion attraction at short center-of-mass separations between the squares. Under certain conditions, when disks are used as depletant, a repulsive barrier forms. The repulsion is attributed to the high densities of disks that impede the approach of the squares. Under certain conditions, the rods are more effective as a depletant than the disks. This effect is attributed to losses in rotational entropy that the rods experience when confined between two approaching squares. The rotational entropy of the squares dominates the total potential of mean force at short center-of-mass separations, even when depletant is included. It was also established that the approach pathway of two squares is dependent on characteristics of the depletant particles. Unlike previous studies that explored the depletion interaction between non-spherical particles of fixed orientation [74, 76], this work allowed the squares to freely rotate. Studying select particle orientations may result in the exclusion of important configurations that may not be anticipated. Collectively, the disks induce vertex-to-vertex or staggered vertex-to-vertex alignment the occurrence of which depends on the disk size and area fraction. Using rods as depletant, the squares prefer both staggered vertex-to-vertex and face-to-face alignment for the shorter rods and face-to-face alignment
for the longer rods. The fact that the staggered vertex-to-vertex alignment is preferred between squares at the minimum value of the potential of mean force when disks or short rods are present is encouraging for the future use of depletion interactions in producing unique self-assembled structures.

This work on depletion interactions between two particles is a natural precursor to studying this effect in ensembles of particles. The influence of hard disks on the structure of hard rods in two dimensions was determined which has received little attention to date. The depletion force of the disks causes increased short-range order between the rods forming bundles. The bundles have increased rotational freedom which causes a decrease in total orientational order under certain conditions. At sufficiently high rod and disk area fractions it is favorable for the rods and disks to microphase separate. Microphase separation in rectangles and disks is an interesting result since bulk rectangles by themselves are not shown to exhibit any phase with a periodic density distribution [cf., Fig. 1.1(c)]. As discussed previously, rectangles are only observed to exhibit the isotropic and nematic phase for \( \alpha = 20 \). Based on the structural characteristics of the rod and disks systems, a phase diagram was constructed that contained three phases of rods and disks. The three phases are the isotropic, nematic, and layered phases. The isotropic phase is characterized by a lack of positional and orientational order to the rods and the nematic phase is characterized by orientational order to the rods but a lack of positional order. The disks are evenly distributed throughout the system in both the isotropic and nematic phases. It was found that the isotropic-to-nematic transition is independent of the area fraction of disks used in this study as the depletion force due to disks is not strong enough to significantly alter the rod ordering at these area fractions. The layered phase is characterized by microphase separated rods and disks where the rods have strong positional and orientational
order and the disks largely occupy the gap between the rods. The nematic and layered phases have similar orientational order to the rods, and it is the result of including sufficiently high area fractions of disks that drives the transition between phases. The rods and disks microphase separate because occupying positions at the ends of the rods, forming layers, results in a free area gain that is entropically favorable for the disks. The layered phase of rods and disks may be a beneficial phase for self-assembly purposes since the rods possess significant positional and orientational order.

Smectic ordering was observed and quantified in charge-stabilized, colloidal Au nanowires that settle onto a glass substrate due to gravity. The MC simulations indicate that these assemblies are brought about by a balance of electrostatic and van der Waals interactions and that a small degree of end charging, associated with roughness of the nanowire ends, can lead to well-aligned nanowire rows. The simulations predict the experimentally observed trend of decreasing smectic order as the nanowire length increases.

Future work can be pursued in several areas. The methods used to modify non-spherical particle assembly discussed in this dissertation could be extended to include the effects of external fields, such as magnetic or electric. The external fields offer a way to influence the ordering of particles without physically contacting the particles. Exploring the assembly of particles on an inhomogeneous substrate, either chemically or physically, is another extension of the present study that will be necessary in producing devices with complex and long-range order. It would also be beneficial to study more complex non-spherical particles such as branched or multifaceted (≥5) particles [154] because the unique geometric features of each particle could potentially be exploited for different applications.
Appendix A

Experimental materials and methods

This section contains the materials and methods information concerning the synthesis and assembly techniques of the gold nanowires discussed in Chapter 5.

Materials. All water used in these experiments was purified to >18 MΩ, using a Barnstead Nanopure filtration system. All chemicals were used as received except where noted. Alumina membranes, pore diameter 0.2 µm, were purchased from Whatman. Orotemp 24 and Ag Cyless R plating solutions were purchased from Technic Inc. Concentrated nitric acid was obtained from JT Baker and 2-mercaptoethanesulfonic acid (MESA) was purchased from Sigma. Sodium hydroxide was purchased from EMD. Ethanol was purchased from Pharmco. Concentrated ammonium hydroxide was purchased from EM Science.

Optical Microscopy. Optical microscopy was performed on a Nikon Eclipse TE300 inverted microscope with a Xe lamp and a Photometrics CoolSNAP HQ camera. The objectives used were a Plan Fluor 100 oil objective (NA 1.30) and a Plan Apo 60 oil objective (NA 1.40). Reflected brightfield images were taken using white light with Image-Pro Plus software (version 4.5; Media Cybernetics).

Nanowire Synthesis. The gold nanowires were grown by electrochemical deposition in the pores of alumina membranes following previously reported
methods [155, 156]. The resulting nanowires were imaged by optical methods to determine lengths with at least 50 nanowires were measured to determine length. Three different lengths were used in this work, referred to throughout this manuscript as 2, 4, and 7 μm nanowires. Measured lengths and standard deviations for these particles were: \( L = 1.8 \pm 0.2, 4.3 \pm 0.3, \) and \( 7.0 \pm 0.5 \) μm, respectively. All nanowires were \( D = 318 \pm 45 \) nm in diameter (previously determined by TEM), hence their aspect ratios were approximately 6, 12, and 22.

**Nanowire Derivatization.** Nanowires were functionalized with a coating of MESA to provide electrostatic repulsion. The thiol moiety of this molecule binds to the Au surface of the nanowires, resulting in a monolayer terminated with the negatively-charged sulfonate groups. Nanowire stock solution (\( \sim 10^9 \) nanowires in 1 mL ethanol) was pelleted by centrifugation at 8100 g for 1 min and, after rinsing 3 times in water, was resuspended in a 10 mg/mL aqueous solution of MESA. The suspension was then vortexed for two hours followed by rinsing the nanowires three times with 1 mL of water by centrifugation.

**Self-Assembly of Nanowires.** A silicone spacer (Invitrogen CoverWell perfusion chamber gasket) was cleaned with ethanol and placed onto a glass slide, forming wells 9 mm in diameter and 2.5 mm deep. 100 μL of nanowires, at the batch concentration, were sonicated and immediately added to a well and allowed to settle from suspension onto the glass slide. After addition of the nanowires each cell was sealed with a glass slide, which prevented the evaporation of solution allowing the nanowires to form assemblies without being effected by an evaporation front. Each constructed well constituted one sample and at least six different samples were imaged for each nanowire length. After nanowire loading, the sample was allowed to rest on the stage of an inverted microscope. The nanowires nearly always deposit on the substrate as single nanowires, not higher
order aggregates. Final configurations only form once sufficient deposition time has passed, approximately 30 minutes. The bottom-most layer of nanowires was observed on the microscope after letting the nanowires rest overnight.
Bibliography


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Derek Triplett was born in Mt. Pleasant, Pennsylvania. He attended Bucknell University where he obtained his B.S. degree in Chemical Engineering in 2003. After graduation, he joined the Ph.D. program in Chemical Engineering at The Pennsylvania State University. In addition to pursuing his Ph.D., he obtained a Ph.D. minor in Computational Science. Derek Triplett is a member of the American Institute of Chemical Engineers.