Interactions between particulate inclusions in a smectic-*A* liquid crystal

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We study theoretically the smectic mediated interactions between pointlike inclusions in a lamellar phase. The two-body interaction is derived and we discuss the virial expansion in the limits of weak and strong interactions. The leading order finite density corrections to the interaction potential are calculated using a mean field theory, which allows the particle density, potential, and effective smectic moduli to be calculated self-consistently. The effective bending modulus of the membranes is found to increase linearly with the particle density. We also give the structure factor $S(\mathbf{q})$ for small but finite particle density. [S1063-651X(97)50602-7]

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INTRODUCTION

It is well known that the physical properties of many systems are highly sensitive to the presence of impurities or defects. A dramatic example is the increased conductivity observed in impure semiconductors [1]. Liquid crystalline systems have been of interest to physicists for many decades [2] and it seems natural to seek to understand the role of impurities in these systems too. We might also be motivated by the numerous industrial applications of liquid crystals or a marked similarity with certain biological systems, e.g., cell membranes, which are known to contain many impurities [3,4]. Some theoretical [5] and experimental [6] studies of the interaction between particles embedded in a single (or pair of) membrane(s) have been carried out. In addition we recently [7] presented a description of aggregation processes involving particles incorporated into a bulk ($3d$) lamellar phase in which the aggregates were treated as noninteracting. Our interest in such bulk systems has been fueled by recent experimental studies [8,9]. It is our aim here to study the interactions between particulate inclusions residing in such a bulk smectic phase.

This paper is organized as follows: In Sec. I we briefly discuss the background theory and introduce our model for the particle-layer interactions. We obtain the interaction potential for two particles embedded in a bulk smectic-*A* phase. We employ these results in Sec. II to construct a self-consistent mean field theory for the two-particle interactions at finite density. We calculate the linear correction to the interaction potential and find that this can be interpreted in terms of a *stiffening* of the membranes, with their compressibility unchanged. This is in contrast to one earlier study, albeit on a somewhat different system, which predicted a decrease in the bending modulus [10]. In Sec. III we discuss the static structure factor for scattering from impurities embedded in a smectic phase. Finally we briefly discuss the far-field contribution to the second virial coefficient for finite particle densities. We present brief conclusions in Sec. V. Throughout, we employ units in which $k_BT=1$.

I. THEORY FOR PARTICLE-SMECTIC COUPLING

In the smectic phase the layers are *on average* flat and equidistant with layer spacing d and normal in the z direction. Deformation of the average layer position away from this state may conveniently be parametrized by the continuous scalar displacement field u, which represents the normal displacement of the layers in the z direction. Such a description leads to the so-called Landau–de Gennes Hamiltonian [2,11,12]. We model the effect of pointlike particles in the smectic phase by including a term $\sim\rho\partial_z u$ in the energy density that represents the lowest order coupling between the particle density $\rho(\mathbf{r})$ and the local layer compression (or expansion) $\partial_z u$. (The reader may be surprised to learn that coupling terms like $\sim\rho\nabla_\parallel^2 u$ lead to identical results. This subtle point will be discussed in a future article.) We omit terms scaling like $\sim\rho^2$, which corresponds to direct interparticle interactions, as these depend on microscopic details of the particles involved. It is our aim here to study only the membrane-mediated interparticle interactions. Our coupling term is formally the simplest in that it is the only term quadratic in $\{\rho,u\}$ involving only a first derivative that is acceptable on symmetry grounds. The Hamiltonian $\mathcal{H}$ now reads

$$\mathcal{H}=\frac{B}{2}\int d^3\mathbf{r}[(\partial_z u)^2+\lambda^2(\nabla_\parallel^2 u)^2+\beta\rho\partial_z u]. \qquad (1)$$

In this expression $\nabla_\parallel$ is the gradient operator in the x-y plane, $\lambda=\sqrt{K/B}$ is a length characteristic of the smectic (typically of the order of the layer spacing d), and B and K are respectively the compressional and bending moduli of the smectic. The coupling constant β, with dimensions of volume, controls the amplitude of the local deformation. Its value depends on the microscopic details of the particle-layer interactions. The particles either provide a local inwards pinch ($\beta>0$) or outwards push ($\beta<0$) to the neighboring layer. Certain proteins [3,9] are known to bind to aqueous surfactant membranes more or less fixing the layer separation very locally. In such systems β could be chosen so that a

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single particle fixes the local layer separation at d^*. Such a condition may be shown to imply [7] $\beta \simeq \lambda d(d-d^*)$.

Minimization of Eq. (1) and subsequent calculations are most easily performed in Fourier space. The Fourier transform is defined by $f_{\mathbf{q}}=\int d^3\mathbf{r} f(\mathbf{r}_\parallel,z)e^{i(\mathbf{q}_\parallel\cdot\mathbf{r}_\parallel+q_z z)}$ with $\mathbf{r}_\parallel$ and $\mathbf{q}_\parallel$ vectors in the x-y plane. Minimizing Eq. (1) with respect to $u_{\mathbf{q}}$ the energy is given by [7]

$$\mathcal{H}=\int \frac{d^3\mathbf{q}}{(2\pi)^3} G_{\mathbf{q}}\rho_{\mathbf{q}}\rho_{-\mathbf{q}}=\int d^3\mathbf{r}' \int d^3\mathbf{r} G(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}'), \tag{2}$$

where

$$G_{\mathbf{q}}=-E_0\lambda d^2 \frac{q_z^2}{q_z^2+\lambda^2 q_\parallel^4}, \tag{3}$$

with

$$E_0=\frac{\sqrt{KB}\beta^2}{8\lambda^2 d^2}, \tag{4}$$

a number characterizing the energy scale of the interactions and, in real space

$$G(\mathbf{r})=\frac{E_0}{8\pi}\left(\frac{d}{z}\right)^2\left(1-\frac{r_\parallel^2}{4\lambda|z|}\right)\exp-\frac{r_\parallel^2}{4\lambda|z|}. \tag{5}$$

The fact that Eq. (5) diverges in the limit $z\to 0$ does not reflect an underyling problem in the theory since the energy is well behaved for densities $\rho(\mathbf{r})$ that are smoothly varying [13]. The two-body interaction potential for $z \gg d$ is approximately $U_{12}(\mathbf{r})=2G(\mathbf{r})$ [the factor 2 arises because of the intrinsic double counting in Eq. (2)].

From Eq. (5) we see that the interaction between two particles is long ranged in the z direction and is anisotropic and radially nonmonotonic. This anisotropy is characterized by the paraboloid $r_\parallel^2=4\lambda|z|$, which also appears in the classical problem of the interaction between two dislocations in smectic A [2], although the precise functional form is rather different in this case. One can also show that the energy scale for the interaction potential E_0 is equal to the (self-) energy of a single isolated particle αE_0, to within a numerical prefactor α of order unity [7]. A quantitative estimate of this prefactor formally requires an improvement in Eq. (1) and also depends on microscopic details.

II. FINITE DENSITY CORRECTIONS TO THE TWO-BODY INTERACTION: A SELF-CONSISTENT MEAN FIELD THEORY

We now examine the effect of surrounding particles on the two-body interaction potential. We will employ a mean field theory in which the particle density and potential fields are determined self-consistently. Such an approach has been employed with success in many other physical problems. Perhaps the best known example is the Debye-Hückel theory for electrolytes. In the present work we use the smectic potential ϕ (in k_BT units) determined via our modified Landau–de Gennes functional (1). We assume Boltzmann statistics for the distribution of particles and solve the linearized version of the resulting equations to obtain corrections to the two-body interaction potential.

We calculate the potential field $\phi(\mathbf{r})$ due to a particle at the origin and its associated correlated neighbors. Thus the energy required to move an infinitesimal number of inclusions δn from infinity to $\mathbf{r}$ is $\delta n\phi(\mathbf{r})$.

Invoking Boltzmann statistics the density field near the particle is of the form

$$\rho(\mathbf{r})=\overline{\rho e}^{-\phi(\mathbf{r})}+\delta(\mathbf{r}), \tag{6}$$

where $\overline{\rho}$ is the density at infinity and the term $\delta(\mathbf{r})$ fixes one particle at the origin.

We may linearize Eq. (6) whenever $\phi \ll 1$, which is satisfied whenever the energy scale $E_0 \ll 1$. The linearized form of Eq. (6) is

$$\rho(\mathbf{r})=\overline{\rho}[1-\phi(\mathbf{r})]+\delta(\mathbf{r}) \Rightarrow \rho_{\mathbf{q}}=\overline{\rho}[(2\pi)^3\delta(\mathbf{q})-\phi_{\mathbf{q}}]+1. \tag{7}$$

Our second equation relates the potential ϕ to the density via the bare two-body Green's function G. From Eq. (2) we have

$$\phi(\mathbf{r})=\int d^3\mathbf{r}' G(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') \Rightarrow \phi_{\mathbf{q}}=G_{\mathbf{q}}\rho_{\mathbf{q}}. \tag{8}$$

Solving Eqs. (7) and (8) for ϕ_q and substituting Eq. (3) we find [14]

$$\phi_{\mathbf{q}}=-\frac{E_0\lambda d^2}{1-\overline{\rho}E_0\lambda d^2}\frac{q_z^2}{q_z^2+\lambda'^2 q_\parallel^4}, \tag{9}$$

where

$$\lambda'=(1-\overline{\rho}E_0\lambda d^2)^{-1/2}\lambda, \tag{10}$$

a result that is valid for $q_z \ll 1/d$. In some sense Eq. (10) indicates that the range of the interactions is increasing with the particle density. Transforming Eq. (9) we find that the real space potential is well approximated by the following form for $z \gg d$:

$$\phi(\mathbf{r})=\frac{E_0}{8\pi(1-\overline{\rho}E_0\lambda d^2)^{1/2}}\left(\frac{d}{z}\right)^2\left(1-\frac{r_\parallel^2}{4\lambda'|z|}\right)\exp-\frac{r_\parallel^2}{4\lambda'|z|}. \tag{11}$$

We may calculate the correction to the zero density interaction potential either by expanding Eq. (11) directly in powers of $\overline{\rho}$ or, equivalently, by expanding Eq. (9) before transforming to real space. Writing the real space potential $\phi=G+\delta\phi$ we find

$$\delta\phi(\mathbf{r})=\frac{\overline{\rho}\lambda d^2E_0^2}{16\pi}\left(\frac{d}{z}\right)^2\left[1+\frac{r_\parallel^2}{4\lambda|z|}-\left(\frac{r_\parallel^2}{4\lambda|z|}\right)^2\right]\exp-\frac{r_\parallel^2}{4\lambda|z|}, \tag{12}$$

where we neglect terms of $O(\overline{\rho^2})$. This function is plotted in Fig. 1. This finite density correction to the interactions can be identified with weakly correlated three-body interactions.

Finally we can examine the influence of the particles on the *effective* moduli K' and B'. These moduli are those which mimic the effect of the finite particle density. In the limit of zero particle density they are merely the bare smectic

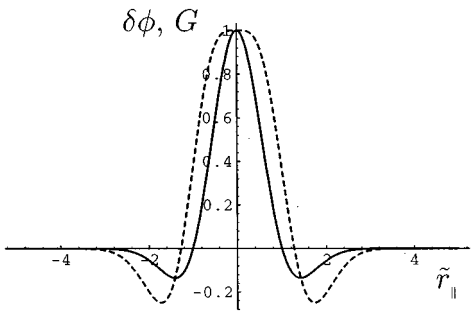

FIG. 1. Plot of the bare potential, or Greens function $G(\mathbf{r})$ (solid line) Eq. (5) and the finite density corrections to the potential $\delta\phi$ (broken line) Eq. (12) against $\tilde{r}_\parallel = r_\parallel/(4\lambda|z|)^{1/2}$. The function $G(\mathbf{r})$ is shown in units where $(E_0/8\pi)(d/z)^2=1$ and the correction $\delta\phi$ is in units where $(\overline{\rho\lambda}d^2E_0^2/16\pi)(d/z)^2=1$.

moduli K and B introduced in Sec. I. However, identifying the scaling $E_0 \propto \sqrt{KB}$ Eq. (4) and $\lambda=\sqrt{K/B}$ we see that $E_0'=E_0(1-\overline{\rho E}_0\lambda d^2)^{-1/2}$ and Eq. (10) together imply a renormalization of K to

$$K'=\frac{K}{1-\overline{\rho E}_0\lambda d^2}, \tag{13}$$

with $B'=B$ unchanged at leading order. Equation (13) indicates an increase in the effective bending modulus with particle density.

III. STATIC STRUCTURE FACTOR

Static scattering measurements measure the ensemble average of the Fourier transform of the density-density correlation function [15]

$$S(\mathbf{q})=C_\alpha^2\frac{1}{N}\left\langle \int\int d^3\mathbf{r}d^3\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\right\rangle, \tag{14}$$

where C_α is the scattering amplitude per inclusion and N is the total number of particles. We wish to calculate this function for scattering from inclusions incorporated in a lamellar phase and assume that this signal can be isolated from that scattered by the lamellae. If we treat the inclusions as pointlike and neglect the details of the short range interactions we may write $S(\mathbf{q})$ in terms of the two-body potential $\phi(\mathbf{r})$ by invoking Boltzmann statistics

$$S(\mathbf{q})=C_\alpha^2\overline{\rho}\int d^3\mathbf{r}e^{i\mathbf{q}\cdot\mathbf{r}-\phi(\mathbf{r})}. \tag{15}$$

By assuming that the potential ϕ is small, which is often a reasonable approximation for uncharged lyotropic systems, we may expand the exponential in Eq. (15) to obtain $S(\mathbf{q})$ for small but finite $\mathbf{q}$.

$$S(\mathbf{q})=-C_\alpha^2\overline{\rho\phi}_\mathbf{q}, \tag{16}$$

where $\phi_\mathbf{q}$ is given by Eq. (9). This prediction allows for a test of the present theory on two grounds. Firstly a structure factor of the form $S(\mathbf{q})\sim q_z^2/(q_z^2+\lambda'^2q_\parallel^4)$ would provide strong evidence that the particle-layer coupling in a given system is well described by the $\sim\rho\partial_z u$ term in Eq. (1). Secondly the finite density corrections calculated in Sec. II predict variation of the length λ' with particle density according to Eq. (10).

IV. AVERAGE PARTICLE INTERACTIONS AND THE SECOND VIRIAL COEFFICIENT

For dilute systems an expansion of the free energy density F/V in powers of the particle concentration $\overline{\rho}$ can usually be performed. Provided that such an analytic expansion exists the second virial coefficient B_V is given by [16]

$$B_V=\frac{1}{2}\int d^3\mathbf{r}(1-e^{-U_{12}(\mathbf{r})}), \tag{17}$$

where U_{12} is the two-body interaction potential for particles separated by a vector $\mathbf{r}$ and the zero of free energy is taken to be the pure smectic phase. If we consider only the long range membrane mediated interactions, neglecting any additional microscopic short range forces, we can estimate the far field contribution to B_V, in both the limits $E_0\ll 1$ and $E_0\gg 1$.

The weak interaction limit $E_0\ll 1$ may often be appropriate for lyotropic phases, in which the characteristic energy scale $E_0\lesssim 1$. In this regime the far field contribution B_V^{far} may be calculated by expanding the exponential factor in Eq. (17). The second order term is found to give the leading order far field contribution

$$B_V\simeq -E_0^2\lambda d^2 \quad \text{for } E_0\ll 1, \tag{18}$$

which is negative, implying that the net interactions are attractive. This result necessarily neglects all additional short range interactions and involves crudely cutting off the volume integral in Eq. (17) at $z=\nu d$ (with ν of order unity). The numerical prefactor depends on the choice of this cutoff.

The opposite, strong interactions, limit may often be relevant for particles incorporated in thermotropic liquid crystals, such as the diblock copolymer lamellar phases. In this limit we can no longer expand the exponential $e^{-U_{12}}$ in Eq. (17) everywhere but can make a crude estimate of the far field contribution to B_V by (i) integrating Eq. (17) by steepest descents in the regime where $U_{12}\gg 1$ and (ii) expanding the exponential when $U_{12}\ll 1$. We proceed by crudely cutting off the integral at $z=\nu d$, as before, and find

$$B_V^{\text{far}}\simeq -\lambda d^2E_0^{-3/2}\exp[E_0/(4\pi e^2\nu^2)] \quad \text{for } E_0\gg 1. \tag{19}$$

This represents a large (exponential) average attraction between particles.

We emphasize again that these results neglect any additional short range interactions not described by the linear coupling term $\beta\rho\partial_z u$ in Eq. (1).

CONCLUSION

We have studied the effect of particulate inclusions in a bulk smectic-A phase and have derived equations for the energy of an arbitrary distribution of particles. These results are used to develop a self-consistent mean field theory for the particle distribution, which is used to study the effect of fi-

nite particle density on the effective two-body interaction potential. The correction to this potential is computed and we find that although the effective compressional modulus of the phase is unchanged, the effective bending modulus increases linearly with the particle density according to Eq. (13). This result is in contrast to one, rather different, study of membrane impurities, which predicted a decrease in the bending modulus [10], but is in qualitative agreement with the trend observed for membranes densely decorated with PEG lipids [17]. In addition both of these studies show a change in B (an increase in the first and a decrease at large densities in the second). The qualitative differences with the present theory are unsurprising in view of the differences between the systems. We give the static structure factor for the particles and suggest that direct measurements of this may provide a direct test of our theory. We also briefly discuss the second virial coefficient for the mixed particle-lamellar system, noting that the far-field interactions are always attractive on average.

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