

Isotropic-nematic transition in hard-rod fluids: Relation between continuous and restricted-orientation models

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We explore models of hard-rod fluids with a finite number of allowed orientations, and construct their bulk phase diagrams within Onsager's second virial theory. For a one-component fluid, we show that the discretization of the orientations leads to the existence of an artificial (almost) perfectly aligned nematic phase, which coexists with the (physical) nematic phase if the number of orientations is sufficiently large, or with the isotropic phase if the number of orientations is small. Its appearance correlates with the accuracy of sampling the nematic orientation distribution within its typical opening angle. For a binary mixture this artificial phase also exists, and a much larger number of orientations is required to shift it to such high densities that it does not interfere with the physical part of the phase diagram.

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I. INTRODUCTION

Understanding the phase behavior of colloidal suspensions of rodlike particles requires an accurate description of their microscopic properties. Fluids of hard rods may be considered as the simplest systems on which the models incorporating particle orientational degrees of freedom can be tested [1,2]. One of the exact theoretical results dates back to Onsager [3] who analyzed the transition from a uniform isotropic phase to an orientationally ordered nematic phase in a fluid of monodisperse hard needles. He realized that the average pairwise (rod-rod) excluded volume is reduced in the nematic phase compared to that in the isotropic phase, and argued that the resulting gain of free volume (and hence translational entropy) compensates the loss of orientation entropy (due to the nematic ordering) at sufficiently high concentrations of rods [3]. Onsager derived a nonlinear integral equation for the orientation distribution function, a key quantity of the theory, which is constant in the isotropic phase and peaked about the director in the nematic phase. He circumvented the problem of explicitly calculating the nematic orientation distribution function (ODF) by adopting a variational ansatz, which was numerically checked to be rather accurate later [1].

The generalization of the Onsager model to binary mixtures of rods showed the possibility of strong fractionation [4,5] and even nematic-nematic demixing at sufficiently high density, driven by a competition between orientation entropy and ideal mixing entropy [6–8]. The functional forms of ODF's in these studies were either variational Gaussian [5,7], truncated expansions in Legendre polynomials [4], or numerically determined on an angular grid [6] or on a scaled angular grid [8]. In all these cases the focus was on describing the system with a continuum of orientations.

An alternative approach is to study models with a finite number N of allowed orientations while the positions of the centers of mass of the rods remain continuous. The first such model was proposed by Zwanzig [9], with orientations of a rod to be restricted to $N=3$ mutually perpendicular directions $\hat{\omega}_i, i=\{1, \dots, N\}$. Despite its inability to resolve the orienta-

tional structure of the one-particle distribution function in any detail, it has been successfully applied to explore wetting phenomena near a single hard wall and in a slit [10], or phase diagrams of polydisperse systems [11,12]. The main advantage of such discrete models in comparison with the continuous ones is their computational simplicity. The combination of spatial inhomogeneity and/or polydispersity with a continuum of orientations is rather demanding numerically, and the computational efforts can be reduced significantly by discretizing the orientations [11,13,14]. The hope has, of course, always been that with an increase of the number of allowed orientations one would smoothly approach the continuum limit. Here we show that this is *not* the case.

The possibility of a continuous interpolation between results for the discrete models on the one hand and Onsager-like solutions on the other has first been questioned by Straley [15] in studies of models with dodecahedral ($N=6$) and icosahedral ($N=10$) symmetries. He concluded that they do not trend towards the continuum solution due to the single allowed orientation within the typical opening angle ($\approx \pi/9$) of the nematic distribution at coexistence. Unfortunately, one cannot proceed the sequence of models with $N=3, 6, 10$ any further, since a larger fully symmetric set of orientations on the unit sphere does not exist. In order to be able to study the effect of discretizing the allowed orientations we give up part of the symmetry of the set, and this allows us to connect continuous and discrete models. We apply our method not only to a one-component system of rods, but also to binary mixtures, which may be considered as the simplest polydisperse systems.

This paper is organized as follows. In Sec. II we derive the grand potential functional for a model with a discrete number of allowed rod orientations from the Onsager functional. We calculate bulk equations of state for specific orientational sets, and determine the number of orientations required to resemble the continuous Onsager solution. In Sec. III we apply the method to construct bulk phase diagrams of binary mixtures of thin and thick rods. We demonstrate that their structure can be significantly modified due to orientational discretization. A summary and some discussion of our results will be presented in Sec. IV.

II. MONODISPERSE RODS

Consider a fluid of hard rods of length L and diameter D ($L \gg D$) in a macroscopic volume V at temperature T and chemical potential μ . The ‘‘Onsager’’ grand potential functional $\Omega[\rho]$ of the one-particle distribution function $\rho(\hat{\omega})$ can be written, within second virial approximation, as [3]

$$\beta\Omega[\rho(\hat{\omega})] = \int d\hat{\omega} \rho(\hat{\omega}) (\ln[\rho(\hat{\omega})\nu] - 1 - \beta\mu) + \frac{1}{2} \int d\hat{\omega} d\hat{\omega}' E(\hat{\omega}, \hat{\omega}') \rho(\hat{\omega}) \rho(\hat{\omega}'), \quad (1)$$

where $\beta = (kT)^{-1}$ is the inverse temperature, ν is the rod’s thermal volume, and $E(\hat{\omega}, \hat{\omega}')$ is the excluded volume of rods with orientations $\hat{\omega}$ and $\hat{\omega}'$. The function $\rho(\hat{\omega})$ is normalized as $n = \int d\hat{\omega} \rho(\hat{\omega})$, with n the bulk number density (which depends on $\beta\mu$). The minimum condition $\delta\Omega[\rho(\hat{\omega})]/\delta\rho(\hat{\omega}) = 0$ on the functional leads to the nonlinear integral equation

$$\ln[\rho(\hat{\omega})\nu] + \int d\hat{\omega}' E(\hat{\omega}, \hat{\omega}') \rho(\hat{\omega}') = \beta\mu, \quad (2)$$

to be solved for the equilibrium distribution $\rho(\hat{\omega})$.

Models with a discrete number N of allowed rod orientations can be systematically derived from the continuous model (1) by dividing the unit sphere into solid sectors $\Delta\hat{\omega}_i$, ($i=1, \dots, N$) around vectors $\hat{\omega}_i$, and fixing the rod density $\rho(\hat{\omega}) = \rho(\hat{\omega}_i)$ within each sector as well as the excluded volume $E(\hat{\omega}, \hat{\omega}') = E(\hat{\omega}_i, \hat{\omega}_j)$ for every pair of sectors. The grand potential functional $\Omega[\rho_i]$ of such an ‘‘orientationally discretized’’ fluid with the density $\rho_i = \rho(\hat{\omega}_i)\Delta\hat{\omega}_i$ and the excluded volumes $E_{ij} = E(\hat{\omega}_i, \hat{\omega}_j)$ is

$$\beta\Omega[\rho_i] = \sum_{i=1}^N \rho_i (\ln[\rho_i\nu] - 1 - \beta\mu) + \frac{1}{2} \sum_{i,j=1}^N E_{ij} \rho_i \rho_j - \sum_{i=1}^N \rho_i \ln \Delta\hat{\omega}_i, \quad (3)$$

with normalization $n = \sum_{i=1}^N \rho_i$ and $\Delta\hat{\omega}_i$ being the volume of the solid sector $\Delta\hat{\omega}_i$. The last term in Eq. (3) represents the contribution due to the discretization procedure into the grand potential Ω , i.e., the intrinsic difference between continuous and discrete models. For a homogeneous distribution of vectors $\hat{\omega}_i$ on the unit sphere and $\Delta\hat{\omega}_i = \Delta\hat{\omega}$ (i.e., for the models with $N=3, 6$, and 10 [15]), it trivially shifts the chemical potential $\beta\mu_d = \beta\mu + \ln \Delta\hat{\omega}$, which does not have any consequence for the solutions ρ_i at a fixed n , and for the thermodynamics of the isotropic-nematic transition. However, when $\Delta\hat{\omega}_i$ is not the same for all i , it acts as an external orientational field that tends to favor the larger sectors over the smaller ones. This becomes explicit if we consider the Euler-Lagrange equations that correspond to the discrete functional [or equivalently the analog of Eqs. (2)]

$$\ln[\rho_i\nu] + \sum_{j=1}^N E_{ij} \rho_j = \beta\mu + \ln \Delta\hat{\omega}_i, \quad (4)$$

now to be solved for ρ_i . Note that the equation of state $p = p(n, T)$ does not pick up an additional term from the discretization,

$$\beta p = n + \frac{1}{2} \sum_{i,j=1}^N E_{ij} \rho_i \rho_j, \quad (5)$$

but the distributions ρ_i to be inserted into it do depend on the discretization.

Further discussion requires a specification of the set of allowed orientations $\hat{\omega}_i$, $i=1, \dots, N$ and the associated solid sectors $\Delta\hat{\omega}_i$. Unfortunately, it is impossible to completely cover a surface of the unit sphere by equal regular spherical M polygons, where M indicates the number of polygon’s sides (only five Platonic solids exist). But symmetries of the function $\rho(\hat{\omega})$ can be explicitly included into the set of vectors $\hat{\omega}_i$ in order to simplify the problem. For the present study we fix the \hat{z} axis of the coordinate system to be parallel to the nematic director \hat{n} and assume uniaxial symmetry of the function $\rho(\hat{\omega}) = \rho(\theta)$, with $\theta = \arccos(\hat{\omega} \cdot \hat{n})$ the angle between $\hat{\omega}$ and \hat{n} . The azimuthal angle is denoted by ϕ , and hence we characterize a vector $\hat{\omega} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ by the angles θ and ϕ . The ‘‘up-down’’ symmetry of the nematic phase reduces the orientational space to half the upper hemisphere, i.e., $\theta \in [0, \pi/2]$ and $\phi \in [0, \pi]$. As we do not expect any azimuthal symmetry breaking we restrict attention to N_ϕ uniformly distributed values for ϕ for every allowed θ . We consider a uniform distribution of N_θ polar angles $\theta \in [0, \pi/2]$, i.e.,

$$(\theta_k, \phi_l) = \left(\frac{\pi(k-1)}{2(N_\theta-1)}, \frac{\pi(l-1)}{N_\phi-1} \right), \quad k=1, \dots, N_\theta, \quad l=1, \dots, N_\phi, \quad (6)$$

as well as a uniform distribution of N_θ values of $\cos \theta \in [0, 1]$, i.e.,

$$(\theta_k, \phi_l) = \left(\arccos \left[1 - \frac{k-1}{N_\theta-1} \right], \frac{\pi(l-1)}{N_\phi-1} \right), \quad k=1, \dots, N_\theta, \quad l=1, \dots, N_\phi. \quad (7)$$

The solid sectors $\Delta\hat{\omega}_i$ are determined by bisecting the angles between the vector $\hat{\omega}_i$ and its nearest neighbors, and the corresponding volumes are given by $\Delta\hat{\omega}_i = \int_{\Delta\hat{\omega}_i} \sin \theta d\theta d\phi$, such that $\sum_i \Delta\hat{\omega}_i = 4\pi$.

Figure 1 shows the dimensionless pressure $p^* = \beta p L^2 D$ as a function of the dimensionless bulk density $n^* = n L^2 D$ for the grid (6) with different N_θ and $N_\phi = 5$. The plateaux (of the solid lines) correspond to the isotropic-nematic coexistence, obtained by equating pressure and chemical potential in the two phases. For $N_\theta \leq 9$ the transition occurs between the iso-

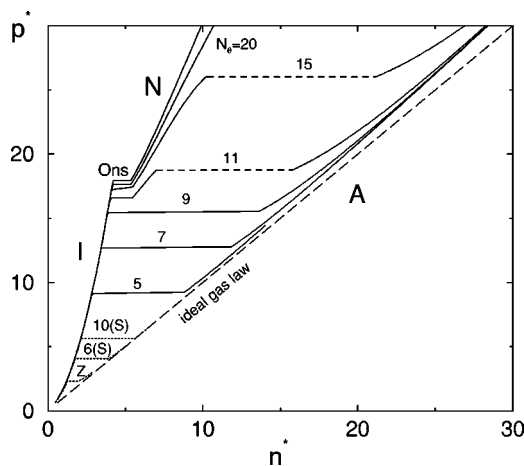


FIG. 1. Equation of state for models with different number of allowed polar angles N_θ . Positions of the phase transitions are indicated by the horizontal lines. The continuous Onsager solution (Ons) can be reproduced in the present density interval with $N_\theta \geq 50$. The dotted lines correspond to equations of state for the Zwanzig (Z), dodecahedral (6S) and icosahedral (10S) models [15]. The dashed horizontal lines correspond to a spurious nematic-nematic (N - A) transition due to poor discretization of the allowed orientations.

tropic phase (I) and an (almost) perfectly aligned nematic phase (A) with the pressure being close to the ideal gas pressure. Note that such grids correspond to a single θ within the “Onsager” opening angle, i.e., $0 \leq \theta_1 \leq \pi/18 < \theta_2$. As soon as $0 \leq \theta_1 < \theta_2 \leq \pi/18$, or $N_\theta > 9$, the distribution function $\rho(\theta)$ at isotropic-nematic coexistence starts to converge to the continuous solution. These results are in full agreement with the previous explanation of Straley [15]. Equations of state for the model (7) are very similar to Fig. 1 but start to resemble Onsager-like distribution function for $N_\theta > 80$ due to the poor sampling of $\hat{\omega}_i$ near the nematic director. Equations of state for the Zwanzig ($N=3$), dodecahedral ($N=6$), and icosahedral ($N=10$) models were calculated using the original formulations [15], and are included for comparison. Our results for $N_\theta \leq 9$ seem to converge well to these existing results.

For $N_\theta > 20$ the pressure of the high-density nematic phase clearly demonstrates a linear dependence on the bulk density, i.e., $\beta p(n) \sim n$. With increasing N_θ it gradually approaches a limiting scaling behavior $\beta p(n) = 3n$, established for the continuous Onsager solution by means of a scaling argument [16].

The discretization of the rod’s allowed orientations shows the existence of an “artificial transition” from a less-ordered nematic phase (N) to a near-perfectly aligned phase (A) for $N_\theta > 9$, as indicated by the dashed horizontal lines in Fig. 1. It occurs due to the same competition between excluded volume and orientational entropy as in the IN transition, and puts an additional constraint on the description of the nematic bulk state by restricted-orientation models. Below we argue that it has important consequences for discrete models of (polydisperse) hard-rod mixtures, where separation into nematic phases with different composition occurs at sufficiently high densities.

III. BINARY MIXTURES

Consider a binary mixture of thin (D_1) and thick (D_2) hard rods of equal length L and the diameter ratio $d = D_2/D_1 = 4$ in a macroscopic volume V at temperature T and chemical potentials μ_1 and μ_2 , respectively. The “Onsager” grand potential functional for this system can be written as [1]

$$\beta\Omega[\{\rho_\sigma(\hat{\omega})\}] = \sum_{\sigma=1}^2 \int d\hat{\omega} \rho_\sigma(\hat{\omega}) \{ \ln[\rho_\sigma(\hat{\omega}) \nu] - 1 - \beta\mu_\sigma \} + \frac{1}{2} \sum_{\sigma,\sigma'=1}^2 \int d\hat{\omega} d\hat{\omega}' E_{\sigma,\sigma'}(\hat{\omega}; \hat{\omega}') \times \rho_\sigma(\hat{\omega}) \rho_{\sigma'}(\hat{\omega}'), \quad (8)$$

with normalization $n_\sigma = \int d\hat{\omega} \rho_\sigma(\hat{\omega})$. It is known from previous work [17–19] that the bulk phase diagram of this system exhibits (i) strong fractionation at isotropic-nematic (I - N_2) coexistence, (ii) nematic-nematic (N_1 - N_2) coexistence ending in a consolute N_1 - N_2 point at sufficiently high pressure, and (iii) an I - N_1 - N_2 triple point. The discrete version of this model follows directly from Eq. (3) as

$$\beta\Omega[\{\rho_{\sigma i}\}] = \sum_{\sigma=1}^2 \sum_{i=1}^N \rho_{\sigma i} (\ln[\rho_{\sigma i} \nu_\sigma] - 1 - \beta\mu_\sigma) + \frac{1}{2} \sum_{\sigma,\sigma'=1}^2 \sum_{i,j=1}^N E_{\sigma i;\sigma' j} \rho_{\sigma i} \rho_{\sigma' j} - \sum_{\sigma=1}^2 \sum_{i=1}^N \rho_{\sigma i} \ln \Delta \hat{\omega}_i, \quad (9)$$

with the densities $\rho_{\sigma i} = \rho_\sigma(\hat{\omega}_i) \Delta \hat{\omega}_i$, the excluded volumes $E_{\sigma i;\sigma' j} = E_{\sigma\sigma'}(\hat{\omega}_i, \hat{\omega}_j)$ and the number densities normalization $n_\sigma = \sum_{i=1}^N \rho_{\sigma i}$. Figure 2 shows the phase diagrams for discrete systems in the p^* - x representation with the dimensionless pressure $p^* = \beta p L^2 D_1$ and the mole fraction of thick rods $x = n_2/(n_1 + n_2)$, for several orientational grids (6) with $N_\theta = 11$ (a), 20 (b), 30 (c), 50 (d), and $N_\theta = 10$. Note that all four discretizations are such that they reproduce the physical Onsager-like I - N transition at $x=0$ and $x=1$, at pressures $p^* \approx 17.7$ and 4.4, respectively. However, the existence of the artificial aligned nematic phase A gives rise to spurious I - A , N_1 - A , and N_2 - A phase equilibria, where I , N_1 , and N_2 are the physical isotropic and nematic phases. (For the coarsest discretization with $N_\theta = 11$ [Fig. 2(a)] the N_1 phase is stable in a very narrow region beyond the resolution of the picture.) Upon refining the discretization from $N_\theta = 11$ the I - N_2 - A triple point (∇) shifts to higher pressures, and combines with the I - N_1 - A triple point (Δ) at $N_\theta = 30$ [Fig. 2(c)] to form the physical I - N_1 - N_2 triple point (now denoted by ∇) and an artificial N_1 - N_2 - A triple point (Δ) at slightly higher pressure. Further grid refinements to $N_\theta = 50$ yield the physical phase diagram with an I - N_1 - N_2 triple point and N_1 - N_2 consolute point as in Ref. [17], but with a spurious N - A coexistence at pressures beyond the “physical” part of the phase diagram. At these pres-

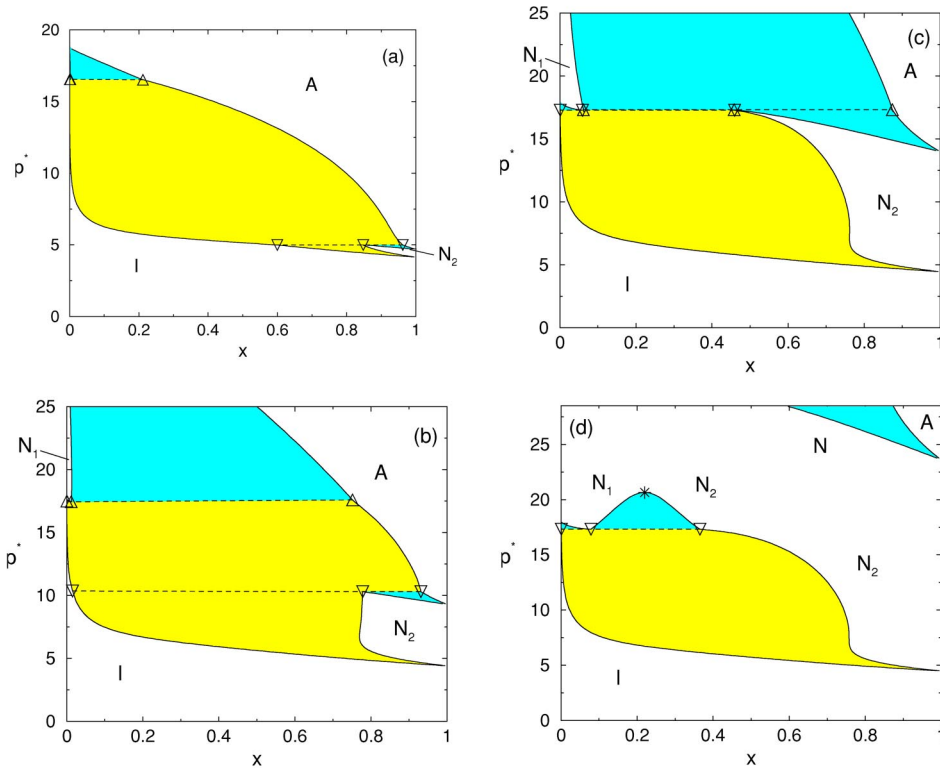


FIG. 2. Bulk phase diagrams of a binary thin-thick mixture of hard rods (diameter ratio $D_2/D_1=4.0$, equal length $L \gg D_2$), in the pressure-composition representation, with p^* the dimensionless pressure and x the mole fraction of the thicker rods. We distinguish the low-pressure isotropic phase (I), high-pressure nematic phases (N_1 and N_2), aligned phase A , upper (Δ) and lower (∇) triple phase coexistence and an N_1 - N_2 critical point (*). The grey regions, enclosed by the binodals, denote the two-phase regimes, and the tie lines that connect coexisting phases, are horizontal.

sures one does not distinguish N_1 and N_2 nematic phases, but the single nematic phase denoted by N here.

IV. SUMMARY AND DISCUSSION

We have explored the connections between continuous and restricted orientation models of monodisperse and binary hard-rod fluids (in the Onsager “needle” limit $L \gg D$). Our main finding is that a discretization of the orientations leads to the existence of a nonphysical almost perfectly aligned nematic phase (A) at high densities. If the discretization is coarse, i.e., the number of allowed orientations is small, then the A phase can coexist with the isotropic phase (I), and at sufficiently fine discretization with the nematic phase N . We also found that the continuum limit requires a finer orientation grid for a mixture than the one-component fluid.

In order to reduce the number of discrete orientations in binary mixtures, we have explored several models with a nonuniform discretization of the angular space. In particular, the physical phase diagram of binary mixtures of thin and thick rods with $d=4.0$ can be reproduced with $N_\theta=30$ if $2N_\theta/3$ points are uniformly distributed in the interval $[0, \pi/4]$ and the remaining $N_\theta/3$ points in $[\pi/4, \pi/2]$. Note that this does not remove the conceptual problem, it rather shifts the problem to identifying correlations between the

structure of the phase diagram and the employed numerical grids. However, this procedure can be tedious, e.g. for interfacial problems or highly polydisperse fluids, since studying these correlations involves the calculation of complete phase diagrams. Nevertheless we used and checked this scheme ourselves in studies of free planar interfaces of binary hard-rod mixtures [18,19].

Clearly, our results are strongly influenced by the adopted limit $L \gg D$, but we would expect similar effects, although weaker, for finite L/D ratio. An additional interesting issue was raised by an anonymous authoritative source, who pointed out the importance of all virial coefficients in the Zwanzig model, even in the Onsager limit $L \gg D$. As the second virial theory is exact for freely rotating needles [3], one can try to relate an increase in the number of virial coefficients necessary to recover the Onsager limit to the decrease of the number of allowed orientations. This suggestion requires studies of models with higher virial coefficients, which are far from trivial and beyond the scope of this work.

Findings of the present work could be relevant for the study of inhomogeneous and/or polydisperse fluids of rods, which are computationally more demanding and hence impose the use of a rather coarse grid of orientations in order to be tractable and practical. It shows that care must be taken with such rather coarse grids, since they can give rise to an artificial, discretization-induced aligned nematic phase.

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