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Entropy of Rodlike Particles: Continuum versus Lattice Representations

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Entropy of Rodlike Particles: Continuum versus Lattice Representations

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The computationally tractable discrete lattice model is compared to a more realistic representation of rodlike particles, which allows continuous variation of rod position and orientation. This continuous-placement Monte Carlo method provides a measurement of the combinatoric entropy of rod configurations. Comparisons reveal that the discrete lattice model overestimates the entropy of short rods and of disordered phases. Three fundamental reasons for these predictive errors are discussed.

Keywords: axial ratio, combinatoric entropy, discrete lattice model, Monte Carlo, orientational entropy, rodlike particles

INTRODUCTION

It is now widely accepted[1–6] that the isotropic-to-nematic (I-N) phase transition can be explained on the basis of hard-core repulsive (steric hindrance) forces. This is not to imply that intermolecular attractive forces have no effect on the behavior of real systems, but rather that, since the basic phenomenon can be explained in the simpler terms of steric hindrance alone, the attractive forces can then be treated as perturbations on the (athermal) model system.

Near mid-century, two distinct theoretical approaches were developed to explain the I-N transition on the basis of steric hindrance. Onsager[7] modeled the system as a (continuum) gas of long rods. Flory,[8] on the other hand, developed a discrete lattice model that represents the rods as sequences of occupied lattice cells. These distinct theories appear to have spawned two branches of subsequent investigations. The two lines of investigation can be roughly differentiated on the basis of their respective representations of the rodlike particle system. One branch generally maintains representation of the system as a continuum,[9–20] with the rods being allowed continuous orientational and positional freedom, while the other branch

persists in modeling the system as a lattice, with rod position and, to various extents, rod orientation, variable in discrete increments.[1,21-29] This broad distinction will serve to focus attention on the main intent of the present work, which is to address the limitations of the discrete lattice representation in modeling the continuum.

It is somewhat inconsonant to model phases that have limited or no positional order in terms of a discrete lattice, in which the lattice cells (possible sites of the monomers) themselves have strict positional order. It would seem that such an approach is more suitable for modeling solid phases. However, the lattice models are generally more amenable to the incorporation of the complexities of real rodlike molecule systems (flexibility, polydispersity, orientation-dependent attractive forces, etc.) because they are generally simpler in terms of computation.[30] Thus, the discrete lattice approaches are still actively evolving in the quest to understand liquid crystalline phase transitions; that is, to predict the critical concentrations of the phase transitions, the nature of the transitions (first order or continuous), and the arrangements of the rods before, during, and after their alignment. However, we have found only one published work[31] that seeks to address the problems that may be introduced by representing what are essentially liquid-like phases (in terms of positional order) in the context of discrete positional possibilities: Okamoto[31] ran dynamic Monte Carlo for two-dimensional systems of flexible, athermal polymers. He varied the lattice cell size and, apparently, tested continuous placement with bond angles restricted to 0 and $\pi/2$. He found "appreciable" differences in pressure and osmotic pressure between the lattice and the continuum systems at high concentrations. However, he did not investigate the fundamental reasons for the differences.

METHODS

We have developed a continuum Monte Carlo (CMC) technique and an associated method of directly measuring the combinatoric entropy, S_c, as realistic configurations of rods are built up to fill a pre-set orientation distribution. Through comparisons of our measurements to the predictions of the Flory-type[1,8] discrete lattice model (DLM), the specific differences between discrete lattice and continuum representations are enumerated. In this paper, our attention is restricted to one- and two-dimensional, athermal systems of rigid rods, with long-range order imposed on the anisotropic phases. The fundamental problems that result from the DLM representation are expected to be qualitatively identical to the problems encountered in DLM representations of three-dimensional systems.

We refer to our numerical experimental method as a Monte Carlo technique in the sense that a random number generator is used to control specific events. Most of the numerical studies in the field that are classed as Monte Carlo investigations[4,16-20,31-35] are in effect "annealing" or "dynamic" schemes that a) begin with a set configuration of molecules, b) use random numbers to control shifts of the position and/or orientation of individual molecules, c) accept or reject each move on the basis of a set of criteria related to simple particle infringement (but that may incorporate more complex energetic interactions), and d) seek to arrive at the

equilibrium configuration, which is signified by lack of continued change in state-determining parameters. These are very powerful techniques for simulating equilibrium rod configurations on a local scale over the entire range of concentrations; however, they cannot impose global orientation distributions, and they cannot be used to investigate the free energy of a given distribution at non-equilibrium concentrations. Therefore, the annealing approach is not well-suited for our purpose of direct comparison to the results of Flory's DLM.

Our continuum Monte Carlo technique starts with a blank placement square. Rods are added one at a time, their positions determined by use of a random number generator and their orientations chosen randomly from a pre-set distribution. The positions and orientations are continuously variable; that is, they are not restricted by discrete lattice cells. (Strictly speaking, the positions and orientations are selected on a discrete lattice, because we are using a digital computer. However, the method approximates the continuum closely since the resolution of the lattice is typically 10^8 times the length of the rods.) Periodic boundary conditions are used. If a candidate rod is found to overlap an existing rod, then a new candidate position is generated at random; the process continues until the new rod is successfully placed. Once rods are placed, they are not allowed to move. After each new rod has been placed, the placement algorithm pauses and the fraction of appropriate vacancies remaining, F_v, is measured by repeated attempts to fit "wandering" test rods.[16,36,37] These test rods are not actually within the configuration; they are used as probes to measure F_v through determination of the fraction of the test rods that do not impinge on existing rods. In this manner, we generate a measure of F_v as a function of rod concentration for the particular axial ratio and global orientation distribution being tested. These F_v values are used to calculate the combinatoric entropy, S_c.

As we build up the assemblage, rods are placed with various orientations, eventually filling a pre-determined global orientation distribution. When we intend to measure the vacancies in a nematic phase, the orientations are constrained to the desired distribution from the beginning. Thus, even when we have placed only a few rods, and the concentration is very low, those few rods are aligned. On the other hand, when we intend to measure the vacancies in the isotropic phase, the rods are forced to remain randomly oriented even at high concentration. We are not attempting to mimic conditions of equilibrium in this procedure. At equilibrium, we expect low concentrations of rods to be randomly oriented (isotropic phase) and high concentrations of rods to be aligned (nematic phase). However, using our CMC method, we cannot predict the state of the system at equilibrium without first knowing the free energies of the various possibly distributions through a range of concentrations. Thus we constrain the orientations to a predetermined distribution, build up the rod concentration—measuring the fraction of appropriate vacancies remaining as each new rod is added—and use this information to determine the free energy of this particular phase through the range of concentrations tested.

For both the DLM and the CMC methods, the orientational entropy, S_o, is calculated directly from the imposed, pre-set orientation distribution. The combinatoric entropy, S_c is calculated via use of lattice statistics in the DLM (see Flory

and Ronca[1], Equations 1, 2, 4, and 11) whereas in the CMC, S_c is calculated, as mentioned above, using the measured vacancy fraction values. The reduced free energies ($G/T = -S_o - S_c$) of the isotropic phase and a range of nematic phases with controlled orientation distribution shapes and varying degrees of alignment (distribution widths) are then calculated as functions of rod concentration. The common tangent method[38] is then employed to determine the phase diagram for the particular nematic orientation distribution shape being studied. Details of these techniques are discussed by Chick.[36]

RESULTS

Comparisons of curves plotting log vacancy fractions versus rod concentration reveal the predictive problems of the DLM:

Figure 1 compares these curves for two-dimensional configurations with isotropic distributions at three axial ratios. The solid curves are from polynomials fit to the CMC measurements. The DLM results (dotted curves) indicate increasing overestimation of occupiable vacancy fractions as the axial ratio is decreased. On a relative free energy basis, the DLM "favors" short rods, a result that is universal to all types of orientation distributions.[36]

In Figure 2 we see that, for a fixed axial ratio ($X = 25$), the DLM overestimates the fraction of vacancies of a more disordered two-dimensional configuration (wider orientation distribution) relative to its estimation of vacancies in a more ordered configuration (narrower orientation distribution). To understand this, compare the relative separation between the two sets of curves. On a relative free energy basis,

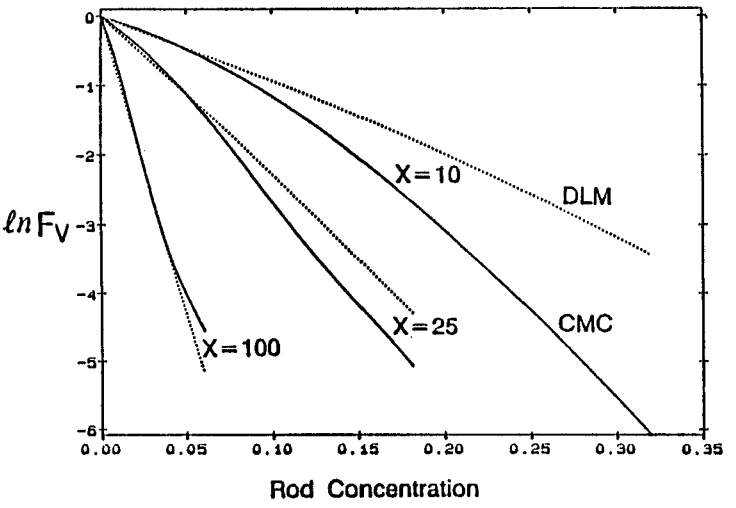

FIGURE 1 Curves of log vacancy fraction versus rod concentration for two-dimensional, monodisperse, isotropic configurations of rods at three axial ratios. Measurements by our continuous Monte Carlo technique are shown as solid lines. As the axial ratio ($\times$) is decreased, the discrete lattice model (dotted lines) increasingly overestimates the fractions of occupiable vacancies. This means that, on a relative free energy basis, the DLM "favors" short rods.

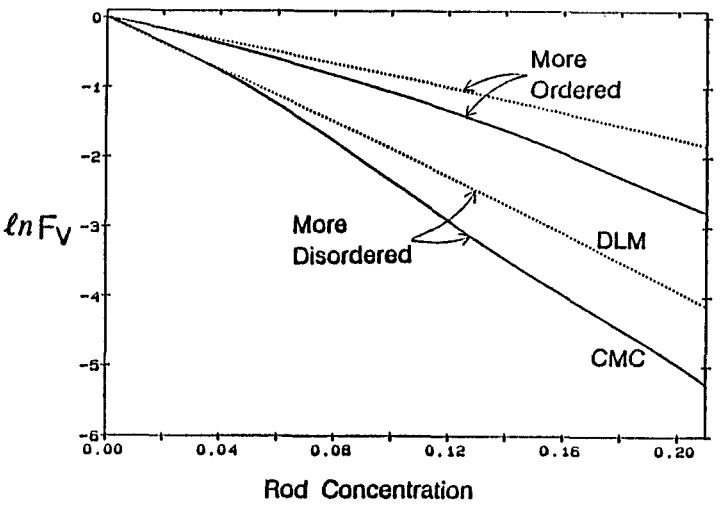

FIGURE 2 Curves of log vacancy fraction versus rod concentration for two-dimensional nematic configurations of rods with an axial ratio of 25. The rod orientations are normally distributed. The DLM overestimates the fraction of occupiable vacancies for both the more disordered and the more ordered configurations. However, on a relative basis, the DLM overestimates vacancies for the more disordered phase to a greater extent.

the DLM "favors" more disordered phases, and again, this result is universal to all orientation distribution shapes,[36] although the error is less serious than the DLM's tendency to favor short rods.

The tendency of the Flory and Ronca model to favor disorder is well known,[2,3,39,40] and results in overestimation of the rod concentration at the biphasic boundaries and of the order parameter of the nematic phase in the biphasic region. Nevertheless[36] a series of offsetting errors results in the DLM's moderately successful predictions for *monodisperse*, athermal systems. However, the DLM's tendency to favor short rods has not been reported previously, and raises doubts about the viability of the DLM for predicting the behavior of *polydisperse* systems, wherein the short rods tend to congregate within the isotropic phase while the long rods reside in the anisotropic phase.

DISCUSSION

In this section, we examine three of the fundamental reasons why the DLM fails to accurately predict the true fraction of occupiable vacancies. A fourth reason, that the DLM fails to account for the ingrowth of short-range order, is discussed elsewhere,[36] wherein it is shown that our CMC method detects the effect of the ingrowth of short-range order on vacancy fraction curves, and in which methods of accounting for short-range order are proposed.

Crossing Rods

Because the rods in the Flory lattice model are a single cell wide and are arranged in "stair-step" sequences, the model does not preclude rods from crossing, as shown

in Figure 3. If vacant cells on either side of an existing rod share a common corner, they can be part of the trajectory of a new rod. Obviously, rods that are perfectly aligned—comprised of a single sequence—cannot cross. The likelihood of rods crossing should be increased as the dispersion of the orientations increases and should be maximum in an isotropic distribution.

Easy Fitting Into Tight Spaces

The second problem that can be directly attributed to the discreteness of the lattice model is that rods can touch or can be placed into tight spaces too easily, that is, with much higher probability than is justifiable in a real system. This problem is most clearly illustrated by reference to a one-dimensional system: Consider the problem of placing the third block in a row that is four blocks long, as shown in Figure 4. In all three situations shown, the first block has been placed such that it "wraps around" the periodic boundary. The three different situations are created by different placements of the second block. In situation A, the second block has been placed next to one end of the first, leaving the largest possible vacancy for placement of the third block. If these blocks occupied discrete sites in a one-dimensional lattice, with placements originally possible at (exactly) 0, 1, 2, or 3 (4 is equivalent to 0 because of the periodic boundary), then the probability of successfully placing the third block in A would be $2/4 = 0.5$, signified by the two dots in the figure. In contrast, if the blocks were placed with continuous variation of position, then the centerpoint of the third block would have to fall in the range from 2 to 3 out of the originally possible range of 0 to 4, giving a placement probability of 0.25, as signified by the arrow-tipped line. In situation B, the probability of successfully placing the third block into spaces just large enough to accommodate it, using a *non-discrete* choice of position, is vanishingly small because there are exactly two positions for successful placement out of the *infinitely many*

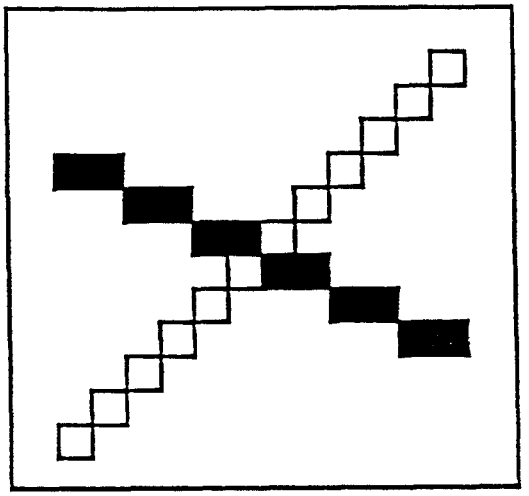

FIGURE 3 Flory and Ronca's discrete lattice model (DLM) allows mutually disoriented rods to cross, provided that their segments do not overlap.

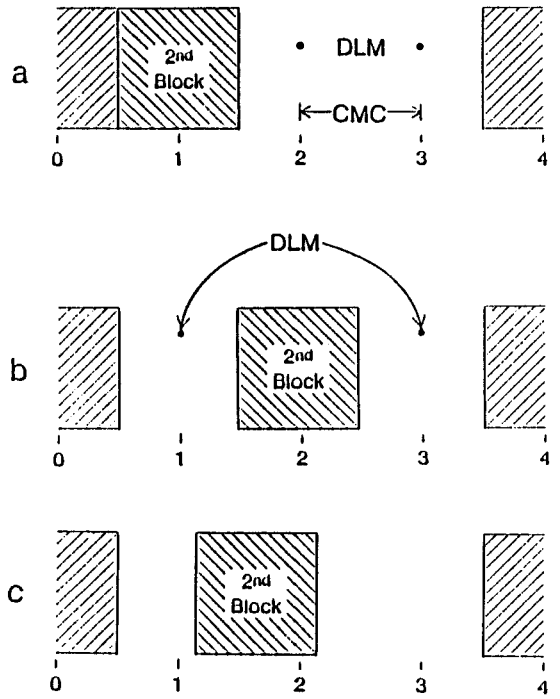

FIGURE 4 One-dimensional block placement situations. Row is four blocks long, with the first block having been placed such that it overlaps the periodic boundary. Discrete-type placement allows the blocks to occupy positions with centerlines exactly at integers, whereas continuum-type placement allows the centerpoints to occupy any of the infinitely many positions along the line segment from 0 to 4: a) Second block has been placed such that the DLM will find two successful placement positions (points) for the third block out of the four originally possible positions. CMC will successfully place the third block in one quarter of all attempts. b) Placement probability for the DLM is the same as in a. Placement probability for CMC is 2 out of infinity, or zero. c) The second block has been placed such that the space remaining to its left is wasted; the space is not large enough to accommodate another block.

positions in the original range of possible placements. Yet if a *discrete* choice of position was used, then the placement probability would again be 2/4, as it was in situation A. (Situation C could not happen in a discrete lattice, because the second block has not been placed exactly at an integer position; we return to this case later.) In general, we can see that the DLM overestimates the ease with which a block can be fit into a "tight" space. It is clear that the errors resulting from rods fitting too easily into tight spaces translates into overestimation of the combinatoric entropy by the DLM. The resulting error in estimation of the combinatoric entropy can be substantial.[36]

Both the problems of rods crossing and of too easily fitting into tight spaces can be eliminated by altering the lattice model. Instead of using cells that are exactly the width of the rods, we increase the resolution of the lattice, such that rods are many cells wide. The placement probability is still expressed in terms of the tractable lattice statistics, but when the resolution of the lattice (number of cells in the rod width) is increased to approach infinity, the model approaches continuum-type placement results. This is illustrated in Figure 5, which shows results for this high

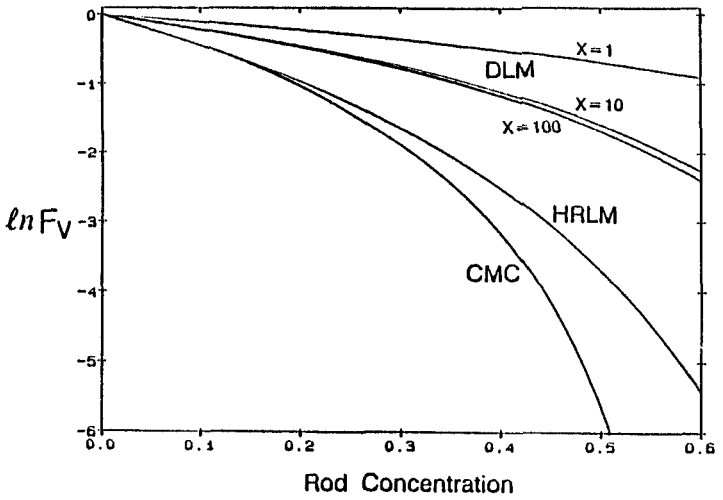

FIGURE 5 Curves of log vacancy fraction versus rod concentration for perfectly aligned rods in a two-dimensional system. CMC and HRLM distinguish no effect of axial ratio on the fraction of occupiable vacancies. DLM incorrectly predicts a dependence on axial ratio, and its predictions substantially overestimate the fractions of occupiable vacancies. Discrepancy between HRLM and CMC at high rod concentrations is due to the ingrowth of wasted space, which is accounted for by CMC, but not by either lattice model.

resolution lattice model (HRLM[36]), for the DLM, and for continuous Monte Carlo, all adapted for determining the vacancy fractions of perfectly aligned rods.

Wasted Space

The error remaining between the vacancy fraction curve from the HRLM and that for CMC is due to the ingrowth of wasted space (in this case of perfectly aligned rods). As rods are added to the system, some of them will be placed sufficiently close to one another such that all or some of the space between them is "wasted;" that is, another rod cannot be fit between them. Space is wasted in *both* DLM and continuous representations of rod configurations. The lattice models (both Flory's DLM and our HRLM) do not account for wasted space in the calculation of vacancies because the probability relations contain values for the *total* number of vacant cells, rather than the number of cells that are arranged contiguously such that they could be occupied by new rods. CMC effectively accounts for wasted space because rods simply cannot be placed where they cannot fit. Flory and Irvine[28] discussed the existence of unoccupied space, discovered by comparing molecular dimensions to total system volume in neat liquids of *p*-phenylenes, which are rigid rodlike molecules subject to orientation dependent mutual interactions. Their theory was adjusted to take wasted space into account by introducing a reduced volume term, the ratio of the volume occupied by the molecules to the total volume of the system. Thus, although their theory compensates for wasted space, it is not explicitly accounted for in the predictions of vacancy fractions.

Wasted space occurs in Figure 4, situation C, where the space to the left of the second block is wasted. Whereas the wasted space in two-dimensional systems

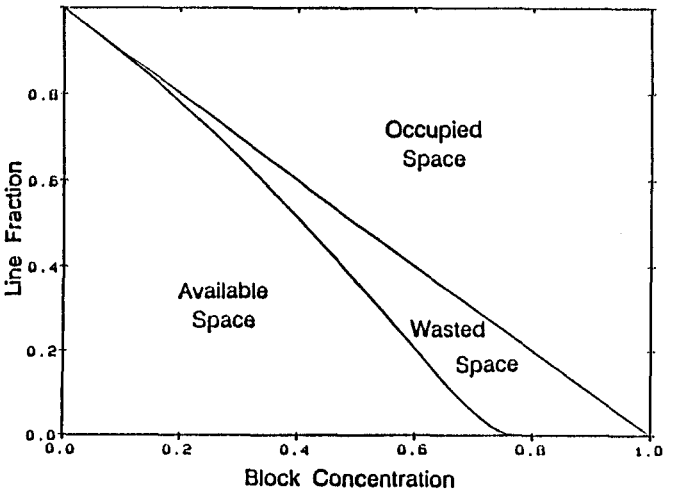

FIGURE 6 CMC-generated measurement of the ingrowth of wasted space as blocks are placed into a one-dimensional system, like that shown in Figure 4, but 500 blocks long. The upper line simply registers the space occupied by blocks as blocks are added. The lower curve is a measurement of the total line fraction comprised occupiable vacancies (available space). At a given concentration, the distance between the two lines represents the ingrowth of wasted space, which is comprised of vacancies that are too narrow to accommodate a block.

often occurs by multi-body interactions, that in one-dimensional systems is always due to simple pair-interactions, and is therefore much more easily quantified. CMC can be run such that, as blocks are placed in a row, the creation of wasted space is monitored. Figure 6 is a plot of the available space (line fraction) remaining as a function of block concentration. The area between the two lines represents the ingrowth of wasted space as the blocks are placed. Failure to account for wasted space will cause the DLM to favor disordered phases and short rods.[36]

CONCLUSIONS

A unique, continuous-placement Monte Carlo technique, which measures the combinatoric entropy of rod configurations, was used to demonstrate that the discrete lattice representation of rodlike particles results in the assignment of relatively lower free energy to disordered phases and to phases containing short rods. These predictive problems result in part from the discrete lattice model a) allowing rods to cross, b) allowing rods to be placed too easily into tight spaces, and c) counting wasted space as occupiable space. Use of a high resolution lattice model eliminates a and b; wasted space can be accounted for in lattice models by methods discussed elsewhere.[36] It is evident (see Figure 1) that resolution of these problems should improve theoretical predictions for polydisperse systems.

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