Different phases of a system of hard rods on three dimensional cubic lattice

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Abstract. We study the different phases of a system of monodispersed hard rods of length $k$ on a cubic lattice, using an efficient cluster algorithm able to simulate densities close to the fully-packed limit. For $k \leq 4$, the system is disordered at all densities. For $k = 5, 6$, we find a single density-driven transition, from a disordered phase to high density layered-disordered phase, in which the density of rods of one orientation is strongly suppressed, breaking the system into weakly coupled layers. Within a layer, the system is disordered. For $k \geq 7$, three density-driven transitions are observed numerically: isotropic to nematic to layered-nematic to layered-disordered. In the layered-nematic phase, the system breaks up into layers, with nematic order in each layer, but very weak correlation between the ordering directions of different layers. We argue that the layered-nematic phase is a finite-size effect, and in the thermodynamic limit, the nematic phase will have higher entropy per site. We expect the systems of rods in four and higher dimensions will have a qualitatively similar phase diagram.

Keywords: classical Monte Carlo simulations, classical phase transitions, numerical simulations, phase diagrams
**1. Introduction**

A system of long hard rods in three dimensional continuum is known to undergo a phase transition from a disordered isotropic phase to an orientationally ordered nematic phase with increasing density [1]. At even higher densities, a system of spherocylinders will show a smectic/columnar phase, having partial translational order along with orientational order [2, 3], or solid-like phases [4]. Physical systems where such transitions are observed include aqueous solutions of tobacco mosaic viruses [5], liquid crystals [6], oxygen monolayers adsorbed on molybdenum surfaces [7], carbon nanotube nematic gels [8] and chlorine atoms adsorbed on silver [9]. In two dimensions, there is no true ordered phase, but a system of needles undergoes a Kosterlitz–Thouless type transition into a high density phase with power law correlations [10–12].

The corresponding problem on lattices where the orientation of rods is restricted to the lattice directions (also known as the Zwanzig model [13]) has also been studied in parallel. Consider a system of monodispersed rods of length $k$ that occupy $k$ consecutive lattice sites along any one of the lattice directions. Two rods cannot overlap. Early work based on virial expansion [13], high density expansions [14] and the Guggenheim approximation [15], predicted a transition from the low-density disordered phase to a nematic-ordered phase, as the density is increased. It is clear that at densities near full packing, nematic order will not survive, as there are exponentially many disordered configurations. But the nature of the high-density disordered phase is not well-understood [6, 16]. In two dimensions, numerical simulations have shown that this phase has no orientational long-range order, but there could be some other more subtle
order. In three dimensions, what is the nature of different phases in the lattice model of hard rods? This is the primary question that we address in this paper. We find that the high-density phase does not have nematic ordering, where rods preferentially align themselves parallel to each other. Instead, for $k > 4$, they develop a smectic-like order, where the densities of two of the three orientations have large, nearly equal values, and the density of rods of third orientation is very small and the different layers are nearly independent. Within a layer, it is possible to pack rods so that there is a non-zero entropy per rod for any density of rods, and this entropy remains non-zero, even at close-packing. Making different layers nearly independent maximizes the entropy, while satisfying the hard-core constraints at high density. We do obtain a nematic phase, but only at intermediate densities, and only for $k \geq 7$. The determination of the rich structure of different possible orderings in this simple model is the main new finding of this paper. We expect that the behavior in dimensions $d > 3$ would be qualitatively similar.

We first summarize known results for the model in two and three dimensions. In two dimensions, for $k = 2$ (dimers), it may be shown rigorously that the system is disordered at all densities [17], while at full packing, the system is power-law correlated [18, 19]. For $k \leq 6$, Monte Carlo simulations show that the system is disordered at all densities [16]. For $k \geq 7$, the system undergoes two transitions: first from a low-density disordered phase to an intermediate density nematic phase, and second from the nematic phase to a high density disordered phase [16, 20, 21]. While the first transition belongs to the Ising and 3-state Potts universality classes on square [22–24] and triangular lattices [23, 25] respectively, the universality class of the second transition has been difficult to resolve [20, 21]. For large enough $k$, the existence of the nematic phase may be rigorously proved [26]. The model may also be solved exactly on a tree-like lattice, corresponding to a Bethe approximation, and shows a nematic phase for $k \geq 4$, but does not exhibit a second transition [27]. Density functional theory for rods give a similar result [28]. The problem of rods may also be generalized to hard rectangles of size $m \times d$ or hard squares of size $m \times m$. For large aspect ratio, the system of rectangles shows four phases with increasing densities: disordered to nematic to columnar to solid-like phases. The detailed phase diagrams for different choices of $m$ and $d$, and the behavior of phase boundaries in some special limits may be determined in [29–32]. The $m \times m$ hard square models undergo a single density-driven transition from a disordered phase to a high-density columnar phase [33–42].

In three dimensions, dimer models ($k = 2$) at full packing on bipartite lattices are known to show a Coulomb phase, with algebraic decay of orientational correlations [19], while for non-bipartite lattices, the correlations decay faster, and in some exactly solved cases, correlations are strictly zero beyond a finite range [43]. Not much is known for larger values of $k$. It would be expected that, like in the continuum, there will be an isotropic–nematic transition as the density is increased above zero. Theories based on Bethe approximation [15], density functional theory [28], and exact solutions on tree-like lattices [27] predict a first order isotropic–nematic transition for $k \geq 4$. However, the topological structure of Bethe or tree-like lattices does not allow for the possibility of having flippable squares of size $k \times k$. This is unlike the case of hypercubic lattices, where the possibility of flippable squares of size $k \times k$ leads to a finite entropy per rod at full packing, and leads to a high-density disordered phase, which does not
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occur on tree-like lattices. Also, the minimum value of $k$ for such a transition to occur in three dimensions is not known.

In this paper, we study the problem of a monodispersed system of rods of length $k$ using grand canonical Monte Carlo simulation using an algorithm with cluster moves. For $k \leq 4$, we find that the system remains disordered, and is in the isotropic phase, at all densities. When $k = 5, 6$, we observe a single transition from a low density disordered phase in which the fractional number of different orientations is nearly equal, to a layered-disordered phase in which the fractional number of one orientation becomes very small, and the system develops a layer-like structure, where each layer is a plane with most of the rods being of two orientations lying within the plane, and very weak correlations between different layers. When $k \geq 7$, at intermediate densities, we numerically observe two other phases: a nematic phase, and a new phase that we call the layered-nematic phase. In the layered-nematic phase, each plane has two-dimensional nematic order, but there is no overall bulk nematic order. At even higher densities, the nematic order within a layer is also lost. This transition is essentially a 2d transition, as different layers are nearly independent. We argue that the observation of the layered-nematic phase in our simulations is a finite size effect, and in the thermodynamic limit, when there is nematic order within a layer, aligning the orientation of different layers is entropically favored, and the nematically-ordered phase will have higher entropy than the layered-nematic phase.

The rest of the paper is organized as follows. In section 2, we define the model precisely, and describe the grand canonical Monte Carlo scheme that is used to simulate the system. Section 3 describes the different phases— isotropic, nematic, layered-nematic and layered-disordered—that we observe in our simulations. In section 4, we use perturbation theory to argue that the layered-nematic phase observed in simulations is an artifact of finite system sizes, and the observed behavior should cross over to nematic order for length-scales greater that some crossover scale $L^* (\rho)$, where $\rho$ is the density of covered sites. Section 5 consists results of detailed simulations for systems with $k = 2, 3, \ldots, 7$. The minimum length of rods that is needed for each of the phases to exist is determined. The critical densities and chemical potentials, and other critical parameters, are determined for $k = 5, 6, 7$. We end with a summary and discussion of results in section 6.

2. Model description and Monte Carlo algorithm

Consider a cubic lattice of size $L \times L \times L$ with periodic boundary conditions. The lattice sites may be occupied by rods that occupy $k$ consecutive lattice sites in any one of the three mutually orthogonal directions. The rods interact only through excluded volume interactions, i.e. a lattice site may be occupied by at most one rod. We associate a weight $e^{\mu}$ with each rod, where $\mu$ is the chemical potential rescaled by temperature. We will call rods oriented in the $x$, $y$ and $z$-directions $x$-mers, $y$-mers and $z$-mers respectively. The site of a rod with the smallest $x$, $y$ and $z$-coordinates will be called its head.

We use grand canonical Monte Carlo simulations to determine the different phases in the hard rod model as a function of the density, for different rod-lengths $k$. Conventional

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algorithms with local evaporation and deposition moves fail to equilibrate the system (within available computer time) at large densities because the system gets stuck in long-lived metastable states. Instead, we implement a Monte Carlo algorithm with cluster moves [20, 44] that has recently proved useful in equilibrating systems of hard particles with large excluded volume interactions at densities close to one [20, 44] and even at full packing [39].

The Monte Carlo algorithm that we use is the following: remove all the $x$-mers, leaving all $y$-mers and $z$-mers undisturbed. The empty intervals in each row in the $x$-direction, separated from each other by $y$-mers or $z$-mers, is now re-occupied by $x$-mers with the correct equilibrium probabilities. The calculation of these probabilities reduces to a one-dimensional problem which may be solved exactly (see [20, 39, 45] for details). The evaporation and deposition move satisfies detailed balance as the transition rates depend only on the equilibrium probabilities of the new configuration. Following evaporation and deposition of $x$-mers, we repeat the set of steps with $y$-mers, and then with $z$-mers.

To reduce equilibration and autocorrelation times at high densities, we also implement a flip move. If there is a $k \times k$ square that is fully covered by $k$ parallel $k$-mers, then we can flip the orientation of $k$-mers, within this square, without affecting any other rods, as shown in the schematic diagram in figure 1. Clearly, the flip move does not violate the hard-core constraint, and satisfies detailed balance. We define one Monte Carlo time step as updating every row in the $x$, $y$- and $z$- directions (total of $3L^2$ rows), and $L^3$ (in case of small system sizes) or $L^3/k^2$ (in case of large system sizes) flip moves.

The flip move is crucial for equilibrating the system at densities close to full packing. Figure 2 shows the time evolution of density $\rho$ for a system with $k = 7$, starting from nematic initial conditions in which most of the rods lie in the $x$-direction, using the evaporation-deposition algorithm with and without the flip move. The value of $\mu$ is such that the equilibrium configuration does not have nematic order (see section 5 for details). When the flip move is present, $\rho$ reaches its equilibrium value in about $3 \times 10^5$ Monte Carlo steps. On the other hand, when the flip move is absent, the system does not reach equilibrium even after $10^7$ Monte Carlo steps.

The algorithm is easily parallelized as all the rows can be updated simultaneously. The flip move may also be parallelized by choosing a plane and then choosing one of the $k^2$ sublattices randomly. All $k \times k$ squares whose bottom left corner lies in

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**Figure 1.** Schematic diagram illustrating the flip move in the Monte Carlo algorithm. If there is a $k \times k$ square, that is fully covered by $k$ parallel $k$-mers as shown in (a), then the orientations of the $k$-mers within the square are flipped to the configuration shown in (b).
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In this section, we describe and define the different phases that we observe in our Monte Carlo simulations. Let \( \rho_x, \rho_y \) and \( \rho_z \) be the density of sites occupied by \( x \)-mers, \( y \)-mers and \( z \)-mers respectively, and \( \rho = \rho_x + \rho_y + \rho_z \) is the total fraction of sites occupied by \( k \)-mers. Consider the two-dimensional vector

\[
Q = |Q| e^{i\theta} = \rho_x + \rho_y e^{2\pi i} + \rho_z e^{4\pi i}.
\]  

We define the bulk nematic order parameters as

\[
Q_N = \langle |Q| \rangle,
\]  

\[
P_2 = \langle \cos (3\theta) \rangle,
\]

where \( \langle \cdots \rangle \) denotes average over the equilibrium probabilities.

**Isotropic phase:** In the isotropic phase, the system is disordered, with \( \rho_x \approx \rho_y \approx \rho_z \). The probability distribution of \( Q \) is centered about the origin, and the order parameters take the value \( Q_N \approx 0 \) and \( P_2 \approx 0 \).

**Nematic phase:** In the nematic phase, a majority of the rods are of one orientation, while the rods of the other two orientations have smaller, roughly equal densities. If \( x \) is the preferred direction, then \( \rho_x \gg \rho_y \approx \rho_z \), as can be seen in the temporal evolution of three densities shown in figure 3(a). A snapshot of a randomly chosen
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...xy plane, as shown in figure 3(b), clearly shows that most rods are x-mers. In the nematic phase, \( Q_N \approx \rho \) and \( P_2 \approx 1 \).

Layered-nematic phase: In the layered-nematic phase, there is spontaneous symmetry breaking; one of the xy, yz or zx planes is selected, and the density of rods that are oriented perpendicular to this plane is suppressed (see figure 4(a)), making the system layered. If the chosen plane is the xy plane, then \( \rho_x \approx \rho_y \gg \rho_z \). In the layered-nematic phase, within a xy-plane, the rods have two-dimensional nematic order. This may be seen in the snapshots, shown in figures 4(b)-(d), of three randomly chosen xy planes. Each of the planes has two-dimensional nematic order, but could be majority x-mers or y-mers. Also, the majority orientation within a plane changes frequently with time in our simulations. This is demonstrated in figure 4(e), where the time evolution of the local nematic order parameter \( n_x(z) - n_y(z) \) is shown for four xy planes, where \( n_x(z) \) and \( n_y(z) \) are the densities of sites occupied by x-mers and y-mers in layer z. There are roughly equal number of planes with majority x-mers and majority y-mers, as may be seen from the double-peak probability distribution function \( P(n_x - n_y) \), shown in figure 4(f), which is obtained by averaging over the various xy planes and over time. If the system has layered-nematic phase, \( Q_N \approx \rho/2 \) and \( P_2 \approx -1 \).

Layered-disordered phase: In the layered-disordered phase, like in the layered-nematic phase, a majority of the rods lie in one of the xy, yz or zx planes (see figure 5(a)). Let the chosen plane be the xy plane, i.e. \( \rho_x \approx \rho_y \gg \rho_z \). In the layered-disordered phase, unlike the layered-nematic phase, the rods within a xy plane do not have nematic order, i.e. \( n_x(z) \approx n_y(z) \) for each layer z. This may be seen in the snapshots, shown in figures 5(b)-(d), of three randomly chosen xy planes, where in each of the planes, there are roughly equal number of x-mers and y-mers present. The nematic order in each plane fluctuates about zero, as may be seen from the time evolution of the nematic order of four planes as shown in figure 5(e) as well as probability...
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Figure 4. (a) Time evolution of the densities of rods along the three orientations in the layered-nematic phase when \( \mu = 5.55 \) and \( \rho \approx 0.914 \) for \( k = 7 \) and \( L = 112 \). The initial configuration has nematic order, where most of the rods are in the \( x \)-direction. (b)–(d) Snapshots of three randomly chosen \( xy \) planes after equilibration. In each of the planes, either horizontal or vertical rods are in majority. (e) Time evolution of \( n_x(z) - n_y(z) \), where \( n_x(z) \) and \( n_y(z) \) are the densities of \( x \)-mers and \( y \)-mers is layer \( z \), for \( z = 0, 24, 49, 74 \). The nematic order in each plane keeps switching between majority \( x \)-mers and majority \( y \)-mers. (d) The probability distribution \( P(n_x(z) - n_y(z)) \), averaged over time and all planes, exhibits two symmetric peaks.

distribution (see figure 5(f)) of the local nematic order parameter \( n_x(z) - n_y(z) \). In the layered-disordered phase, \( Q_N \approx \rho/2 \) and \( P_2 \approx -1 \).

We find that onset of the layered disordered phase in 3d for \( k = 7 \) occurs at approximately \( \rho_{2,3d} \approx 0.914 \pm 0.01 \) (figure 4(d)), which is not very different from the corresponding value in two dimensions (\( \rho_{2,2d} \approx 0.917 \pm .005 \)) [20]. This is consistent with the picture that at high densities, the layers are only very weakly coupled, the transition
from nematic (or layered nematic) to the layered disordered phase is essentially driven by the two-dimensional transition within a layer.

The bulk order parameters $Q_N$ and $P_2$ do not distinguish between the layered-nematic and layered-disordered phases, and take the values $Q_N \approx \rho/2$ and $P_2 \approx -1$ for both phases. Though we observe both these phases in our simulations, we argue in the
next section that the layered-nematic phase has lower entropy per site than the nematic phase, and is thus a metastable phase.

4. The instability of the layered-nematic phase

In this section, we discuss the instability of the layered-nematic phase. We argue that the layered-nematic phase seen in our simulations is the result of finite size of our samples, and different layers would be expected to develop alignment—and hence the usual nematic order, if we could study samples of much larger sizes. This is done using a perturbative expansion similar to the high density expansion developed for hard squares and rectangles [32, 33, 38, 40, 45].

We start by considering a system in which the activities of rods in different directions are different: in the \( x \)- and \( y \)-directions, it is \( z \), but in the \( z \)-direction it is \( z' \). When \( z' = 0 \), the different \( z \)-layers decouple, and the problem reduces to the problem of \( k \)-mers on a two dimensional square lattice. We assume that \( z \) is such that in each layer there is nematic ordering, but in different layers, it may be in different directions.

We consider the spontaneous-symmetry broken state \( \{ \sigma \} \), where the ordering direction in the layer \( z = i \) is \( \sigma_i \), taking values \( \pm 1 \), depending on the mean orientation being in the \( x \) or \( y \)-directions. There are \( 2^L \) such states, for the \( L \times L \times L \) lattice, say with fixed boundary conditions that enforce the specified layered order.

When \( z' = 0 \), the states with different \( \{ \sigma \} \) are degenerate. We now develop a perturbation theory for the partition function \( \mathcal{L}_{\{\sigma\}}(z, z') \) in powers of \( z' = e^{\mu'} \) [32, 38]:

\[
\mathcal{L}_{\{\sigma\}}(z, z') = \mathcal{L}_{\{\sigma\}}(z, 0) \left[ 1 + A_{\{\sigma\}}(z) z' + B_{\{\sigma\}}(z) z'^2 + \ldots \right].
\]

Define \( \eta(\vec{R}) \) as the indicator variable that takes a value 1 in a configuration, iff one can place the head of a \( z \)-mer at \( \vec{R} \), and zero otherwise. Then it is easy to see that

\[
A_{\{\sigma\}} = \sum_{\vec{R}} \langle \eta(\vec{R}) \rangle_{\{\sigma\}}
\]

and

\[
B_{\{\sigma\}} = \sum_{\vec{R}_1, \vec{R}_2} \langle \eta(\vec{R}_1) \eta(\vec{R}_2) \rangle_{\{\sigma\}},
\]

where the sum over \( \vec{R}_1 \) and \( \vec{R}_2 \) is over all position of two non-overlapping \( z \)-mers. The expectation values of products of \( \eta(\vec{R}) \) values factorize into terms that depend on correlations of unoccupied sites within a layer. Clearly, we get \( A = L^3 \epsilon^k \), independent of \( \{\sigma\} \), where \( \epsilon = 1 - \rho \) is the density of holes in the unperturbed problem. Hence, any difference between layer-orderings only shows up in the coefficient \( B \).

Let us denote the probability that, in a 2d layer, both sites \((x, y)\) and \((x + \Delta_1, y + \Delta_2)\) are unoccupied as \( \alpha(\vec{\Delta}) \) or \( \beta(\vec{\Delta}) \), when the nematic ordering in the plane in \( x \) or \( y \)-respectively, with \( \vec{\Delta} = (\Delta_1, \Delta_2) \). Then, \( B_{\{\sigma\}}(z) \) is a sum of terms of the form \( \alpha(\vec{\Delta})^r \beta(\vec{\Delta})^s \), where \( r \) is the number of planes with \( x \)-ordering that intersect both rods, and \( s \) is the corresponding number of planes with \( y \)-ordering. By symmetry in the \( x \) and \( y \) directions,
there will also be a term $\alpha^s \beta^r$ for the same $\{\sigma\}$ corresponding to separation $r = (\Delta_2, \Delta_1)$ between the rods. But we notice that, for all $\alpha, \beta \geq 0$, and integers $r, s \geq 0$,
\[
\alpha^r \beta^s + \alpha^s \beta^r \leq \alpha^{r+s} + \beta^{r+s}. \tag{7}
\]
This implies that the second correction term is greater when all in-plane nematic orientations are parallel than when they are not. Thus, the concentration of $z$-rods induces an effective aligning interaction between nearby layers. Note that this interaction term is proportional to the volume of the system, and would dominate over the degeneracy $2^L$ term coming from the number of different states $\{\sigma\}$. This is an order-by-disorder mechanism, where the degeneracy between different equal-weight states $\{\sigma\}$ is lifted, once the perturbation $z'$ is introduced.

However, the excess free energy in the ordered nematic state per unit volume is only of $\mathcal{O}(|\rho'/k|^3)$, where $\rho'/k$ is the number density of $z$-mers. In our simulations, for larger values of $\mu$, $\rho'$ becomes very small, for instance in $L = 112$ and $k = 7$, from figure 6, we see that $\rho'(\mu = 5.42) = 0.023$ and $\rho'(\mu = 5.43) = 0.0009$, just beyond the onset of the layered nematic phase, decrease by a factor of 20 in $\rho'$, when $\mu$ is increased by 0.01. One expects to see configurations with non-parallel nematic order between layers with significant weight if the disordering term $L \ln 2$ is of same order as the the ordering term $L^3(\rho'/k)^2$. Hence, we expect that for $L > L^* \sim k/\rho'$, the ordering term will win, and nematic ordered state will dominate. However, in our simulations, for $\mu = 5.42, k = 7$, $\rho' \approx 0.023$, so $L^*$ is of order 300. For lower values of $\mu$, $\rho'$ is larger, and we do see the nematic order. In the other case of $\mu = 5.43, L^*(\rho' = 0.0009) \sim 7000$. This is much higher than the system size $L = 112$, implying that the layered-nematic phase is favored for $\mu = 5.43$.

We now estimate $L^*$ for large $k$, by estimating the the free-energy cost of changing the orientation of one $z$-layer (say, the layer $z = 0$), to be along $y$-axis, while the remaining layers are all aligned in the $x$-direction. Let $S_a$ be the state of fixed chemical potential $z$, where all the $k$-mers are aligned in the $x$-direction. We denote by $S_b$ the state where the $z = 0$ layer has orientation along the $y$-direction, and all other rods are oriented in the $x$-direction. Let $\mathcal{L}^{(a)}(z, z')$ and $\mathcal{L}^{(b)}(z, z')$ denote the grand partition function of these two cases, where $z$ and $z'$ are the activities of the rods in the $xy$ plane and those perpendicular to it respectively. Then $\Delta F_{b,a} = -\ln \mathcal{L}^{(b)}(z, z') + \ln \mathcal{L}^{(a)}(z, z')$ is the free energy cost of creating a mis-aligned layer in the nematically ordered state $S_a$. These partition functions have a perturbation expansion in powers of $z'$ as defined in equation (4). As explained above, we get $A_a = A_b$. Then, it is easy to see that to second order in $z'^2$, we obtain
\[
\Delta F_{b,a} = [B_b(z) - B_a(z)] z'^2. \tag{8}
\]
As noted above, this calculation requires the knowledge of the vacancy–vacancy correlations within a layer as a function of density. This is non-trivial, but we note that typically, the nematic order is near 1, and to a good approximation, the qualitative behavior of vacancy–vacancy correlations is the same as that in the problem where all the rods are constrained to lie in the same direction within a plane. Then the problem reduces to a one dimensional problem, for which the behavior of correlations is known. Let $g(R, \epsilon)$ be the vacancy–vacancy pair correlation function of a gas of hard $k$-mers in one dimension:

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Figure 6. (a) The variation of $\langle \rho' \rangle$, the minimum of the densities of the rods of different orientations, with $\mu$ for $L = 112$ and $k = 7$ in the vicinity of transition from nematic phase to a layered-nematic phase. $\rho'$ has a discontinuity as $\mu$ changes from $\mu = 5.42$ to $\mu = 5.43$, representing the onset of a layered phase. The lower values of $\langle \rho' \rangle$ stabilize the layered-nematic phase for finite system sizes. (b) Corresponding probability distribution $P(Q_N)$ near the vicinity of nematic-layered transition. The peak of $P(Q_N)$ jumps as $\mu$ changes from $\mu = 5.42$ to $\mu = 5.43$.

$$g(R, \epsilon) = \epsilon^{-2} \left[ \text{Prob (site } x \text{ and } x + R \text{ are both unoccupied)} \right],$$  \hspace{1cm} (9)

where $\epsilon = 1 - \rho$ is the density of empty sites.

The calculation of $g(R, \epsilon)$ is straightforward. Given a configuration of $k$-mers on a line, we construct another configuration, where the gaps between rods are the same as in the first configuration, but the size of each rod is only 1. In this gas, different sites are uncorrelated, and the fractional density of unoccupied sites is $\epsilon' = \epsilon k / [1 + (k - 1)\epsilon]$. Then, it is easy to obtain

$$g(R, \epsilon) = \epsilon^{-1} \sum_{m=0}^{\lfloor (R-1)/k \rfloor} \frac{(R - 1 - mk + m)}{R - 1 - mk} \epsilon'^{R - mk} (1 - \epsilon')^m. \hspace{1cm} (10)$$

In particular, for $r \leq k$, we have $g(r, \epsilon) = \epsilon^{-1} \epsilon'^r$. Also, it is straightforward to obtain $g(mk + 1, \epsilon) \approx \epsilon^{-1} \epsilon' \exp(-m \epsilon')$, where $m$ is an integer smaller than $\epsilon'^{-1}$, and fixed $\epsilon' \ll 1$, corresponding to the limit $\epsilon k \ll 1$. We note that $g(mk + 2, \epsilon)$ is smaller than $g(mk + 1, \epsilon)$ by a factor $\epsilon'$ for small $m$. Thus, $g(R, \epsilon)$ will show prominent oscillations of period $k$ for $R \ll k\epsilon'^{-1}$. These oscillations may be seen in figure 7, where $g(R, \epsilon)$ has been numerically evaluated for $k = 7$ and $\epsilon = 0.02$. It shows oscillations of period 7, before converging to 1 for large $R$.

To compute $\Delta F_{b,a}$, it is easily seen that the most dominant contribution, when two rods are present in the $z$-direction, arises when both rods have heads in the same plane with the same $y$-coordinates, and intersect the plane $z = 0$. The calculation is straightforward, and gives

$$\Delta F_{b,a} = kL^2 z^2 \epsilon 2^k \sum_{R=1}^{\infty} [g(R, \epsilon) - 1][g(R, \epsilon)]^{k-1}, \hspace{1cm} (11)$$

$$= kL^2 z^2 \epsilon 2^k S(k, \epsilon). \hspace{1cm} (12)$$

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In the sum in equation (11), the main contribution is from terms with $R = mk + 1$, where $m = 0, 1, \ldots (\epsilon' k)^{-1}$. All these terms have roughly the same contribution $(\epsilon' / \epsilon)^{k}$. Thus, we expect that the sum $S(k, \epsilon) \sim (\epsilon' / \epsilon)^{k}$. However, $\epsilon' / \epsilon \sim k \exp(-\epsilon k)$. Hence, we conclude that within second order perturbation theory

$$\Delta F_{b,a} \sim L^2 \epsilon' k e^{-k^2 (z' \epsilon')^2}.$$  \hfill (13)

The transition from the nematic to layered-disordered phase occurs at vacancy density $\epsilon \sim k^{-2}$ [20], corresponding to $\epsilon' \sim k^{-1}$. If we put $z' = z \sim k$, and $\Delta F_{b,a} = \ln 2$, we obtain $L^* \sim k^{1/2}$ for large $k$. For $k = 7$, $L^* \sim 340$, in fair agreement with our earlier estimate. However, $L^*$ increases rapidly with $k$. For example, it is $L^* \sim 2 \times 10^{12}$ for $k = 20$. Thus, while the layered nematic phase is thermodynamically unfavored, it will be observed in finite-sized simulations.

5. Phase diagram and critical behavior

We numerically determined the order parameters $Q_N$ (see equation (2)) and $P_2$ (see equation (3)) as function of $\rho$ for different $k$ as shown in figure 8. We first determine $k_{\text{min}}$, the minimum value of $k$ required for each of the phases to appear.

5.1. $k_{\text{min}}$

From figure 8, it is evident that for $k \leq 4$, both $Q_N$ and $P_2$ are zero for all values of $\rho$. There are no phase transitions, and the system is in the disordered isotropic phase for all densities.
For $k = 5$ and $k = 6$, $Q_N$ increases from 0 to 0.5 at high densities, while $P_2$ simultaneously decreases from 0 to $-1$. These values are indicative of the layered phase, and show that the system undergoes a single transition from an isotropic phase to a layered phase. Thus, for observing a layered phase, $k \geq k_{\text{layered}}^{\text{min}} = 5$. We note that there is no nematic phase when $k = 5, 6$. The critical values for the isotropic-layered transition are: $\mu_c(5) \approx 3.82$ and $\rho_c(5) \approx 0.874$ and $\mu_c(6) \approx 1.0$ and $\rho_c(6) \approx 0.68$.

When $k = 7$, it may be seen from figure 8 that $Q_N$ increases from zero to $\approx \rho$, and then decreases to $Q_N \approx \rho/2$. Simultaneously, $P_2$ increases to 1, and then drops sharply to $-1$. These values are indicative of nematic and layered phases. We conclude that a nematic phase exists for $k \geq k_{\text{nematic}}^{\text{min}} = 7$. In our simulations, we find that the layered
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5.2. $k = 5, 6$

Rods of length $k = 5$ are the smallest to show the layered-disordered phase at high densities. We first show that this phase is stable, and that the Monte Carlo algorithm equilibrates the system at these densities. To show the stability, we compare the order parameters $Q_N$ and $P_2$ for two different system size in figure 9. The data has only a very weak dependence on the system size, showing that the finite size effects are not important, and that the layered phase is stable in the thermodynamic limit. The critical values for the transition is $\mu_c(5) \approx 3.82$ and $\rho_c(5) \approx 0.874$, estimated by determining the value of $\mu$ for which the probability distribution for $Q_N$ shows a double-peaked structure.

To check that our simulations do not suffer from slow down due to jamming problems at high values of $\mu$ and densities $\rho$, we observed the evolution with two different initial conditions: one corresponding to a nematic phase and the other corresponding to an isotropic phase, and checked that the final state is independent of the initial conditions. The time evolution of $|Q|$ is shown in figure 10 for both of these initial conditions. Clearly, the system loses memory of the initial conditions quite rapidly, and the order parameter reaches a value close to 0.5, indicative of the layered phase.

We now study of the isotropic to layered-disordered transition. In the symmetry-broken state, there are three possible choices of the layering orientation. By analogy to the three state Potts model, we expect that this transition should be first order. The numerical data is consistent with a first order transition. First, we show in figure 11(a) the probability distribution of the order parameter $Q_N$ near the transition point. The distribution has two peaks for values of $\mu$ close to the transition point, one near $Q_N \approx 0$, corresponding to the isotropic phase and the other close to $Q_N \approx 0.25$, corresponding to the layered phase. Double peaked distributions are a signature of first order transitions and coexistence of different phases. This can be further confirmed by looking at two-dimensional density plots of $P(Q)$, as shown in figures 11(b)–(e), where as $\mu$ is increased, the simultaneous presence of peaks at the origin and at $\pi/3$, $\pi$ and $5\pi/3$ can be seen in figures 11(c) and (d).
Further evidence of the first order nature may be obtained by studying the Binder cumulant:

\[ U_N = 1 - \frac{\langle |Q|^4 \rangle}{2 \langle |Q|^2 \rangle^2} \]  

In a continuous transition, the value of the Binder cumulant at the critical point is independent of the system size, providing a convenient tool to obtain the critical point \[ [46] \]. The Binder cumulant becoming negative is a signature of the transition being first order. \( U_N \) is zero in the isotropic phase and \( \frac{1}{2} \) in the completely ordered phase. The variation of \( U_N \) with \( \mu \) is shown in figure 12. The Binder cumulant becomes negative near the transition point, with its minimum decreasing with system size. The Binder cumulant becoming negative is a strong signature of the transition being first order.

The results for \( k = 6 \) are very similar to that for \( k = 5 \). The system undergoes a single transition from isotropic to layered phase with critical parameters are approximately \( \mu_c(6) \approx 1.0 \) and \( \rho_c(6) \approx 0.68 \). We note that the critical values are smaller than that for \( k = 5 \).

5.3. \( k = 7 \)

When \( k = 7 \), the system undergoes a transition from an isotropic phase to a nematic phase at low densities, and from a nematic phase to a layered phase at high densities (see figure 8). Here, we analyze the nature of the transitions, as well as the nature of the layered phase. We first discuss the isotropic–nematic transition. As in the case of \( k = 5, 6 \), there are three symmetric nematic phases corresponding to the three different orientations. By analogy with the three state Potts model, we expect that the transition will be first order in nature. The dependence of the order parameter \( Q_N \) and the Binder cumulant \( U_N \) on \( \mu \) for different system sizes are shown in figure 13. \( Q_N \) does not
Figure 11. (a) Probability distribution $P(|Q|)$ near the isotropic-layered transition for $L = 50$ and $k = 5$. (b)–(e) Two dimensional color plots for $P(Q)$ for various values of $\mu$ near the isotropic layered transition for $L = 50$ and $k = 5$. 

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show any sign of a discontinuity, nor does the Binder cumulant become negative, both being signatures of a first order transition. Likewise, the probability distribution for $Q_N$, shown in figure 14 does not show a bimodal distribution for any values of $\mu$ near the critical point. In the absence of signatures for a first order transition, we estimate the critical parameters to be $\mu_c \approx -0.23$ corresponding to $\rho_c \approx 0.556$, from the crossing of the Binder cumulants for different system sizes. The three state Potts model in three dimensions has a very weak first order transition, that is difficult to detect in numerical simulations, and we expect that the same difficulty holds for the problem of rods. Our simulations do not find clear evidence of the nature of this phase transition.

We now examine the transition from nematic to layered phase. For $k = 7$ and $L = 112$, we find a range of $\mu$ ($5.43 < \mu < 5.60$) for which the system finds itself in the layered-nematic phase. We check that this phase is stable for the finite systems we have studied, by simulating with initial conditions that are isotropic, nematic and

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layered-disordered. Also, we note that the transition from nematic to layered nematic is accompanied by a sharp decrease in $\rho'$. However, as we do not expect this to be a thermodynamic phase transition, we did not undertake a detailed study of the layered-nematic phase.

6. Summary and discussion

To summarize, we studied the problem of monodispersed hard rods on a three dimensional cubic lattice, using grand canonical Monte Carlo simulations and theoretical
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methods to obtain the phases for rods of length \(k\). We showed that for \(k \leq 4\), the system is in a disordered isotropic phase at all densities \(\rho\), and there are no phase transitions. For \(k = 5, 6\), the system undergoes a single transition into a high density layered-disordered phase, where the system breaks up into two dimensional layers, but disordered within a layer. For \(k = 7\), we find that as density is increased, the system makes a transition into a nematic phase. Further increase of density results in a layered-disordered phase.

We also observe a layered-nematic phase between the nematic and layered-disordered phases, which we argued is a finite-size effect. By developing a perturbation expansion in terms of number of \(z\)-mers, we estimated the system size that is required for the layered-nematic phase to be destabilized into a nematic phase to be \(L^* \sim k^{(k-1)/2}\). Thus, \(L^*\) increases rapidly with \(k\) with \(L^* \sim 340\) for \(k = 7\). Therefore, in simulations of systems with larger \(k\), we expect that there will be a range of densities for which the layered nematic phase will be observed.

For values of \(k > 7\), we expect that the phase diagram remains qualitatively the same as that for \(k = 7\). We expect the critical density for the isotropic-nematic transition to decrease with increasing \(k\), as is confirmed by Monte Carlo simulations of systems with \(k = 8, 9, 10\). As seen from figure 15, \(\rho_c\) decreases from 0.556 for \(k = 7\) to 0.364 for \(k = 10\). Near the isotropic–nematic transition, the \(O(\rho^2)\) term in the expansion of pressure as a function of density should be of approximately the same magnitude as the first term of \(O(\rho)\). Since the second virial coefficient for hard rods of length \(k\) varies as \(k^2\) in all dimensions (for large \(k\), the critical number density of rods scales as \(k^{-2}\) or, equivalently, the critical covered density \(\rho_c^{I-N} \sim k^{-1}\), consistent with the estimate given in [47], where the numerical data for \(k = 7, 8, 16, 25\) in three dimensions obey \(\rho_c^{I-N} \sim k^{-1}\). On the other hand, the nematic–layered transition is essentially a two-dimensional transition, as different layers are nearly independent. Thus, we expect that the critical density for this transition varies as \(1 - a/k^2\) for large \(k\), as in two dimensions [16].

These arguments are easily extended to higher dimensions. For large enough \(k\), we will expect an isotropic–nematic transition at a critical density that scales as \(k^{-1}\). A nematic phase may be thought of as a union of parallel lines, with hard core constraint along a line, and the problem becomes essentially one dimensional, with weak correlations between different lines. In the high-density phase, we expect that the system will break to two-dimensional layers, with only weak interaction between different layers. The critical density will be nearly independent of \(d\) for \(d \ll k\). This critical density will vary as \(1 - a/k^2\) for large \(k\). Preliminary simulations in four dimensions are consistent with the above observations.

From the results of the paper, it is clear that for \(k \geq 5\), the fully packed phase shows spontaneous symmetry breaking by selecting the layering plane. It is thus qualitatively different from the case with \(k \leq 4\). Extending the problem of rods to cuboids would result in a much richer phase diagram, as expected from the corresponding case of hard rectangles in two dimensions. However, simulation of such systems is a challenging task.
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Acknowledgments

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Note added After the submission of our our article, another Monte Carlo study of the same system has appeared in print [47]. This study uses local evaporation–deposition moves to reach the equilibrium state. The results obtained are qualitatively the same as ours. However, because of difficulties of equilibrating at high densities, this study could not access the isotropic-layered transition for the same as ours. However, because of difficulties of equilibrating at high densities, this study could not access the isotropic-layered transition for $k = 5$ or the nematic-layered transition for $k = 7$. But the system sizes are somewhat larger than ours, and some numerical evidence for the first order nature of the isotropic–nematic transition was found.

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