

QUADROPOLAR FORCES AND AGGREGATION OF NEMATIC DROPLETS

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The electrostatic quadrupolar interaction between spherical nematic droplets in an isotropic (and nonconducting) liquid is calculated. It is found to have an anisotropic form $U_q \propto 1/R^5$, where R is the distance between droplets, with repulsion for droplets having parallel orientation of the quadrupole moments and attraction at oblique angles around the orthogonal orientation. In an external magnetic field aligning the orientations of the quadrupole moments, a competition of the quadrupolar repulsion and van der Waals attraction ($U_{vdW} \propto 1/R^6$) leads to a specific spatial organization of droplets which is in fact often reported in experimental observations (see the monograph [1] and references cited therein).

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1. A nematic liquid crystal is uniform in its ground state, which, however, is very rarely attained in practice. The structure and properties of suspensions (in particular, nematic droplets in an isotropic liquid matrix) pose a number of theoretical and experimental questions which are interesting both from the standpoint of practical applications of liquid crystals and also because phenomena of this kind are of fundamental interest in their own right.

There is one rather evident consequence of nematic ordering that nevertheless, as far as we know, has never been considered before. As is well known [2], the nematic order parameter is a second-order tensor and has all the properties of the quadrupole moment of a charge distribution. Therefore generally nematics are quadrupolar ferroelectrics (and their isotropic phase is accordingly a quadrupolar paraelectric in which the nematic fluctuations enhance the quadrupolar susceptibility). In spite of this fairly strong statement, in the general case for large (ideally infinite) systems it does not lead to any directly observable predictions, primarily because quadrupolar forces are not very long-ranged. They are proportional to $1/R^5$, and for large systems this contribution to the energy can be represented (in terms of a Fourier expansion) as being proportional to q^2 (actually to a certain anisotropic combination of $q_i q_j$), and therefore the quadrupolar interactions in principle give some corrections to the bare contributions to the total free energy of the system which scale as q^2 (e.g., compressibility or orientational deformations). From the standpoint of translational symmetry, however, nematics are equivalent to isotropic liquids and must therefore have isotropic ($\propto q^2$) compressibility. Thus the anisotropic quadrupolar contribution to the compressibility in nematics should by definition be zero. The only consequence of quadrupolar forces for bulk nematics is a renormalization of the Frank elastic moduli, which can be represented in the form $K_{ii} = K_{ii}^0 + K_{ii}^Q$, where K_{ii}^0 is the bare value related to forces more short-ranged than the quadrupolar forces, e.g.,

steric forces, and K_{ii}^Q is the contribution from the quadrupolar interactions. It is clear that such a separation has no relevant physical meaning, and we will not discuss it further in this paper.

The above statement does not necessarily hold for small (mesoscopic) systems, where quadrupolar forces can lead to fairly pronounced phenomena. For a nematic droplet the director distribution field inside the droplet depends on the strength of surface anchoring, the elastic constants, and the droplet size. In the next section some particular configurations having quadrupolar symmetry of the director field will be presented. For such configurations the total orientational quadrupole moment of a droplet is nonzero. On the other hand, in the general case (when the chemical bonds in the material are not purely covalent, and actually they never are 100% covalent — see, e.g., [3] or the more recent monograph [4]) the droplets should also have an electrostatic quadrupole moment (recall that nematic liquid crystals are quadrupolar ferroelectrics). Therefore an orientational quadrupole moment of the droplet will inevitably lead to an electrostatic quadrupole moment. The latter can create an observable (and not extremely small) electric field around such a droplet (for a droplet radius of the order of 10^{-4} cm it can be as large as 1 V/cm; see the estimates below).

Nevertheless, even for mesoscopic objects the director distribution inside a droplet (and the shape of the droplet itself) is determined mainly by its surface tension and anchoring energy (and, of course, the nematic elastic moduli) and not by the electrostatic quadrupolar energy. Indeed, the electric field created by a quadrupole moment on the droplet surface scales as $E_Q \propto (D_0/L^4)$, where L is the droplet radius and D_0 is the total quadrupole moment, which can be estimated as $D_0 = d_0 N$, where d_0 is the molecular quadrupole moment and N is the number of molecules in the droplet, i.e., $N = (4\pi L^3/3a^2l)$. It is customarily believed that for most thermotropic nematics the molecules can be represented as hard rods having a well-defined length l and diameter a . Therefore the quadrupolar contribution to the energy is

$$F_{eQ} \simeq \int E^2 d^3 r \simeq \frac{d_0^2}{a^4 l^2} L \quad (1)$$

This should be compared to the conventional anchoring and surface energy of the nematic droplet, $F_s \simeq WL^2$, where $W \propto T/a^2$ if it is a typical surface energy or $\propto T/l^2$ for the anchoring energy. Thus in any case for

$$L > \frac{d_0^2}{a^4 l^2 W} \simeq l_b \quad (2)$$

(where the so-called Bjerrum length l_b (see, e.g., [5]) is usually of the order of 10 \AA , and therefore the condition (2) is always satisfied for any real nematic droplet with $L \simeq 10^5 - 10^4 \text{ \AA}$), and the shape (and director distribution) of the nematic droplet is determined mainly by the conventional surface energy.

However, let us stress once again that the quadrupolar forces (though they give only small corrections to the thermodynamic properties) are not negligible. For example, using the rough estimates given above, one can find that for a droplet with $L \simeq 10^{-4}$ cm the quadrupolar electric field around it will be about $E_Q \simeq 1 \text{ V/cm}$.

2. From what we have said above it is clear that under the condition (2) the director distribution in a nematic droplet can be found in the standard way [2] by minimization of the Frank elastic energy with suitable boundary conditions. In fact, a simple qualitative analysis of possible director configurations shows that for a spherical droplet with

any boundary condition (the only exception being an infinitely strong radial anchoring), the director distributions always have quadrupolar symmetry. We might mention, for example, bipolar structures with two surface point defects (so-called boojums), which can be realized for tangential boundary conditions, or more-sophisticated (but also possessing quadrupolar symmetry) structures which arise in the case of tilted orientation of the director on the droplet surface and which correspond to two boojums, one hedgehog, and one disclination ring (see [6]). All these configurations can be characterized by a quadrupolar preferred direction $\mathbf{m} \equiv -\mathbf{m}$ (e.g., for the bipolar structure \mathbf{m} is a unit vector along the direction between two poles). Thus the quadrupole moment of such a configuration can be represented in the form

$$D_{ik} = \tilde{D}_0(m_i m_k - \frac{1}{3} \delta_{ik}), \quad (3)$$

and the only difference between different quadrupolar configurations is the numerical coefficient (of the order of 1/10) which relates \tilde{D}_0 and D_0 . We henceforth neglect this difference, or, more accurately, consider this numerical factor to be included in the definition of \tilde{D}_0 .

The quadrupole-quadrupole pair interaction between droplets having quadrupole moments $\hat{D}^{(1)}$ and $\hat{D}^{(2)}$ for distances R larger than the size of each droplet can be found easily for the case when the droplets have no charge and no dipole moment [7]:

$$F_{int} = \frac{1}{12} D_{\alpha\beta}^{(2)} \frac{\partial}{\partial x_\alpha} \frac{\partial}{\partial x_\beta} [D_{\gamma\delta}^{(1)} \frac{n_\gamma n_\delta}{R^3}] \quad , \quad (4)$$

where \mathbf{n} is a unit vector along \mathbf{R} . Using (3) and performing the calculations, we find

$$F_{int} = \frac{\tilde{D}_0^{(1)} \tilde{D}_0^{(2)}}{12R^5} [(\mathbf{m}_1 \mathbf{m}_2)^2 - 20(\mathbf{n} \mathbf{m}_1)(\mathbf{n} \mathbf{m}_2)(\mathbf{m}_1 \mathbf{m}_2) - 5((\mathbf{n} \mathbf{m}_1)^2 + (\mathbf{n} \mathbf{m}_2)^2) + 35(\mathbf{m}_1 \mathbf{n})^2 (\mathbf{n} \mathbf{m}_2)^2 + \frac{4}{3}] \quad (5)$$

In the general case F_{int} is a function of three angular variables: θ_1 , θ_2 , and $\varphi_1 - \varphi_2$ (where θ_i and φ_i are, respectively, the polar and azimuthal angles between \mathbf{m}_i and \mathbf{n}).

Although the complete investigation of this function can be done only numerically, some particular configurations of relevance to us can rather easily be calculated analytically. Namely, one can show that attraction takes place only for nearly orthogonal orientations¹⁾ of \mathbf{m}_1 and \mathbf{m}_2 , while for nearly parallel vectors \mathbf{m}_i we have always repulsion. Expression (5) has a zero average over a sphere, as it should for quadrupolar symmetry.

Obviously $F_{int}(R, \theta_1, \theta_2, \varphi_1 - \varphi_2)$ is a noncentral potential, and the force on the nematic droplet has both radial and angular (torque) components. Therefore when we have many droplets interacting with each other in many different directions, and also as a result of Brownian motion, these droplets will always find a way towards the global angular minimum. This implies that the droplets would tend to organize themselves into chains with alternating orthogonal orientations of the quadrupole moments of neighbor-

¹⁾ The angular interval in which attraction takes place can be characterized by a certain angle between \mathbf{n} and one of the vectors \mathbf{m} , which is varied from $\arccos\sqrt{4/15}$ to $\arccos\sqrt{2/3}$, and the maximum is achieved for precisely orthogonal orientations.

ing droplets. One can consider organization of this type as an analogy of ferroelectric domains for quadrupolar ferroelectrics.

It is easy to estimate the characteristic time for chain formation controlled by the Stokes friction force $6\pi\eta Lu$, where η is the viscosity of the liquid and u is the velocity of a droplet. The interdroplet distance R is proportional to $\phi^{-1/3}L$, where ϕ is the droplet concentration. Therefore using expression (5) for quadrupolar attraction and equating the frictional and quadrupolar forces, one can estimate the characteristic time as

$$\tau \simeq \frac{\eta a^4 l^2}{d_0^2} L^2 \phi^{-7/3}. \quad (6)$$

Here (as well as later on) we ignore the entropy of mixing of the droplets, treating them as macroscopic objects, and, of course, the estimate (6) is valid only for small ϕ , when $R \gg L$.

Interesting phenomena can appear when we apply an external magnetic field to the system. Recall that the droplets are not only quadrupolar ferroelectrics but also conventional nematics having a diamagnetic anisotropy χ_a . Therefore a sufficiently strong magnetic field can provide alignment of the droplet quadrupole moments. The necessary condition for this alignment is

$$\chi_a^2 H^2 L^3 > \frac{\bar{D}^2}{R^5} \quad (7)$$

i.e., the magnetic energy must overcome the quadrupolar attraction. From (7) we find the critical field

$$H_c = \frac{d_0}{\sqrt{\chi_a a^2 l}} \frac{1}{L} \quad (8)$$

(we have assumed here that $R \simeq L$). Natural estimates of the parameters appearing in (8) give $H_c \simeq 10^3$ – 10^4 G.

However to avoid director deformations inside a droplet (and the consequent reduction of the droplet quadrupole moments) under the influence of this field, it must be smaller than the critical field for the Fréedericksz transition [2], [9]

$$H_F = \sqrt{\frac{K}{\chi_a}} \frac{1}{L}. \quad (9)$$

Comparing (8) and (9), we get the condition

$$d_0 < \sqrt{K} a^2 l. \quad (10)$$

Estimating K as T/l , we conclude that the condition (10) is equivalent to the condition

$$l_b < l \left(\frac{l}{a} \right),$$

which can be satisfied for real nematics.

Under these conditions (namely in an external magnetic field $H_c < H < H_F$) the quadrupolar forces give repulsion between droplets (as can be easily seen from (5)), and the chain structure will therefore be broken. To find the structure which will arise as a result of this quadrupolar repulsion ($\propto 1/R^5$) one has to take into account the others forces acting in such a system. The most relevant among these are the van der Waals forces. These forces lead primarily to a certain contribution to the internal energy

of each droplet. This internal contribution can be calculated using the general method elaborated by Dzyaloshinskii, Lifshitz, and Pitaevskii (see, e.g., [10]; some features of this contribution which are specific to nematics and which give, in particular, a renormalization of the Frank moduli, have been studied in [11]).

For us it is more relevant that the van der Waals forces lead to attraction between droplets. This attraction is anisotropic; in any case, however, the average over a sphere is nonzero. Thus we have a rather unusual situation: a system of particles with, say, "long-range" ($1/R^5$) repulsion and "short-range" ($1/R^6$) attraction.

The detailed calculation of all possible configurations for such systems would address a very complicated kinetic (and statistic) problem which is beyond the scope of our paper. A more modest aim we have is to describe qualitatively the consequences of quadrupolar forces. At this level it is clear that in the presence of both forces (the quadrupolar and van der Waals) the droplet distribution can be characterized by a certain specific length scale Λ . The above discussion of the forces assumed $1/R^5$ or $1/R^6$ laws for the interactions between isolated molecules. To find the total interactions between two mesoscopic spheres one has to sum of all individual interactions. This reduces to evaluation of the following integral:

$$I = \int d^3r_1 \int d^3r_2 \frac{1}{S^\alpha}, \quad (11)$$

where

$$S^2 = [(R + 2L - r_2 \cos \theta_2 - r_1 \cos \theta_1)^2 + (r_2 \sin \theta_2 - r_1 \sin \theta_1)^2], \quad (12)$$

and the exponent $\alpha = 3$ for the van der Waals interactions and $\alpha = 5/2$ for the quadrupolar interactions. In the simplest case $R \ll L$ it follows from (11)–(12) that

$$I_{\text{vdW}} \propto \frac{L}{R}, \quad I_Q \propto \ln \frac{L}{R}.$$

Now we are in position to estimate the characteristic cluster scale as the scale at which the van der Waals attraction is of the same order as the quadrupolar repulsion. Putting together all dimensional factors, we get

$$\Lambda \simeq \frac{h\nu\alpha_0^2 a^4 l^2}{d_0^2} \ln \frac{L}{l},$$

where α_0 is the electronic polarizability and ν is a characteristic frequency that can be identified with the first ionization potential of the molecules, which usually falls in the ultraviolet region (the meaning of all the others parameters has been explained above).

3. We calculated the electrostatic quadrupolar interaction between spherical nematic droplets in an isotropic (and nonconducting) liquid. It has an anisotropic form $U_q \propto 1/R^5$, where R is the distance between droplets, with repulsion for droplets having parallel orientation of the quadrupole moments and with attraction at oblique angles around the orthogonal orientation. In an external magnetic field ordering the orientations of the quadrupole moments, a competition of the quadrupolar repulsion and van der Waals attraction ($U_{\text{vdW}} \propto 1/R^6$) leads to a specific spatial aggregation of droplets that has in fact been reported often in experimental observations (see, e.g., [1], [8], [9], [12], [4], [13]). Results analogous to those given above should be applicable as well to colloidal suspensions of quadrupolar polarizable particles in a less-polarizable nonconducting fluid.

Obviously the above description is rather simplistic and does not include any unwelcome effects, namely:

i) Charge screening. To neglect this effect we assumed that the isotropic liquid is ideally nonconducting.

ii) Depletion [14], [13]. It leads only to a short-range attraction between spheres with a characteristic scale of the order of l .

iii) Coarsening and coalescence. Neglecting these processes is a good approximation at a sufficiently small droplet concentration.

iv) Flexoelectric polarization. Flexoelectricity in nematic liquid crystals is a phenomenon that has been studied in many publications for over a decade (see, e.g., [2], [8]). It is known [2] that deformations of the director field in nematics can create a polarization

$$\mathbf{P}_f = e_1(\mathbf{n}\text{div}\mathbf{n}) + e_3(\text{rot}\mathbf{n}) \times \mathbf{n},$$

which involves two coefficients with dimensions of electric potential. In the case of molecules which are very asymmetric in shape and carry a strong electric dipole moment μ_d the flexoelectric coefficients might reach values of order μ_d/l^2 . In all other cases (and in particular in the case under consideration, when the molecules do not have a permanent dipole moment) they will be smaller. Rough estimates of these coefficients based on calculations of the fraction of the molecules which achieve the necessary ordering of their dipoles to ensure the maximum packing density give [8]

$$e \propto N^{1/3}/T,$$

where N is the number of molecules per unit volume. Thus the corresponding electric field (proportional to $N^{1/3}$) will be small in comparison to the quadrupolar field, which is proportional to N . Note also the following difference between the two kinds of polarizations. The quadrupolar polarization (at least in principle) can be nonzero even for $\mathbf{n} = \text{const}$, while the flexoelectric polarization is proportional to gradients of \mathbf{n} .

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1. P.Drzaic, *Liquid Crystal Dispersions*, World Scientific, Singapore (1995).
 2. P.G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford (1974).
 3. A.I.Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York (1973).
 4. D.Myers, *Surfaces, Interfaces, and Colloids*, VCH Publishers, New York (1991).
 5. J.N.Israelashvili, *Intermolecular and Surface Forces*, Academic Press, Orlando (1985).
 6. G.E.Volovik and O.D.Lavrentovich, *JETP* **58**, 1159 (1983).
 7. L.D.Landau and E.M.Lifshitz, *The Classical Theory of Fields*, Pergamon Press, New York (1974).
 8. S.Chandrasekhar, *Liquid Crystals*, Cambridge Univ. Press, New York (1977).
 9. E.Dubois-Violette and O.Parodi, *J. Phys. (Paris)* **30**, Colloque C4-57 (1969).
 10. I.E.Dzyaloshinskii, E.M.Lifshitz, and L.P.Pitaevskii, *Adv. Phys.* **10**, 165 (1961).
 11. I.E.Dzyaloshinskii, S.G.Dmitriev, and E.I.Kats, *JETP* **41**, 1167 (1976).
 12. W.B.Russel, D.A.Saville, and W.R.Schowalter, *Colloidal Dispersion*, Cambridge University Press, Cambridge (1989).
 13. P.Poulin, V.Cabuil, and D.A.Weitz, *Phys. Rev. Lett.* **79**, 4862 (1997).
 14. Y.Mao, M.E.Cates, and H.N.W. Lekkerkerker, *Phys. Rev. Lett.* **75**, 4548 (1995).

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