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Interaction of foreign macroparticles in a cholesteric liquid crystal

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We calculate the interaction energy between spherical macroparticles immersed in a cholesteric liquid crystal due to the elastic deformation of the director field. We assume weak anchoring on the surface of the macroparticles and obtain the expression of the interaction energy that is valid for particle radius and interparticle distance sufficiently smaller than the cholesteric pitch. The resultant form of the interaction energy is more complex than that in a nematic liquid crystal. One of the characteristics is its dependence on the particle position as well as the interparticle distance, which arises from the intrinsic structure of a cholesteric liquid crystal, i.e., the absence of translational symmetry due to helical periodicity and local nematic ordering whose orientation depends on the position.

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Colloidal suspensions [1,2] of solid or liquid particles dispersed in liquid-crystal hosts constitute a new class of composite materials with unique physical properties [3–7], and the physics therein has attracted boom of interest in recent years. Depending on the relative magnitude of the particle size and the anchoring extrapolation length at the surface of the particle, there appear a variety of superstructures such as linear chains [4,8–10], anisotropic clusters [3,11–13], and periodic lattices [14–16] of suspended particles. In addition to the ordinary colloidal forces, particles immersed in liquid crystals can interact with each other through the orientational Frank elasticity [4,14,17–20]. The elastic interaction consists in the fact that the particle distorts the adjacent director field whose effects extend far and exert a long-range orientational stress on surrounding particles. Since the form of superstructures made by colloidal particles in a liquid crystal is crucially influenced by this elasticity-mediated interaction, the understanding of such an interaction is quite important to predict and control the properties and behaviors of liquid crystal colloids.

In previous papers [14,17–21], the interaction energy between macroparticles has been considered in the nematic liquid-crystal host and one of the present authors (B.I.L.) has developed a theoretical scheme [14] that can be applied to general cases of macroparticles with arbitrary shape and anchoring orientation on the surface as long as the anchoring strength is weak. Since a nematic phase possesses the highest symmetry of all the liquid-crystal phases and the Frank elasticity of a nematic liquid crystal does not have its own characteristic length scale, the resulting interparticle interaction depends only on the particle size and the anchoring extrapolation length if it is finite.

As a host liquid crystal, one can choose other types of liquid crystals with lower symmetries such as smectics or cholesterics. The wide variety of liquid-crystal phases will be of great use and importance because we can seek a wider possibility of creating different superstructures of colloidal suspension. Moreover, it is interesting also from a fundamental point of view to know how the interaction between macroparticles is influenced by the presence of an intrinsic structure of liquid crystals. The purpose of the present paper is, therefore, to extend our previous formulation [14] to other liquid-crystal phases with a lower symmetry, thereby with inherent characteristic length scales. There have already been several theoretical attempts to study the interaction between macroparticles in smectic liquid crystals due to the smectic layer displacement induced by the macroparticles [22–24]. To our knowledge, however, no theoretical studies have been focused on cholesteric liquid crystals as a host fluid, with which we will concern ourselves in this paper. In the case of cholesteric liquid crystals, the twist pitch serves as an additional characteristic length and it is, therefore, of an interest to examine how the existence of this new length scale together with a helical structure would qualitatively as well as quantitatively modify the interparticle interaction law found for the nematic suspensions.

We begin with writing the free energy due to the elastic deformation of the director field $\boldsymbol{n}$. The bulk elastic energy of a cholesteric liquid crystal can be described as [25]

$$F_b=\frac{1}{2}\int d\boldsymbol{r}\{K_1(\boldsymbol{\nabla}\cdot\boldsymbol{n})^2+K_2(\boldsymbol{n}\cdot\boldsymbol{\nabla}\times\boldsymbol{n}+q_0)^2 \\ +K_3(\boldsymbol{n}\times\boldsymbol{\nabla}\times\boldsymbol{n})^2\}, \tag{1}$$

where K_1, K_2, and K_3 are the elastic constants associated with splay, twist, and bend deformations, respectively, and q_0 is the wave number characterizing the cholesteric pitch.

The interaction energy between a macroparticle and a cholesteric liquid crystal can be obtained from the known director distribution on the macroparticle surface and given by

$$F_s=\sum_p \oint_{\Omega_p} d^2SW(\boldsymbol{s})[\boldsymbol{\nu}(\boldsymbol{s})\cdot\boldsymbol{n}(\boldsymbol{s})]^2. \tag{2}$$

Here p is the index labeling the particles and the surface of the macroparticle p is denoted by Ω_p. The integral is taken

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over Ω_p and d^2S is the surface element. The anchoring strength is given by $W(\boldsymbol{s})$ and $\boldsymbol{\nu}(\boldsymbol{s})$ is the unit normal to the surface at the point $\boldsymbol{s}$. In the case of homeotropic anchoring, $W(\boldsymbol{s})<0$ and vice versa for planar anchoring. We restrict ourselves to the case of the weak anchoring ($|W|r_0/K_i \ll 1$, where r_0 is the characteristic dimension of the macroparticles) so that the director field is only slightly deformed by the particles from its ground state,

$$\boldsymbol{n}_0(\boldsymbol{r})=(\cos q_0 z, \sin q_0 z, 0), \tag{3}$$

where we take the pitch axis along the z axis. The director field in a general case can be written as

$$\boldsymbol{n}(\boldsymbol{r})=\{\cos[q_0 z+u(\boldsymbol{r})]\cos v(\boldsymbol{r}), \sin[q_0 z+u(\boldsymbol{r})]\cos v(\boldsymbol{r}), \sin v(\boldsymbol{r})\}, \tag{4}$$

where we have introduced the deformation field $u(\boldsymbol{r})$ and $v(\boldsymbol{r})$ characterizing the deviation from the ground state.

Here we assume that the director field $\boldsymbol{n}(\boldsymbol{r})$ is defined throughout the system, even within macroparticles, and continuous. Such an assumption is justified in the case of weak anchoring and resultant small deformation of the director field. Then we can employ the Fourier representation for the distortion field, which is defined as $u_{\boldsymbol{q}}=\int d\boldsymbol{r} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} u(\boldsymbol{r})$ and $v_{\boldsymbol{q}}=\int d\boldsymbol{r} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} v(\boldsymbol{r})$.

We first substitute Eq. (4) into the bulk energy (1). In the case of small u and v, we have to retain only up to the second order terms in u and v, which can be written as

$$F_b=\frac{1}{2}K\int_{\boldsymbol{q}}\{q^2 u_{\boldsymbol{q}} u_{-\boldsymbol{q}}+(q^2+q_0^2)v_{\boldsymbol{q}} v_{-\boldsymbol{q}}+q_0 u_{\boldsymbol{q}}[(iq_x+q_y) \times v_{-\boldsymbol{q}-q_0\hat{\boldsymbol{z}}}+(iq_x-q_y)v_{-\boldsymbol{q}+q_0\hat{\boldsymbol{z}}}]\}, \tag{5}$$

where $\int_{\boldsymbol{q}}\equiv(2\pi)^{-3}\int d\boldsymbol{q}$ and we have employed the one constant approximation $K_i=K$. $\hat{\boldsymbol{z}}$ denotes the unit vector along the z direction.

In dealing with the surface energy, we make a gradient expansion of the director field $\boldsymbol{n}(\boldsymbol{s})$ around the center of gravity of the macroparticle p, which we will denote by $\boldsymbol{r}_p$. We also restrict ourselves to the case of spherical particles with equal radius R_0 and constant anchoring energy W, although our approach can be easily extended to particles with an arbitrary shape [14]. Then the resultant form of the surface energy is

$$\begin{aligned}F_s=\frac{1}{2}\gamma\sum_p\int_{\boldsymbol{q}}[&\{-i(q_x-iq_y)^2\exp[i(\boldsymbol{q}+2q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]\\&+i(q_x+iq_y)^2\exp[i(\boldsymbol{q}-2q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]\}u_{\boldsymbol{q}}+2\{-(q_0+q_z)\\&\times(q_x-iq_y)\exp[i(\boldsymbol{q}+q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]+(q_0-q_z)(q_x+iq_y)\\&\times\exp[i(\boldsymbol{q}-q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]\}v_{\boldsymbol{q}}],\end{aligned} \tag{6}$$

where we have retained only linear order terms in u and v as in our previous study [14]. The only parameter characterizing the spherical particle is $\gamma\equiv(4/15)\pi R_0^4 W$. We note that as in the previous study [14] we have retained only up to second order terms in the gradients and higher order terms will result in the corrections of the order of $(q_0R_0)^{2n}$ with n being a positive integer. Therefore the treatment above is justified for particles whose radius is sufficiently smaller than the cholesteric pitch.

The distortion profile that minimizes the elastic energy in the presence of macroparticles can be determined through the conditions,

$$\frac{\delta(F_b+F_s)}{\delta u_{\boldsymbol{q}}}=\frac{\delta(F_b+F_s)}{\delta v_{\boldsymbol{q}}}=0. \tag{7}$$

However, in contrast to the case of nematic liquid crystals [14], the presence of the off-diagonal coupling in the bulk energy, the last two terms in Eq. (5), makes the calculation quite difficult. Therefore we naively assume here that these off-diagonal terms can be neglected and will discuss below in what condition this assumption can be justified. Under this assumption, the calculation is greatly simplified and Eq. (7) yields

$$\begin{aligned}u_{\boldsymbol{q}}=\frac{\gamma}{2Kq^2}\sum_p&\{-i(q_x-iq_y)^2\exp[i(\boldsymbol{q}+2q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]\\&+i(q_x+iq_y)^2\exp[i(\boldsymbol{q}-2q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]\},\end{aligned} \tag{8}$$

$$\begin{aligned}v_{\boldsymbol{q}}=\frac{\gamma}{K(q^2+q_0^2)}\sum_p&\{-(q_0+q_z)(q_x-iq_y)\\&\times\exp[i(\boldsymbol{q}+q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]+(q_0-q_z)(q_x+iq_y)\\&\times\exp[i(\boldsymbol{q}-q_0\hat{\boldsymbol{z}})\cdot\boldsymbol{r}_p]\}.\end{aligned} \tag{9}$$

After substituting Eqs. (8) and (9) into the total free energy $F=F_b+F_s$, we can obtain the interaction energy between macroparticles due to the elastic deformation of the director field as $F=\Sigma_{p<p'}U_{pp'}$ with the pairwise interaction $U_{pp'}$ being

$$\begin{aligned}U_{pp'}=\frac{\gamma^2}{8\pi K}\Bigg[&\Bigg\{-\cos(2q_0z)\nabla_\perp^4+\operatorname{Re}\exp(4iq_0R_z)\left(i\frac{\partial}{\partial x}\right.\\&\left.+\frac{\partial}{\partial y}\right)^4\Bigg\}\frac{1}{r_{pp'}}+4\operatorname{Re}\Bigg\{\exp(iq_0z)\nabla_\perp^2\left(q_0-i\frac{\partial}{\partial z}\right)^2\\&+\exp(2iq_0R_z)\left(i\frac{\partial}{\partial x}+\frac{\partial}{\partial y}\right)^2\left(q_0^2+\frac{\partial^2}{\partial z^2}\right)\Bigg\}\frac{e^{-|q_0|r_{pp'}}}{r_{pp'}}\Bigg].\end{aligned} \tag{10}$$

Here $\boldsymbol{r}_{pp'} = (x,y,z) \equiv \boldsymbol{r}_p - \boldsymbol{r}_{p'}$ denotes the distance between two particles and $r_{pp'} = |\boldsymbol{r}_{pp'}|$. $R_z \equiv (1/2)(\boldsymbol{r}_p + \boldsymbol{r}_{p'}) \cdot \hat{\boldsymbol{z}}$ and Re implies taking the real part of a complex expression. We have also employed the abbreviations $\nabla_\perp^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$ and $\nabla_\perp^4 = (\nabla_\perp^2)^2$.

Several remarks are in order. First of all, when deriving Eq. (10), we have neglected the off-diagonal coupling terms in the bulk elastic energy as mentioned before. For vanishingly small q_0, these off-diagonal terms give a contribution to the distortion energy of the order $\gamma^2 q_0/K r_{pp'}{}^4$, while $U_{pp'} \sim \gamma^2/K r_{pp'}{}^5$ from Eq. (10). Therefore the off-diagonal terms can be safely neglected and the resultant formula for the interaction energy (10) holds when $q_0 r_{pp'} \ll 1$, that is, the interparticle distance is sufficiently smaller than the cholesteric pitch.

One might argue that the self-energy, the distortion energy due to one particle, must be properly taken into account because of the absence of translational symmetry due to the cholesteric structure and the resultant possibility of the dependence of self-energy on particle position. We can show, however, that in the case of spherical particle the self energy is independent of the particle position and that such a treatment is not necessary. It can be simply explained by a symmetry argument as follows: the distortion field $\boldsymbol{n}(\boldsymbol{r})$ with one particle located at $\boldsymbol{r}_p$ can be exactly mapped onto the distortion field $\boldsymbol{n}'(\boldsymbol{r})$ with the particle at another point $\boldsymbol{r}_p'$ by a rotation of the laboratory frame by an appropriate angle after a translation by $\boldsymbol{r}_p' - \boldsymbol{r}_p$. Such an argument, however, does not apply when particles have a lower symmetry or when two or more particles are present and not aligned in the direction of the cholesteric pitch (z direction). The inapplicability of the symmetry argument above reveals itself in the dependence of $U_{pp'}$ on $R_z = (1/2)(\boldsymbol{r}_p + \boldsymbol{r}_{p'}) \cdot \hat{\boldsymbol{z}}$, a detailed discussion on which will be given below.

Since the resultant form of the interaction energy (10) is somewhat complicated, we restrict the discussions below to the simple cases where two particles lie perpendicular to or along the cholesteric pitch axis (or z axis). In the former case ($\boldsymbol{r}_{pp'} \perp \hat{\boldsymbol{z}}$), the interaction energy is given by

$$U_{pp'} = \frac{3\gamma^2}{8\pi K r_\perp^5}\{9 + 20\cos 2(q_0 R_z - \phi) + 35\cos 4(q_0 R_z - \phi) + O(|q_0 r_\perp|)\}, \tag{11}$$

where $R_z = (1/2)(\boldsymbol{r}_p + \boldsymbol{r}_{p'}) \cdot \hat{\boldsymbol{z}}$ as defined before, and $r_\perp \equiv \sqrt{x^2 + y^2}$. Since $\boldsymbol{r}_{pp'}$ is perpendicular to the z axis, R_z is equal to the z coordinate of the two particles and $r_\perp = |\boldsymbol{r}_{pp'}|$. The azimuthal angle ϕ is defined as $\phi = \tan^{-1}(y/x)$.

One of the most characteristic properties of the interaction energy (11) is that it depends not only on the relative distance $\boldsymbol{r}_{pp'}$ but also on the position R_z of the two particles. This reflects the breakdown of the translational symmetry in the presence of two particles due to the cholesteric helical structures as noted above. Notice also that $q_0 R_z - \phi$ represents the angle between $\boldsymbol{r}_{pp'}$ and the local orientation of liquid crystals [see Eq. (3)]. Therefore the interaction energy depends on how two particles are placed with respect to the local orientation of cholesteric liquid crystals. In Fig. 1 we plot the interaction energy (11) with $R_z = 0$ (the local nematic orientation is along the x axis). It is clear from Fig. 1 that the interaction is repulsive when two particles lie along or perpendicular to the local nematic orientation and attractive in the oblique direction. The repulsive interaction is stronger parallel than perpendicular to the local nematic orientation. As expected, the interaction closely resembles a quadrupole one in nematics in the case of weak anchoring and it can be easily shown that we recover the interaction energy in a nematic liquid crystal [14] by taking the limit of $q_0 \to 0$.

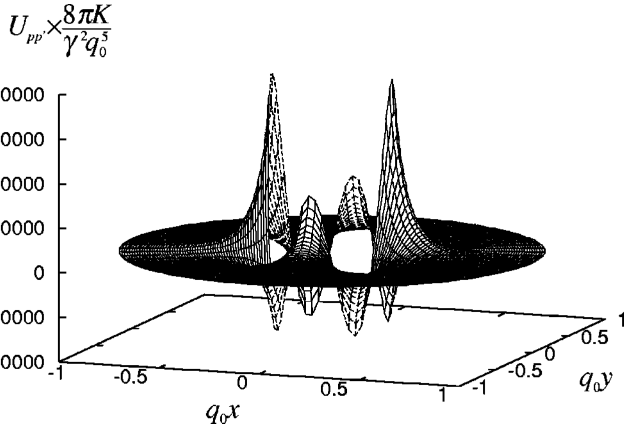

FIG. 1. The pairwise interaction energy $U_{pp'}$ in the case of $\boldsymbol{r}_{pp'}$ perpendicular to the z axis and $R_z = 0$. We show only the region with $q_0 r_\perp > 0.3$ because $U_{pp'}$ diverges at $r_\perp = 0$.

When two particles lie along the cholesteric pitch axis ($\boldsymbol{r}_{pp'} \| \hat{\boldsymbol{z}}$), we obtain, from a straightforward manipulation of Eq. (10),

$$U_{pp'} = \frac{\gamma^2}{8\pi K z^5}[-24\cos 2q_0 z + 16 e^{-|q_0| z}(3 + 3|q_0|z + q_0^2 z^2) \times (2\cos q_0 z + q_0 z \sin q_0 z)] \tag{12}$$

for $z = \boldsymbol{r}_{pp'} \cdot \hat{\boldsymbol{z}} > 0$. Equation (12) is plotted as a function of z in Fig. 2. For $q_0 z \ll 1$, the interaction is repulsive, and the

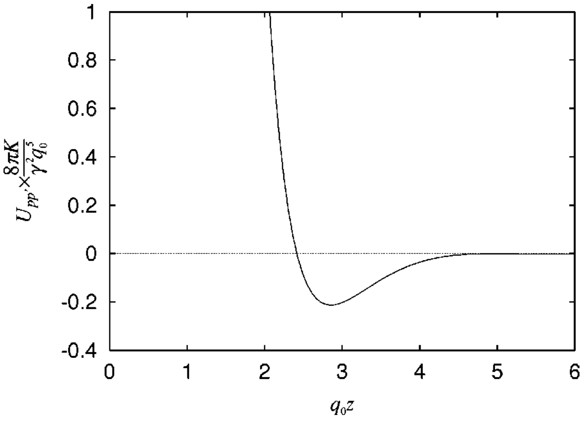

FIG. 2. The pairwise interaction energy $U_{pp'}$ as a function of $z = \boldsymbol{r}_{pp'} \cdot \hat{\boldsymbol{z}}$ when $\boldsymbol{r}_{pp'}$ is parallel to the z axis. $U_{pp'}$ goes to infinity with $z \to 0$.

energy is proportional to z^{-5}. From Fig. 1 we also find that Eq. (12) has its minimum at $q_0 z \simeq 2.85$. Of course we cannot conclude that the interaction energy has its minimum there because the validity of Eq. (12) is guaranteed only for $q_0 z \ll 1$. However, this result, together with the oscillating nature of Eq. (12), might be considered to reflect directly the periodic helical structure of cholesteric liquid crystals. Further quantitative analysis that can be applied to $q_0 z > 1$ will be necessary to determine whether this potential minimum really exists and to elucidate how the interaction will be influenced by the presence of periodic structures. We note that although there have been several theoretical studies to evaluate the interaction energy between inclusions immersed in periodic media like smectics [22–24], their starting point is a more coarse-grained free energy in terms of the layer displacement and the resultant formula of the interaction energy does not reflect the layer structure of the media (for example, it does not depend on the layer spacings).

In conclusion, we have evaluated the interaction energy between two spherical macroparticles immersed in a cholesteric liquid crystal by extending our approach formerly applied to the case of nematic liquid crystals. In the case of weak surface anchoring and small interparticle distance compared to the cholesteric pitch, we have obtained an analytic form of the interaction energy in terms of the position of two particles. The interaction energy has more complex form than those for nematics or smectics in previous theoretical studies and reflects the absence of translational symmetry related to the helical periodicity and local nematic ordering in cholesteric liquid crystals. We, therefore, believe that cholesteric liquid crystals will provide an interesting example as a host fluid of colloidal systems and we encourage experiments to reveal how the force between particles in cholesteric liquid crystals is influenced by the cholesteric structures. Possible future direction of the present study is to extend our calculations to the case of particles with lower symmetries or to incorporate the off-diagonal coupling of the twist and the umbrella modes properly to argue the interaction energy for large interparticle distance.

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