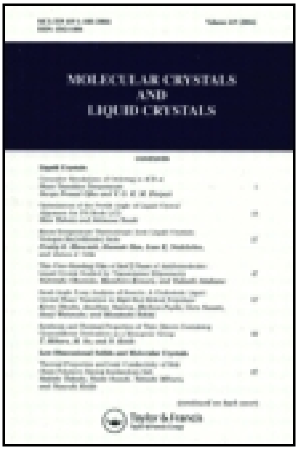

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POWER-LAW FORCES BETWEEN PARTICLES IN A NEMATIC

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Abstract Macroscopic particles of size a immersed in liquid crystalline solvents (e.g. polystyrene spheres in a lyotropic nematic) will exert long-range forces on each other by distorting the order-parameter field around them. As a first step towards a full theory of this novel class of suspensions, we show how to calculate the energy of interaction as a function of the separation $\mathbf{r}$ for $r \gg a$ between particles of various shapes and orientations in a nematic liquid crystal. Our approach can be understood (i) as a continuum description of the concentration field of the particles, with symmetry-allowed couplings between concentration *gradients* and director fields or (ii) in terms of an electrostatic analogy due to Brochard and de Gennes, in which the far-field transverse components of the director distortion are treated as a two-component Coulomb field of which particles of various shapes and orientations are elementary multipolar sources. The results with the greatest potential relevance to the experiments of Raghunathan *et al.* are for spheres: these act like quadrupoles, and the interaction is $\propto \frac{Ka^6}{r^5}$, and attractive for $\mathbf{r}$ oriented in a range around 50° to the nematic axis $\hat{\mathbf{n}}$, although it is repulsive for $\mathbf{r}$ normal or parallel to $\hat{\mathbf{n}}$. The error in a recent calculation in the literature, claiming an always repulsive, r^{-3} interaction, is pointed out.

In recent work[1] by a group at CRPP Pessac, spherical latex particles of 600Å and 1200Å diameter, were successfully suspended in a lyotropic medium (CsPFO + water, which forms disc-like micelles ordering into a nematic at sufficiently low temperatures), and the phase diagram, structure, and dynamics of the mixture studied. Fig.1a sketches the kind of configuration which is expected for normal alignment on the particle surface, and a uniform director field along the z axis at infinity[2]. One can also envisage[2] a tangential configuration, Fig 1b, which leads to two point defects at the poles of the sphere instead of the ring defect. There is an effective long range interaction between two such particles originating in the overlap of their director fields, arising from the broken-symmetry nature of nematic elasticity. We present here a calculation of this interaction.

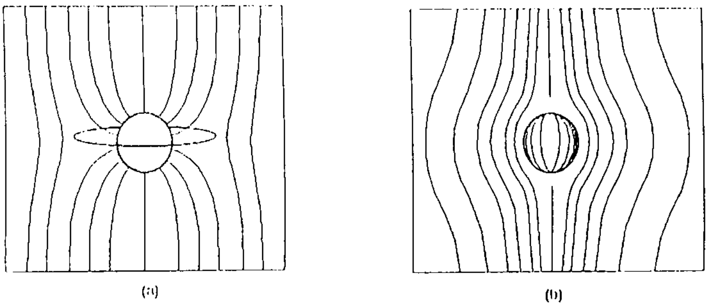

FIGURE 1 Director configuration around a spherical particle in a nematic. (a) Director normal to the surface. (b) Director tangential to the surface.

An *ab initio* approach to calculating the interaction between two suspended particles would address the nonlinear partial differential equation for the director field, imposing suitable boundary conditions on each particle surface and at infinity, and introducing compensating defects such as the ring defect in Fig. 1a around each particle to absorb the incompatibility between these boundary conditions. The detailed defect configuration required to enforce, *e.g.* normal alignment on the particle surfaces, however, changes as the particles are brought closer together[3]. A more modest aim, taking for definiteness the case of normal alignment, would be to *assume* the defect configuration of Fig. 1a around each sphere, but treat the radius of the ring defect as a variational parameter, to be obtained for each value of interparticle separation. Or, persisting with the defect picture, one could calculate in detail the fields around a single sphere, for the optimal radius of the ring, and then superpose the far-fields of two such objects, to get the long-distance part of the interaction as attempted in ref.2.

If all we are after is the leading behaviour of the interaction at large separations, then a strategy exists which isolates the long wavelength physics, bypassing the complexities of the above approaches. Consider therefore a concentration field $c(\mathbf{r})$ of the particles, which couples to the (smoothed out) director field $\mathbf{n}(\mathbf{r})$. Apart from the well known Frank free energy density $\mathcal{F}_F$ of the nematic[4], one includes terms in which concentration gradients ∇c couple to director gradients $\nabla\mathbf{n}$, respecting the equivalence of $\mathbf{n}$ and $-\mathbf{n}$. This gives the following free energy density which keeps the lowest order gradients and hence is the relevant one for long wavelengths.

$$\begin{aligned} \mathcal{F} &= \mathcal{F}_F + A(\nabla c)\cdot[(n\cdot\nabla)n] \\ &+ A'(\nabla\cdot n)(n\cdot\nabla)c \end{aligned} \tag{1}$$

This describes the coupling of concentration fluctuations to bend and splay distortions, twist being excluded for nonchiral situations. We specialise to the case when the director field is nearly uniform and along z, i.e., of the form

$$\mathbf{n} = (n_x, n_y, 1 + \mathcal{O}(n_x^2, n_y^2)) \tag{2}$$

In terms of $\mathbf{n}_\perp \equiv (n_x, n_y)$ and $\nabla_\perp \equiv (\partial_x, \partial_y)$; we can now write

$$\begin{aligned} \mathcal{F} &= \frac{1}{2}K(\nabla \mathbf{n}_\perp)^2 + A(\nabla_\perp c)\cdot(\partial_z \mathbf{n}_\perp) \\ &+ A'(\partial_z c)(\nabla_\perp\cdot n_\perp) \end{aligned} \tag{3}$$

The Frank free energy has been written in the one constant approximation, and twist has been dropped. It is actually straightforward to account for splay- bend anisotropy at this stage by rescaling the z co-ordinate with respect to x and y, and we omit this step for simplicity. One can see that the A' term can be integrated by parts and combined with the A term, dropping the boundary contribution for localised concentration fluctuations. Further, we write, on dimensional grounds $A = \alpha K a^3$, in terms of the radius a of the particles, and one expects $\alpha \sim 1$. Transforming to Fourier space, the free energy now reads (with $c_q = \int d^3\mathbf{r} c(r) e^{iq\cdot r}$, etc.)

$$\begin{aligned} F &= \frac{1}{2}K\Big[\int \frac{d^3q}{(2\pi)^3}(q^2 \mid n_{\perp q} \mid^2) + 2\alpha a^3 \times \\ &\times \int \frac{d^3q}{(2\pi)^3}(iq_\perp c_q)(-iq_z n_{\perp -q})\Big] \end{aligned} \tag{4}$$

Given an imposed concentration fluctuation c_q, one obtains the director distortion by varying (4) with respect to $\mathbf{n}_{\perp q}$ and minimising. This gives

$$\mathbf{n}_{\perp q} = \frac{-\alpha a^3 q_z}{q^2} c_q \mathbf{q}_\perp \tag{5}$$

The idea is now to eliminate the director field and obtain the effective interaction between concentration fluctuations that it mediates. Substituting (5) back into (4) to express the free energy in terms of c_q gives

$$F = -\frac{1}{2}K(\alpha a^3)^2 \int \frac{d^3q}{(2\pi)^3} c_q c_{-q} \left(\frac{q_z^2 q_\perp^2}{q^2}\right) \tag{6}$$

This is of the form

$$\begin{aligned} F &= \int dr dr' c(r) c(r') V(r-r') \\ &= \int \frac{d^3q}{(2\pi)^3} c_q c_{-q} V(q) \end{aligned} \tag{7}$$

where the effective interparticle potential $V(r)$ is the Fourier transform of $V(q)$. We thus have, comparing (6) and (7)

$$V(q) = -\frac{1}{2}K(\alpha a^3)^2 \left[\frac{q_z^2(q^2 - q_z^2)}{q^2}\right] \tag{8}$$

This is the sum of two terms, the first of which, q_z^2, merely shifts the coefficient of $(\partial_z c)^2$ in a gradient expansion of the free-energy cost of concentration fluctuations. The term of interest is the second one, which reads, in real space,

$$V(r) = +\frac{1}{2}K(\alpha a^3)^2 (\frac{\partial}{\partial z})^4 \frac{1}{4\pi r} \tag{9}$$

In terms of the separation of the particles and the angle θ made by this with the z axis, we have

$$V(r) = +\frac{1}{2}K\frac{(\alpha a^3)^2}{4\pi}\frac{1}{r^5}(9 - 90\cos^2\theta + 105\cos^4\theta) \tag{10}$$

Note the angular factor which is positive at $\theta = 0°$ and $90°$ but negative between about 30° and 70°, and has a zero average over a sphere. Terentjev[2] obtains an expression for the force which does not agree with (10). The source of the error is the use of a two-dimensional solution for the director distortion in the three-dimensional calculation[5].

It is illuminating to have an alternative real space interpretation of (10). We sketch this briefly below. Our viewpoint is that of Brochard and de Gennes[6]. The two components n_x and n_y of the director field far from the particles satisfy Laplace's equation, as can be checked by minimising (3). Here one is making both the one-constant and small tilt ($n_x, n_y << 1$) approximations. A localised perturbation near the origin can give rise to multipoles with different l's, each with a $r^{-(l+1)}$ radial dependence and $P_l^m(\cos\theta)\sin(m\varphi)$ or $\cos(m\varphi)$ angular dependence. The lowest order multipole which satisfies the symmetry of Fig.1 is $l = 2$, m=1, since n_x and n_y vary as $\cos\varphi$ and $\sin\varphi$, and vanish at $\theta = 0°$, $90°$, and $180°$, as does $\sin\theta\cos\theta$ which is nothing but $P_2^1(\cos\theta)$. We can straightaway write

$$\begin{aligned} n_x &\sim \frac{a^3}{r^3}\sin\theta\cos\theta\cos\varphi + \ldots \\ n_y &\sim \frac{a^3}{r^3}\sin\theta\cos\theta\sin\varphi + \ldots \end{aligned} \tag{11}$$

Terms falling off faster with r have been neglected, (e.g., $P_4^1(\cos\theta)/r^5$). One can also write (11) in the form

$$\begin{aligned} n_x &= \alpha a^3 \partial_z \partial_x (\frac{1}{4\pi r}) \\ n_y &= \alpha a^3 \partial_y \partial_z (\frac{1}{4\pi r}) \end{aligned} \tag{12}$$

which is seen to be just the real space counterpart of (5), when we put $c_q = 1$ (for a δ function $c(r)$, i.e., a particle at the origin). Clearly, the energy calculation following (5) can now be carried out. We omit the details of the real space integration of the free energy density corresponding to the superposition of two solutions of the type (11) or (12), since it leads to the same result (10) for the interaction. However, we can now add that α is positive in the case sketched in Fig.1a and negative for Fig.1b: the boundary condition at the surface of the particles is encoded completely in the sign and magnitude of the coupling α between concentration and director fluctuations. Further, the pattern shown in Fig.2, when the interparticle line makes an angle of about 45° with the z axis, reveals the origin of the attractive force in this geometry. As the two particles approach each other, the elastic energy associated with the director field in the space between them is actually *lowered* since it assumes a more nearly uniform, albeit tilted, configuration.

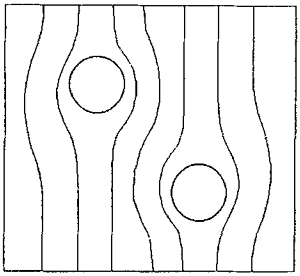

FIGURE 2 Director configuration around a pair of particles with the separation making 45° to the z axis. Note the nearly uniform and tilted orientation between the particles, whose low energy is the source of the attractive interaction for angles in this range.

Given the nature of the forces we have calculated, one expects neither a simple, repulsion stabilised, colloidal suspension nor a straightforward attraction induced clumping into a closely packed configuration. The preliminary indications from the experiments[1] are (i) that the 600Å particles are freely dispersed in the isotropic phase of the lyotropic, as well as in the high-temperature end of its nematic phase. Deep in the nematic phase, the particles condense out into aggregates. The 1200Å particles enter the isotropic phase without diffculty, but are expelled as soon as the system goes nematic. This latter effect is probably because the (self) energy of a single particle of radius a is of order Ka, and could become prohibitive at large a. Modeling the phase behaviour will involve studying the interaction at closer distances of a few particle radii, which is clearly more complex than the long range part we have considered so far[7].

The real space view, based on multipoles, naturally raises the question of what situations would give rise to the lower order multipoles, which fall off even more slowly with distance. As an example, an $l = 1, m = 1$ dirctor pattern has the symmetry to be induced by a carrot- or corkscrew-shaped particle[6]. The $l = 0$ situation is easily seen to describe the pattern around a " tilted stick " , which would of course relax back to an aligned, $l = 2, m = 1$ configuration in the absence of any external torque holding it in an inclined position[6].

Finally, a remark on the kinetics of aggregation is in order here. The rapidly decaying albeit power-law attraction means that the growth of particle clusters in the phase-separated regime will be dominated by Brownian motion rather than the attractive forces we have calculated here.

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