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Molecular Fluids at High Dimensionality

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We extend the analysis of orientational first-order phase transitions in anisotropic molecular fluids at high spatial dimensionality to hard-disk fluids, and then to mixture of hard disks and hard spheres. The effect of hard-sphere admixture depends sensitively on the relative sizes of the two geometrical objects, and large spheres completely quench the disk transition. An introductory study is made of spatially ordered states.

KEY WORDS: Anisotropic fluid; high-dimensional space; phase transition; hard particles; fluid mixture.

1. INTRODUCTION

We are delighted to dedicate this paper to George Stell, who has contributed so much to, and stimulated so greatly, the theory of classical fluids.

As one's interest turns more and more to complex molecular units, it is important to work in a context in which the essential elements come through while the details wait in the wings to be introduced. A major conceptual advance was made long ago by Onsager,[(1)] who realized that much of the phenomenology of structured molecular fluids already appeared at the primitive non-uniform second virial level. More recently, similar considerations have appeared in the analysis of demixing of hard-rod mixtures,[(2, 3, 4)] but we will not attend to the demixing process in the present study. The utility of this drastic simplification was enhanced many

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years later by the observation[5, 6] that suitably scaled systems at high spatial dimensionality were in fact fully described by the second virial level, with the welcome accompaniment of greater analytic simplicity in this same limit. A consequence was that phenomena, such as first-order phase transitions, that were robust under increasing spatial dimensionality could be presented in unusually simple form. This made theoretical analysis easy, but not trivial, and only a few cases were analyzed in full, notably[7] the hard cylinder fluid that Onsager had first considered.

In this paper, we would like to extend the above investigations, first to fluids of hard disks, in which the geometry is a little more involved, where we will find a carbon copy of the spherocylinder nematic orientational transition, and then to disks mixed with a hard sphere fluid. The latter of course serves to weaken the correlations that the disks are using to carry out their ordering, and we will assess the qualitative fashion in which this occurs. We hypothesize that the phenomenology uncovered in our high-dimensional investigation is indeed robust and may be expected to extend to three dimensions.

2. SINGLE SPECIES

A rigid anisotropic molecule is specified by center of mass and suitable angular coordinates $(\vec{r}, \omega)$. We will deal with 3-dimensional molecules that possess a symmetry axis, and it then becomes easy to extend our picture to D-dimensional space by imagining that this property is maintained. The location and orientation of the molecule is hence given by the D-dimensional center of mass $\vec{r}$ and the $D-1$-dimensional set ω of hyperspherical angles; the interaction potential, assumed translation-invariant, by $\phi(\vec{r}-\vec{r}\,', \omega, \omega')$. In fact, we shall in this paper restrict our attention to the case of perfectly hard molecules. Then the familiar[8] density, $\rho(\vec{r}, \omega)$, expansion of the Helmholtz free energy takes the form

$$\begin{aligned}\beta F = &\int \rho(\vec{r}, \omega)[\log \rho(\vec{r}, \omega) - 1]\, d^D r\, d^{D-1}\omega \\ &- \tfrac{1}{2} \int \rho(\vec{r}, \omega)\, \rho(\vec{r}\,', \omega')\, f(\vec{r}-\vec{r}\,', \omega, \omega')\, d^D r\, d^D r'\, d^{D-1}\omega\, d^{D-1}\omega' \\ &- \tfrac{1}{6} \int \rho(\vec{r}, \omega)\, \rho(\vec{r}\,', \omega')\, \rho(\vec{r}\,'', \omega'')\, f(\vec{r}\,'-\vec{r}\,'', \omega', \omega'')\, f(\vec{r}-\vec{r}\,', \omega, \omega') \\ &\times f(\vec{r}\,''-\vec{r}, \omega'', \omega)\, d^D r\, d^D r'\, d^D r''\, d^{D-1}\omega\, d^{D-1}\omega'\, d^{D-1}\omega'' + \cdots \end{aligned} \tag{1}$$

where $f(\vec{r}-\vec{r}', \omega, \omega') = -1$ or 0 as the particles at $(\vec{r}, \omega)$ and $(\vec{r}', \omega')$ do or do not overlap. Here, β denotes reciprocal temperature, and the successive terms in (1) represent ideal gas, second virial, third virial, etc. contributions.

It has been demonstrated[9] in special cases that in the high dimensional limit, up to densities at which the second virial term overwhelms the ideal gas contribution—but significantly lower than close packing—the series (1) truncates at the second virial term. We will hereafter carry out this truncation without further comment. Our focus will be principally on spatially uniform states in which angular isotropy is broken, and to study the transition to the basic nematic phase, we can assume that ρ is only a function of the angle between the molecular symmetry axis and the spatial alignment axis. Hence, to within a constant,

$$\beta f = \frac{\beta F}{V} = \int \rho(\theta)[\log \rho(\theta) - 1] \sin^{D-2}\theta \, d\theta \, S_{D-1} + \frac{1}{2}\int \rho(\theta)\, \rho(\theta')\, \mathscr{V}(\omega, \omega')\, d^{D-1}\omega \, d^{D-1}\omega' \tag{2}$$

where

$$S_D = \int d\omega^{D-1} = \frac{D\pi^{D/2}}{\Gamma\left(\dfrac{D}{2}+1\right)} \tag{3}$$

and

$$\mathscr{V}(\omega, \omega') = -\int d^D\vec{R}\, f(\vec{R}, \omega, \omega') \tag{4}$$

is the overlap integral. For both hard rods and hard disks, the overlap integral takes the form

$$\mathscr{V}(\omega, \omega') = |\sin(\omega, \omega')|\, B \tag{5}$$

where

$$B = L^2(2R)^{D-2}\frac{S_{D-2}}{D-2} \tag{6}$$

for a uniform hard-rod fluid (L is the length of the rod, R is the radius),[7] and

$$B = (2R)^D \frac{\pi S_{D-2}}{(D-2)^2} \tag{7}$$

for the model of infinitely thin disks (R is the radius of a disk). See Appendix A.

In a hyperspherical coordinate system we have

$$\begin{aligned} |\sin(\omega, \omega')| &= \sqrt{1-\cos^2(\omega, \omega')} \\ &= [1-(\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\phi')^2]^{1/2} \end{aligned} \tag{8}$$

Then

$$\begin{aligned} \beta f = &\int \rho(\theta)[\log\rho(\theta) - 1] \sin^{D-2}\theta \, d\theta \, S_{D-1} \\ &+ \frac{B}{2} \int \rho(\theta)\, \rho(\theta')[1-(\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\phi')^2]^{1/2} \\ &\times \sin^{D-2}\theta \, d\theta \sin^{D-2}\theta' \, d\theta' \sin^{D-3}\phi' \, d\phi' \, S_{D-1} S_{D-2} \end{aligned} \tag{9}$$

In the $D \to \infty$ limit, integration over ϕ' can be performed by steepest descent. We obtain

$$\begin{aligned} \beta f = &\int \rho(\theta)[\log\rho(\theta) - 1] \sin^{D-2}\theta \, d\theta \, S_{D-1} \\ &+ \frac{B}{2} \int \rho(\theta)\, \rho(\theta')[1-\cos^2\theta\cos^2\theta']^{1/2} \sin^{D-2}\theta \, d\theta \sin^{D-2}\theta' \, d\theta' \, S_{D-1}^2 \end{aligned} \tag{10}$$

Finding the extremum of (10) under the constraint

$$\int \rho(\theta) \sin^{D-2}\theta \, d\theta \, S_{D-1} = N/V \equiv n \tag{11}$$

we obtain the equation of state

$$\log\rho(\theta) + B \int \rho(\theta')(1-\cos^2\theta\cos^2\theta')^{1/2} \sin^{D-2}\theta' \, d\theta' \, S_{D-1} = \lambda \tag{12}$$

where λ is a Lagrange multiplier. Now we evaluate the integral in (12) by steepest descent under the assumption that in the $D \to \infty$ limit the integrand has a sharp maximum at some $\theta = \theta_0$ (as in the work of Carmesin *et al.*,[11] and similar to the strategy used at high concentration in ref. 3). The result is

$$\rho(\theta) = Ke^{-(D-2)\,\bar{n}(1-\cos^2\theta\cos^2\theta_0)^{1/2}} \tag{13}$$

where $\bar{n}$ has been scaled as $\bar{n} = Bn/(D-2)$, taken to have a finite limit as $D \to \infty$. θ_0 is determined from the equation

$$\bar{n} = \frac{(1+\cos^2\theta_0)^{1/2}}{\sin\theta_0\,\cos^2\theta_0} \tag{14}$$

The normalization constant K can be found from (11) and turns out to be

$$\log\frac{K}{n} = (D-2)(1+\sec^2\theta_0 - \log\sin\theta_0) - \log S_D \tag{15}$$

Assuming the existence of two phases (isotropic with $\rho(\theta) = \text{const}$ and anisotropic with nontrivial $\rho(\theta)$ given by (13)) we can write down the equations for 2-phase equilibrium,

$$\mu_a = \mu_i, \qquad P_a = P_i \tag{16}$$

Free energy, chemical potential and pressure for both phases can be written as

$$\beta f = n(\log n - 1) - n\sigma + \tfrac{1}{2}n^2\tau \tag{17}$$

$$\beta\mu = \log n - \sigma + n\tau \tag{18}$$

$$\beta P = n + \tfrac{1}{2}n^2\tau \tag{19}$$

where for the isotropic phase

$$\sigma = \log S_D \tag{20}$$

$$\tau = B \tag{21}$$

and for the anisotropic phase

$$\sigma = \log S_D + (D-2)\log\sin\theta_0 \tag{22}$$

$$\tau = B\sin\theta_0(1+\cos^2\theta_0)^{1/2} \tag{23}$$

Then the equations of phase equilibrium (16) can be written as

$$\log \frac{n_i}{n_a} + (D-2) \log \sin \theta_0 + [n_i - n_a \sin \theta_0 (1+\cos^2 \theta_0)^{1/2}]\, B = 0 \quad (24)$$

$$n_i - n_a + \frac{1}{2} [n_i^2 - n_a^2 \sin \theta_0 (1+\cos^2 \theta_0)^{1/2}]\, B = 0 \quad (25)$$

compatible with the scaling $n_{i,a} = \frac{D-2}{B} \bar{n}_{i,a}$. In the limit $D \to \infty$ we get the following solution

$$\theta_0 = 0.2773, \qquad \bar{n}_i = 3.376, \qquad \bar{n}_a = 5.478 \quad (26)$$

Since $\bar{n}_i \neq \bar{n}_a$, the transition is first order.

3. UNIFORM MIXTURE OF HARD DISKS AND SPHERES

The phenomenology associated with mixtures can be quite extensive.[10] The elementary case of two hard sphere species with non-additive hard interactions is quite traditional–and almost trivial–in the high dimensional limit, and was analyzed some years ago.[11] When one or more of the species is not isotropic, the situation becomes potentially more interesting and involved. Here, we consider perhaps the simplest of this genre, that of hard (infinitely thin) disks of radius b mixed with hard spheres of radius a. The same-species contributions to the second virial term of the free energy are of course those that have been preciously computed, while the mutual contribution is immediate: the sphere center must be either within a of the perimeter of the disk or within a of the plane of the disk. We readily find

$$\beta F = \sum_{\alpha=1,2} \int \rho_\alpha(r,\omega)[\log \rho_\alpha(r,\omega) - 1]\, d^D r\, d^{D-1}\omega$$
$$- \tfrac{1}{2} \sum_{\alpha,\beta=1,2} \int \rho_\alpha(r,\omega)\, \rho_\beta(r',\omega')\, f_{\alpha\beta}(r-r',\omega,\omega')$$
$$\times d^D r\, d^D r'\, d^{D-1}\omega\, d^{D-1}\omega' + \cdots \quad (27)$$

or

$$\beta f = \frac{\beta F}{V} = \sum_{\alpha=1,2} \int \rho_\alpha(\omega)[\log \rho_\alpha(\omega) - 1]\, d^{D-1}\omega$$
$$+ \frac{1}{2} \sum_{\alpha,\beta=1,2} \int \rho_\alpha(\omega)\, \rho_\beta(\omega')\, \mathscr{V}_{\alpha\beta}(\omega,\omega')\, d^{D-1}\omega\, d^{D-1}\omega' \quad (28)$$

where

$$\mathscr{V}_{\alpha\beta}(\omega, \omega') = -\int f_{\alpha\beta}(R, \omega, \omega')\, d^D R \tag{29}$$

The matrix elements are $\mathscr{V}_{11} = B_{11}$, $\mathscr{V}_{12} = \mathscr{V}_{21} = B_{12}$, $\mathscr{V}_{22} = |\sin(\omega, \omega')|\, B_{22}$, where

$$B_{11} = S_D \frac{(2a)^D}{D}, \qquad B_{12} = S_{D-1} \sqrt{\frac{2\pi a}{a+b}} \frac{(a+b)^D}{(D-1)^{3/2}},$$

$$B_{22} = \pi S_{D-2} \frac{(2b)^D}{(D-2)^2} \tag{30}$$

and a is the radius of a sphere, b is the radius of a disk.

Now let us see how the isotropic-nematic transition is affected by the sphere admixture. First, for the isotropic phase, we set $\rho_\alpha = n_\alpha / S_D$, and the free energy (28) becomes

$$\beta f = \sum_{\alpha=1,2} n_\alpha (\log n_\alpha - 1) - \sum_{\alpha=1,2} n_\alpha \log S_D + \tfrac{1}{2} \sum_{\alpha, \beta=1,2} n_\alpha n_\beta B_{\alpha\beta} \tag{31}$$

with chemical potentials

$$\mu_\alpha = \frac{1}{\beta} \left(\log n_\alpha - \log S_D + \sum_{\beta=1,2} B_{\alpha,\beta} n_\beta \right) \tag{32}$$

and pressure

$$P = \frac{1}{\beta} \left(\sum_{\alpha=1,2} n_\alpha + \frac{1}{2} \sum_{\alpha, \beta=1,2} n_\alpha n_\beta B_{\alpha,\beta} \right) \tag{33}$$

Next, in the putative nematic phase, we can write

$$\rho_1 = n_1 p_1(\theta), \qquad \rho_2 = n_2 p_2(\theta) \tag{34}$$

where $p_1(\theta) = 1/S_D$ and $p_2(\theta) = p(\theta)$. We have

$$\beta f = \sum_\alpha n_\alpha (\log n_\alpha - 1) - \sum_\alpha n_\alpha \sigma_\alpha + \frac{1}{2} \sum_{\alpha,\beta} n_\alpha n_\beta \tau_{\alpha\beta} \tag{35}$$

where

$$\sigma_\alpha = -\int p_\alpha(\omega) \log p_\alpha(\omega)\, d^{D-1}\omega \tag{36}$$

$$\tau_{\alpha\beta} = \int p_\alpha(\omega)\, p_\beta(\omega')\, \mathscr{V}_{\alpha\beta}(\omega, \omega')\, d^{D-1}\omega\, d^{D-1}\omega' \tag{37}$$

In order to find σ_1,σ_2 and τ we have to minimize (28) subject to constraints

$$\int \rho_\alpha(\theta) \sin^{D-2}\theta\, d\theta\, S_{D-1} = N_\alpha / V \equiv n_\alpha \tag{38}$$

where $\alpha = 1, 2$, imposed by Lagrange parameters λ_1, λ_2. The equation with λ_1 is trivial while for λ_2,

$$\log \rho_2(\omega) + \int \rho_1(\omega')\, \mathscr{V}_{12}(\omega, \omega')\, d^{D-1}\omega' + \int \rho_2(\omega')\, \mathscr{V}_{22}(\omega, \omega')\, d^{D-1}\omega' = \lambda_2 \tag{39}$$

Using (34), (29)–(30), assuming that $p(\theta) \sin^{D-2}\theta$ is sharply peaked at $\theta = \theta_0$ and integrating via steepest descent, we obtain

$$p(\theta) = Ke^{-(D-2)\,\bar{n}_2 (1 - \cos^2\theta \cos^2\theta_0)^{1/2}} \tag{40}$$

where $\bar{n}_2 = n_2 B_{22}/(D-2)$ and θ_0 is determined from the equation

$$\bar{n}_2 = \frac{(1 + \cos^2\theta_0)^{1/2}}{\sin\theta_0 \cos^2\theta_0} \tag{41}$$

The normalization constant K is readily found:

$$\log \frac{K}{n_2} = (D-2)(1 + \sec^2\theta_0 - \log \sin\theta_0) - \log S_D \tag{42}$$

Using steepest descent again and plugging the expression for $p(\theta)$ into the formulas for σ and τ, we see that

$$\beta\mu_\gamma = \log n_\gamma - \sigma_\gamma + \sum_{\beta = 1, 2} n_\beta \tau_{\gamma\beta} \tag{43}$$

$$\beta P = \sum_{\alpha = 1, 2} n_\alpha + \frac{1}{2} \sum_{\alpha, \beta = 1, 2} n_\alpha n_\beta \tau_{\alpha\beta} \tag{44}$$

with

$$\sigma_1 = \log S_D, \qquad \sigma_2 = \log S_D + (D-2)\log\sin\theta_0 \tag{45}$$

$$\tau_{11} = B_{11}, \qquad \tau_{12} = \tau_{21} = B_{12}, \qquad \tau_{22} = B_{22}\sin\theta_0(1+\cos^2\theta_0)^{1/2} \tag{46}$$

4. ORIENTATIONAL PHASE TRANSITION

For our mixture, phase equilibrium requires

$$\mu_1^i = \mu_1^a, \qquad \mu_2^i = \mu_2^a, \qquad P^i = P^a \tag{47}$$

Using the scaling $n_1 = \bar{n}_1(D-2)/B$, with B yet unknown, and $n_2 = \bar{n}_2(D-2)/B_{22}$, we get the scaled system of equations describing phase equilibrium

$$\log\frac{\bar{n}_1^i}{\bar{n}_1^a} + (\bar{n}_1^i - \bar{n}_1^a)\frac{B_{11}}{B}(D-2) + (\bar{n}_2^i - \bar{n}_2^a)\frac{B_{12}}{B_{22}}(D-2) = 0 \tag{48}$$

$$\log\frac{\bar{n}_2^i}{\bar{n}_2^a} + (D-2)\log\sin\theta_0 + (\bar{n}_1^i - \bar{n}_1^a)\frac{B_{12}}{B}(D-2) + [\bar{n}_2^i - \bar{n}_2^a\sin\theta_0(1+\cos^2\theta_0)^{1/2}](D-2) = 0 \tag{49}$$

$$(\bar{n}_1^i - \bar{n}_1^a)\frac{(D-2)}{B} + (\bar{n}_2^i - \bar{n}_2^a)\frac{(D-2)}{B_{22}} + \frac{1}{2}([\bar{n}_1^i]^2 - [\bar{n}_1^a]^2)\frac{(D-2)^2 B_{11}}{B^2} + (\bar{n}_1^i\bar{n}_2^i - \bar{n}_1^a\bar{n}_2^a)\frac{(D-2)^2 B_{12}}{BB_{22}} + \frac{1}{2}([\bar{n}_2^i]^2 - [\bar{n}_2^a]^2\sin\theta_0(1+\cos^2\theta_0)^{1/2})\frac{(D-2)^2}{B_{22}} = 0 \tag{50}$$

The analysis depends however on the relative sizes of disks and spheres. Consider first the case when the radius a of a sphere is less than the radius b of a disk. Then $B_{12}(D-2)/B_{22} \to 0$ as $D \to \infty$ and for any B the relationship

$$\bar{n}_1^i = \bar{n}_1^a \equiv \bar{n}_1 \tag{51}$$

holds. But the D-dependence of B has not so far been fixed. There are three possibilities as $D \to \infty$: $B/B_{12} \to 0$, $B/B_{12} \to \infty$ and $B/B_{12} \to \text{const}$ (where const can be taken to be 1 without loss of generality). In the first case, the system (48)–(51) has no solution and thus the phase transition is absent. In the second case, a solution does exist, with the coexistence density of the

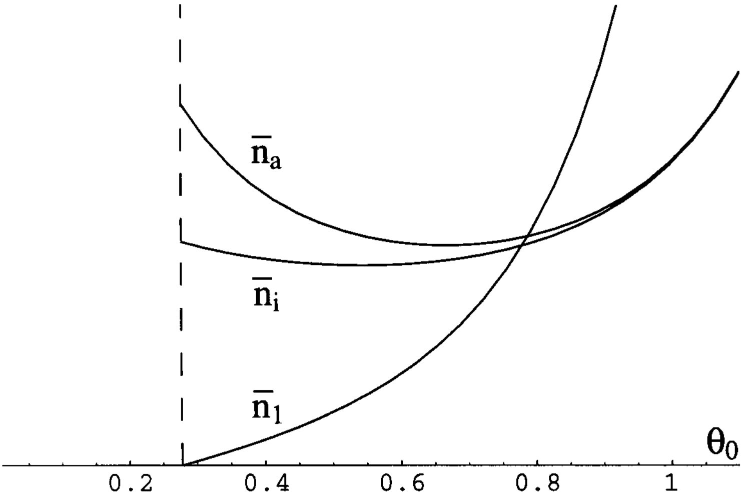

Fig. 1. Scaled coexistence densities of disks (with $\bar{n}_a$, $\bar{n}_i$ corresponding to anisotropic and isotropic phase respectively) and spheres $\bar{n}_1$ (the same in both phases) as functions of the parameter θ_0. Physically meaningful solution exist only for $\theta_0 \geqslant 0.2773$ ($\bar{n}_1 \geqslant 0$).

disks equal to (26). This coexistence density is independent of the density of the spheres and thus the presence of the spheres is irrelevant.

Finally, for $B = B_{12}$ the equilibrium conditions in the limit $D \to \infty$ become

$$\log \sin \theta_0 + [\bar{n}_2^i - \bar{n}_2^a \sin \theta_0 (1 + \cos^2 \theta_0)^{1/2}] = 0 \tag{52}$$

$$\bar{n}_1 (\bar{n}_2^i - \bar{n}_2^a) + \tfrac{1}{2}([\bar{n}_2^i]^2 - [\bar{n}_2^a]^2 \sin \theta_0 (1 + \cos^2 \theta_0)^{1/2}) = 0 \tag{53}$$

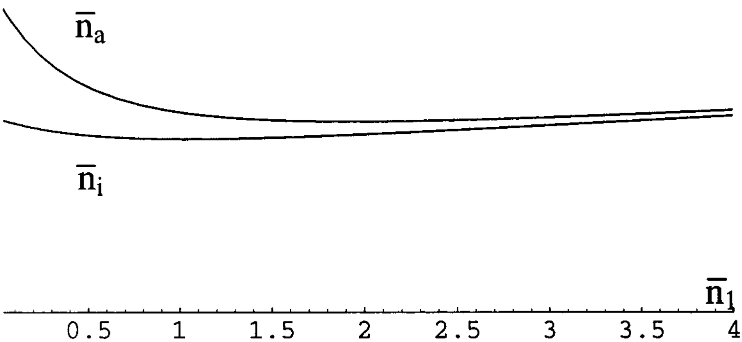

Fig. 2. Dependence of scaled coexistence densities of disks in anisotropic ($\bar{n}_a$) and isotropic ($\bar{n}_i$) phases on the density $\bar{n}_1$ of spheres.

where $\bar{n}_2^a$ is defined by (41). The solution is shown in Figures 1 and 2. The solution exists for $\theta_0 \geqslant 0.2773$, at which point the density of spheres is zero and coexistence densities of disks in isotropic and anisotropic phases are given by (26). For nonzero density of spheres, coexistence densities of disks depend on the density of spheres as shown in the graph. Note that the sphere density in the two disk phases are the same, although this particular aspect may very well not extend to three dimensions.

Now let us consider the case when the radius a of a sphere is greater than the radius b of a disk. In this case the equilibrium condition reduces to the following system of equations

$$(\bar{n}_1^i - \bar{n}_1^a) + (\bar{n}_2^i - \bar{n}_2^a)\,\frac{B_{12}B}{B_{11}B_{22}} = 0 \tag{54}$$

$$\log \sin\theta_0 + (\bar{n}_2^i - \bar{n}_2^a \sin\theta_0(1+\cos^2\theta_0)^{1/2}) + (\bar{n}_1^i - \bar{n}_1^a)\,\frac{B_{12}}{B} = 0 \tag{55}$$

$$(\bar{n}_1^i\bar{n}_2^i - \bar{n}_1^a\bar{n}_2^a) + \frac{1}{2}([\bar{n}_1^i]^2 - [\bar{n}_1^a]^2)\,\frac{B_{11}B_{22}}{BB_{12}} + \frac{1}{2}([\bar{n}_1^i]^2 - [\bar{n}_1^a]^2 \sin\theta_0(1+\cos^2\theta_0)^{1/2})\,\frac{B}{B_{12}} = 0 \tag{56}$$

Analysis shows that for any possible choice of B this system has no solution and therefore we conclude that the phase transition does not occur.

5. FUTURE DIRECTIONS

Elucidation of the isotropic–nematic orientational transition for pure disks and disk–sphere mixtures concludes the first phase of our investigation. There is at least anecdotal evidence leading one to expect a smectic layering with anisotropy transition to occur in the pure disk case at higher density. In order to detect this, we must at least assume inhomogeneity in, say the z-direction. The density of molecules $\rho(\vec{r}, \omega)$, will therefore be a function of z and the angle θ specifying relative orientation of the molecule and the z axis, $\rho(\vec{r}, \omega) = \rho(z, \theta)$. With this assumption, the free energy (1) can be written as

$$\beta f = \frac{\beta F}{A} = \int \rho(z,\theta)[\log \rho(z,\theta) - 1]\, dz \sin^{D-2}\theta\, d\theta\, S_{D-1} + \frac{1}{2}\int \rho(z,\theta)\,\rho(z-Z,\theta')\,\mathscr{V}(Z,\omega,\omega')\, dz\, dZ\, d^{D-1}\omega\, d^{D-1}\omega' \tag{57}$$

where $A = \int d^{D-1}r$,

$$\mathscr{V}(Z, \omega, \omega') = -\int f(\vec{R}, \omega, \omega')\, d^{D-1}R_{\perp} \tag{58}$$

and we have made a change of variables $\vec{R} = \vec{r} - \vec{r}\,'$, with $\vec{R} = \vec{R}_{\perp} + Z\hat{z}$.

This analysis is considerably more involved, and so "for practice", we have chosen to spatially order the fluid by a hard hyperplanar wall boundary. Some details of our preliminary study are presented in Appendix B. Suffice it to say that at high dimensionality, the effect of the wall "heals" very rapidly, with no immediate evidence of layering at higher densities, suggesting that a more delicate multi-scale analysis may be required. This forms the substance of an ongoing investigation.

APPENDIX A. OVERLAP INTEGRAL EVALUATION: HOMOGENEOUS CASE

We wish to evaluate

$$\mathscr{V}(\omega_1, \omega_2) = -\int d^D\vec{R}\, f(\vec{R}, \omega_1, \omega_2) \tag{59}$$

the overlap integral. Here, $f(\vec{R}, \omega_1, \omega_2) = -1$ or 0 as the particles at $(\vec{r}_1, \omega_1)$ and $(\vec{r}_2, \omega_2)$ with relative position $\vec{R} = \vec{r}_1 - \vec{r}_2$ do or do not overlap.

First, we are interested in the overlap of two infinitely thin disks of the same radius a whose relative positions and orientations are specified by the vector $\vec{R}$ connecting their centers and unit vectors $\hat{n}_1$ and $\hat{n}_2$ orthogonal to the disks.

In the coordinate system with the origin exactly half-way between the centers of the disks on the line connecting them, the point with the radius-vector $\vec{r}$ belongs to both disks if and only if the following conditions are satisfied:

$$\left(\vec{r} - \frac{\vec{R}}{2}\right) \cdot \hat{n}_1 = 0 \tag{60}$$

$$\left(\vec{r} - \frac{\vec{R}}{2}\right)^2 \leqslant a^2 \tag{61}$$

$$\left(\vec{r} + \frac{\vec{R}}{2}\right) \cdot \hat{n}_2 = 0 \tag{62}$$

$$\left(\vec{r} + \frac{\vec{R}}{2}\right)^2 \leqslant a^2 \tag{63}$$

In other words, the overlap function f is nonzero iff the above system admits a solution $\vec{r}$ for a given set $\vec{R}$, $\hat{n}_1$, $\hat{n}_2$.

Introducing new orthogonal unit vectors $\hat{v}_1$, $\hat{v}_2$ in the plane defined by $\hat{n}_1$, $\hat{n}_2$,

$$\hat{v}_1 = \frac{\hat{n}_1 + \hat{n}_2}{\sqrt{2A_+}}, \qquad \hat{v}_2 = \frac{\hat{n}_1 - \hat{n}_2}{\sqrt{2A_-}} \tag{64}$$

where

$$A_+ = 1 + \hat{n}_1\hat{n}_2, \qquad A_- = 1 - \hat{n}_1\hat{n}_2, \qquad A = A_+A_- = 1 - (\hat{n}_1\hat{n}_2)^2 \tag{65}$$

We can expand $\vec{R}$ and $\vec{r}$ as

$$\vec{R} = \hat{v}_1 R_1 + \hat{v}_2 R_2 + \vec{R}_0 \tag{66}$$

$$\vec{r} = \hat{v}_1 r_1 + \hat{v}_2 r_2 + \vec{r}_0 \tag{67}$$

where $R_1 = \hat{v}_1 \cdot \vec{R}$, $R_2 = \hat{v}_2 \cdot \vec{R}$, $r_1 = \hat{v}_1 \cdot \vec{r}$, $r_2 = \hat{v}_2 \cdot \vec{r}$, i.e. $\vec{R}_0$ and $\vec{r}_0$ are orthogonal to the plane spanned by $\hat{v}_1$, $\hat{v}_2$. Using these expansions and the inverse of (64),

$$\hat{n}_1 = \frac{1}{\sqrt{2}}(\sqrt{A_+}\hat{v}_1 + \sqrt{A_-}\hat{v}_2), \qquad \hat{n}_2 = \frac{1}{\sqrt{2}}(\sqrt{A_+}\hat{v}_1 - \sqrt{A_-}\hat{v}_2) \tag{68}$$

we obtain from (60), (62) the following equations

$$\sqrt{A_+}\left(r_1 - \frac{R_1}{2}\right) + \sqrt{A_-}\left(r_2 - \frac{R_2}{2}\right) = 0 \tag{69}$$

$$\sqrt{A_+}\left(r_1 + \frac{R_1}{2}\right) - \sqrt{A_-}\left(r_2 + \frac{R_2}{2}\right) = 0 \tag{70}$$

the solution of which is given by

$$r_1 = \sqrt{\frac{A_-}{A_+}}\frac{R_2}{2}, \qquad r_2 = \sqrt{\frac{A_+}{A_-}}\frac{R_1}{2} \tag{71}$$

Similarly, the inequalities (61), (63) reduce to

$$\left(\vec{r}_0 - \frac{\vec{R}_0}{2}\right)^2 \leqslant a^2 - \frac{1}{2}\left(\frac{R_1}{\sqrt{A_-}} - \frac{R_2}{\sqrt{A_+}}\right)^2 \tag{72}$$

$$\left(\vec{r}_0 + \frac{\vec{R}_0}{2}\right)^2 \leqslant a^2 - \frac{1}{2}\left(\frac{R_1}{\sqrt{A_-}} + \frac{R_2}{\sqrt{A_+}}\right)^2 \tag{73}$$

Inequalities (72), (73) describe the set of points in space corresponding to the overlap region of two spheres with centers at $\vec{R}_0/2$ and $-\vec{R}_0/2$ and radii squared $a^2 - \frac{1}{2}(R_1/\sqrt{A_-} - R_2/\sqrt{A_+})^2$ and $a^2 - \frac{1}{2}(R_1/\sqrt{A_-} + R_2/\sqrt{A_+})^2$. This set is not empty iff

$$a^2 - \frac{1}{2}\left(\frac{R_1}{\sqrt{A_-}} - \frac{R_2}{\sqrt{A_+}}\right)^2 \geqslant 0 \tag{74}$$

$$a^2 - \frac{1}{2}\left(\frac{R_1}{\sqrt{A_-}} + \frac{R_2}{\sqrt{A_+}}\right)^2 \geqslant 0 \tag{75}$$

and

$$\sqrt{a^2 - \frac{1}{2}\left(\frac{R_1}{\sqrt{A_-}} - \frac{R_2}{\sqrt{A_+}}\right)^2} + \sqrt{a^2 - \frac{1}{2}\left(\frac{R_1}{\sqrt{A_-}} + \frac{R_2}{\sqrt{A_+}}\right)^2} \geqslant |\vec{R}_0| \tag{76}$$

The overlap integral (59) becomes

$$-\int d^D R\, f(\vec{R}, \omega_1, \omega_2) = -\int dR_1\, dR_2\, d^{D-2}R_0\, f(\vec{R}, \hat{n}_1, \hat{n}_2) \tag{77}$$

Changing variables to ξ_1, ξ_2 defined as

$$\xi_1 = \frac{R_1}{\sqrt{2A_-}} - \frac{R_2}{\sqrt{2A_+}}, \qquad \xi_2 = \frac{R_1}{\sqrt{2A_-}} + \frac{R_2}{\sqrt{2A_+}} \tag{78}$$

and writing conditions (74) –(76) in terms of ξ_1, ξ_2,

$$a^2 - \xi_1^2 \geqslant 0, \qquad a^2 - \xi_2^2 \geqslant 0, \qquad \sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2} \geqslant |R_0| \tag{79}$$

we get $(dR_1 dR_2 = \sqrt{A}\, d\xi_1 d\xi_2)$

$$\sqrt{A}\int_{-a}^{a} d\xi_1 \int_{-a}^{a} d\xi_2 \theta(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2} - |R_0|)\, d^{D-2}R_0 \tag{80}$$

where $\theta(x) = 0$ for $x < 0$, $\theta(x) = 1$ for $x \geqslant 0$. Integration over $d\vec{R}_0$ gives the volume of a $D-2$-dimensional sphere with radius $\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2}$. We obtain

$$\begin{aligned}\sqrt{A}\,\frac{S_{D-2}}{D-2}\int_{-a}^{a} d\xi_1 \int_{-a}^{a} d\xi_2 (\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^{D-2} \\ = |\sin(\hat{n}_1, \hat{n}_2)|\, a^D\, \frac{S_{D-2}}{D-2}\, I\end{aligned} \tag{81}$$

where

$$I = \int_{-1}^{1} dx \int_{-1}^{1} dy(\sqrt{1-x^2} + \sqrt{1-y^2})^{D-2} \tag{82}$$

The integral (82) can be evaluated by the steepest descent method in the limit $D \to \infty$. The leading term of the asymptotics is given by

$$I = \frac{2^D \pi}{D-2} \tag{83}$$

Inserting this into (81) we finally obtain

$$\mathscr{V}(\omega, \omega') = |\sin(\omega, \omega')| \, (2a)^D \frac{\pi S_{D-2}}{(D-2)^2} \tag{84}$$

APPENDIX B. OVERLAP INTEGRAL EVALUATION: INHOMOGENEOUS CASE

In the inhomogeneous case the overlap integral (52) can be written as

$$\begin{aligned} \mathscr{V}(Z, \omega_1, \omega_2) &= -\int f(\vec{R}, \omega_1, \omega_2) \, d^{D-1} R_\perp \\ &= -\int f(\vec{R}, \omega_1, \omega_2) \, \delta(\vec{R} \cdot \hat{z} - Z) \, d^D R \end{aligned} \tag{85}$$

Proceeding as in the homogeneous case (see Appendix A, (60)–(80)) we find

$$\begin{aligned} \mathscr{V}(Z, \omega_1, \omega_2) = \sqrt{A} \int_{-a}^{a} d\xi_1 \int_{-a}^{a} d\xi_2 \theta[(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^2 - |\vec{R}_0|^2] \\ \times \delta(\vec{R} \cdot \hat{z} - Z) \, d^{D-2} R_0 \end{aligned} \tag{86}$$

To perform the integral over $\vec{R}_0$ it is convenient to use the expansion

$$\hat{z} = z_1 \hat{v}_1 + z_2 \hat{v}_2 + \vec{z}_0 \tag{87}$$

where $\vec{z}_0 \in \mathbb{R}^{D-2}$, $z_1 = \hat{z} \cdot \hat{v}_1$, $z_2 = \hat{z} \cdot \hat{v}_2$, $\hat{v}_1$, $\hat{v}_2$ were defined in (64) and $z_0 = \sqrt{1 - z_1^2 - z_2^2}$. Introducing $\hat{v}_0 = \vec{z}_0 / z_0$, we may expand $\vec{R}_0$ as

$$\vec{R}_0 = \xi \hat{v}_0 + \vec{\mathscr{R}} \tag{88}$$

where $\xi = (\vec{R}_0, \hat{v}_0)$ and $\vec{\mathscr{R}} \in \mathbb{R}^{D-3}$. Then

$$\vec{R} \cdot \hat{z} = z_1 R_1 + z_2 R_2 + z_0 \xi \tag{89}$$

$$|\vec{R}_0|^2 = \xi^2 + |\vec{\mathscr{R}}|^2 \tag{90}$$

Inverting (78) we can express R_1 and R_2 in terms of ξ_1, ξ_2:

$$R_1 = (\xi_2 + \xi_1)\sqrt{\frac{A_-}{2}}, \qquad R_2 = (\xi_2 - \xi_1)\sqrt{\frac{A_+}{2}} \tag{91}$$

Then (89) can be written as

$$\vec{R} \cdot \hat{z} = \alpha\xi_1 + \beta\xi_2 + z_0\xi \tag{92}$$

where

$$\alpha = z_1\sqrt{\frac{A_-}{2}} - z_2\sqrt{\frac{A_+}{2}}, \qquad \beta = z_1\sqrt{\frac{A_-}{2}} + z_2\sqrt{\frac{A_+}{2}} \tag{93}$$

and the integral (86) becomes

$$\begin{aligned} \mathscr{V}(Z, \omega_1, \omega_2) = \sqrt{A}\int_{-a}^{a} d\xi_1 \int_{-a}^{a} d\xi_2 \\ \times \theta[(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^2 - \xi^2 - |\vec{\mathscr{R}}|^2] \\ \times \delta(\alpha\xi_1 + \beta\xi_2 + z_0\xi - Z)\, d^{D-3}\mathscr{R}\, d\xi \end{aligned} \tag{94}$$

Integrating over $\vec{\mathscr{R}}$ and then over ξ we get, correspondingly

$$\begin{aligned} \mathscr{V}(Z, \omega_1, \omega_2) = \sqrt{A}\,\frac{S_{D-3}}{D-3} \int_{-a}^{a} d\xi_1 \int_{-a}^{a} d\xi_2 \\ \times \theta[(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^2 - \xi^2] \\ \times [(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^2 - \xi^2]^{(D-3)/2} \\ \times \delta(\alpha\xi_1 + \beta\xi_2 + z_0\xi - Z)\, d\xi \end{aligned} \tag{95}$$

$$\begin{aligned} \mathscr{V}(Z, \omega_1, \omega_2) = \gamma\sqrt{A}\,\frac{S_{D-3}}{D-3} \int_{-a}^{a} d\xi_1 \int_{-a}^{a} d\xi_2 \\ \times \theta[(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^2 - \gamma^2(Z - \alpha\xi_1 - \beta\xi_2)^2] \\ \times [(\sqrt{a^2 - \xi_1^2} + \sqrt{a^2 - \xi_2^2})^2 - \gamma^2(Z - \alpha\xi_1 - \beta\xi_2)^2]^{(D-3)/2} \end{aligned} \tag{96}$$

where $\gamma = 1/z_0$. Finally, introducing dimensionless variables $x = \xi_1/a$, $y = \xi_2/a$ and $\zeta = Z/a$, we obtain

$$\mathscr{V}(\zeta, \omega_1, \omega_2) = \gamma \sqrt{A}\, a^{D-1} \frac{S_{D-3}}{D-3} J(\alpha, \beta, \gamma, \zeta) \tag{97}$$

where

$$J(\alpha, \beta, \gamma, \zeta) = \int_{-1}^{1} dx \int_{-1}^{1} dy\, \theta[(\sqrt{1-x^2} + \sqrt{1-y^2})^2 - \gamma^2(\zeta - \alpha x - \beta y)^2] \\ [(\sqrt{1-x^2} + \sqrt{1-y^2})^2 - \gamma^2(\zeta - \alpha x - \beta y)^2]^{(D-3)/2} \tag{98}$$

Evaluation of the overlap integral (97)–(98) for $D \to \infty$ in a way which would preserve its essential dependence on angular variables and Z is a fairly complicated problem requiring subtle multiscale analysis. The relevant work is now in progress.

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