Restricted-orientation models of hard-rod fluids

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Colloidal suspensions of rodlike particles may be considered as mesoscopic analogs of molecular liquid crystals. Even in the simplest case of pure hard-core interparticle interactions they exhibit a rich phase behavior as a function of density [1, 2]. Theoretical studies of such systems were pioneered by Onsager who analyzed the transition from a uniform isotropic phase to an orientationally ordered nematic phase in a fluid of 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 by adopting a variational Ansatz, but later it was calculated numerically [1].

Another simplifying 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 [4], with orientations of a rod to be restricted to $N = 3$ mutually perpendicular directions $\hat{n}_i, i = \{1, \ldots, N\}$. Despite its inability to resolve the orientational 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 [5], phase diagrams of polydisperse systems [6], etc.

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 [7] in studies of models with dodecahedral ($N = 6$) and icosahedral ($N = 10$)

symmetries. He concluded that they do not trend towards the Onsager solution due to the single allowed orientation within the typical opening angle ($\approx \pi/9$) of the nematic distribution at coexistence. Here we derive a connection between continuous and discrete models in general, and explicitly construct such an interpolation for a specific model.

For 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 grand potential functional $\Omega[\rho]$ of the one-particle distribution function $\rho(\hat{\omega})$ can be written, within second virial approximation, as [3]

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

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 set of nonlinear integral equations

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

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 $\Delta\hat{\omega}_i, (i = 1,\ldots,N)$ around vectors $\hat{\omega}_i$, and fixing the rod density $\rho(\hat{\omega}) = \rho(\hat{\omega}_i)$ within each sector as well as 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 "orientationally discretized" fluid with the density $\rho_i = \rho(\hat{\omega}_i)\Delta\hat{\omega}_i$ is

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

with normalization $n = \sum_{i=1}^{N}\rho_i$. The last term in (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), 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 corresponds to the discrete functional

(or equivalently the analog of Eqs. (2))

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

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 discretization,

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

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 $\hat{\omega}_i, i = 1, \ldots, N$ and the associated solid angles $\Delta\hat{\omega}_i$. 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 5 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 the nematic director $\hat{n}$. 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 orientational space to the half of 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 have considered a uniform distribution of N_θ polar angles $\theta \in [0, \pi/2]$, i.e.

$$(\theta_k, \phi_l) = \Big(\frac{\pi(k-1)}{2(N_\theta - 1)}, \frac{\pi(l-1)}{N_\phi - 1}\Big), \quad k = 1, \ldots, N_\theta, \quad l = 1, \ldots, N_\phi, \tag{6}$$

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

$$(\theta_k, \phi_l) = \Big(\arccos\Big[1 - \frac{k-1}{N_\theta - 1}\Big], \frac{\pi l - 1}{N_\phi - 1}\Big), \quad k = 1, \ldots, N_\theta, \quad l = 1, \ldots, N_\phi \tag{7}$$

with the conventional definition of $\Delta\hat{\omega}_i = \int_{\Omega_i} \sin\theta d\theta d\phi$.

Figure 1 shows the dimensionless pressure $p^* = \beta p L^2 D$ as a function of the dimensionless bulk density $n^* = nL^2D$ 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 isotropic phase and an (almost) perfectly aligned nematic phase with the pressure essentially equal to the 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

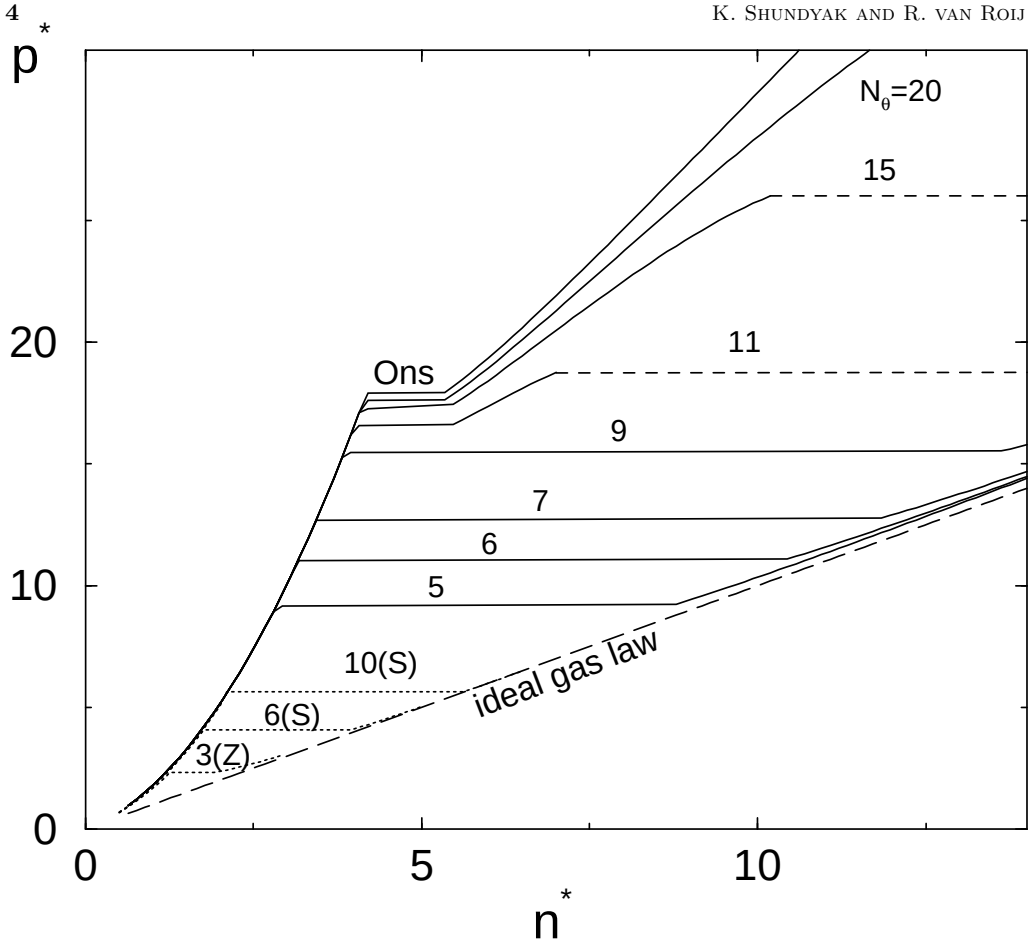

Fig. 1. – Equation of state for models with different number of allowed polar angles N_θ. Positions of the phase transitions are indicated by the horizontal lines. The continuous Onsager solution (Ons) can be reproduced in the present density interval with $N_\theta \geq 50$. Dotted lines correspond to equations of state for the Zwanzig (3Z), dodecahedral (6S) and icosahedral (10S) models [7]. The dashed horizontal lines correspond to a spurious nematic-nematic transition due to poor discretization of the allowed orientations.

$0 \leq \theta_1 < \theta_2 \leq \pi/18$, 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 [7]. 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, and are included for comparison. Our results for $N_\theta < 9$ seem to converge well to these existing results.

For $N_\theta > 20$ the pressure of the high-density nematic phase clearly demonstrates 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 [8].

The discretization of the rod's allowed orientations shows the existence of an "artificial transition" from a less-ordered nematic phase to a near-perfectly aligned phase (indicated by the dashed horizontal lines in Fig.1), even for $N_\theta > 9$. This occurs due to the same competition between excluded volume and orientational entropy, and puts another constraint on the description of the nematic bulk state by restricted-orientation models.

In conclusion, we have explored a connection between continuous and restricted orientation models. A discrete set of orientations starts to resemble Onsager's continuous results when several orientations are present within an opening angle of about $\pi/9$. These results are important in the study of spatially inhomogeneous systems of rods, where a fully continuous approach seems to be particulary difficult due to the coupling between orientational and translational degrees of freedom of the constituent particles. One should then be aware of artifacts due to too coarse a discretization of the allowed angles.

1. – Acknowledgements

We would like to thank J.P. Straley for useful correspondence. This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the "Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO)".

REFERENCES

[1] G.J. Vroege and H.N.W. Lekkerkerker, Rep. Progr. Phys. **55**, (1992) 1241.
[2] S. Fraden, in *Observation, Prediction and Simulation of Phase Transitions in Complex Fluids*, edited by M.Baus et al. (Kluwer, Dordrecht, 1995), p. 113.
[3] L. Onsager, Ann. N.Y. Acad. Sci. **51**, (1949) 627 .
[4] R. Zwanzig, J. Chem. Phys. **39**, (1963) 1714.
[5] R. van Roij, M. Dijkstra and R. Evans, Europhys. Lett. **49**, (2000) 350.
[6] N. Clarke, J.A. Cuesta, R. Sear, P. Sollich and A. Speranza, J. Chem. Phys. **113**, (2000) 5817.
[7] J.P. Straley, J. Chem. Phys. **57**, (1972) 3694.
[8] R. van Roij and B. Mulder, Europhys. Lett. **34**, (1996) 201.