

Paranematic interaction between nanoparticles of ordinary shape

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(Received 5 January 2005; revised manuscript received 5 April 2005; published 16 June 2005)

We propose a general approach to the description of the long-ranged interaction between nanoparticles (1–10 nm) of ordinary shape in the paranematic phase, i.e., nematic liquid crystal in the isotropic phase. In general case interaction potential is attractive of Yukawa form with derivatives. But it can be anisotropic despite the isotropy of the paranematic phase. The origin of such anisotropy is the shape of nanoparticles. Particular potentials for spherical and cylindrical particles are considered. For the case of nanocylinders anisotropic part of the interaction potential can lead to the orientational ordering of them in the isotropic phase of nematic liquid crystals.

DOI: 10.1103/PhysRevE.71.062701

PACS number(s): 77.84.Nh

I. INTRODUCTION

Colloidal media formed by particles suspended in liquids are a widely abundant important state of matter and have attracted much interest in science, technology and medicine [1,2]. Dispersed liquid crystals with macroscopic inclusions of a foreign substance are particular of such systems. Ordered structures of colloidal particles can give rise to bulk phenomena that are very different from those displayed by disordered structure. Order as it is known also greatly affects the electro-optical and rheology properties of colloidal dispersion. Including particles form various structures which are observed in liquid crystal mesophase [5–10]. In recent years a great deal of interest has developed to understand the interaction and phase behavior of colloidal particles dispersed in the nematic phase or in the isotropic phase of a nematogenic compound [13–20]. The paranematic phase is the isotropic phase of the nematic liquid crystals. The introduced particles in such liquid can result to orientational ordering at the expense of the formation of the solvent area. The existence of such deformed areas will result in effective interaction, when these areas are overlapped [13,14,17,18]. Such interaction is known on short distances. In the nematic phase orientational ordering exists on the long distance. The deformation of the elastic field results in the long-ranged interaction between particles which are included in the nematic liquid crystal [3,4,8,11]. In the nematic phase colloids experience a specific interaction because they induce competing distortions of the nematic director field. In the isotropic phase the surface of colloidal particles induces a local nematic order, giving rise to the short-ranged interaction [12–18]. The same sort of induction of the parameter at the surface of the separate introduced particle can occur and is usual in liquids. For spherical particles energy of interaction through change of order parameter in the paranematic phase was counted in Refs. [13,14]. Analytical results of this problem were given in the works of Refs. [17] and [18]. In the majority of interesting cases the introduced particles do not have the spherical form and thus it is interesting to receive dependence of energy of interaction on the form, orientation, and parameters of ordering in such media.

We propose a general approach to the description of the long-ranged interaction between nanoparticles (with size about 1–10 nm) of ordinary shape in paranematic phase based on the self-consistent approach. The type of the far-field interaction among particles is determined by the distance and orientation and is strongly dependent on the temperature. In the paranematic phase we obtain the attractive interaction which can be the answer for the segregation of them with the formation of soft solid with high concentration. We offer an advanced earlier approach [3] to apply it for the paranematic phase. For the case of high concentration of particles we find that their collective influence is reduced to the change of the screening length. The offered approach allows us to receive energy of interaction in the paranematic phase depending on the form and boundary conditions on the surface of a separate particle. It is shown that the interaction carries anisotropic character. Interaction can give rise to an orientational ordering in the system of the introduced particles, which are brought in the paranematic phase.

II. ENERGY OF THE SYSTEM: PARANEMATIC PHASE PLUS NANOPARTICLES

For the weak induced nematic order in the isotropic phase, the quadratic Landau–de Gennes expansion of the bulk free-energy density has the form

$$F_b = \frac{1}{2} \int dV a Q_{ij}(\mathbf{R}) Q_{ij}(\mathbf{R}) + L Q_{ij,k}(\mathbf{R}) Q_{ij,k}(\mathbf{R}), \quad (1)$$

where the comma indicates derivation and summation over repeated indices is implied. Here $a > 0$ and $L > 0$ quantify the cost of creating a distortion of the nematic phase. For simplicity, we take a one-constant approximation. At the quadratic order, the corresponding surface free-energy density is

$$F_s = \frac{1}{2} \sum_p \oint dS W [Q_{ij}(\mathbf{r}_s) - Q_{ij}^0] [Q_{ij}(\mathbf{r}_s) - Q_{ij}^0], \quad (2)$$

where W measures the anchoring strength. Here Q_{ij} is the tensorial order parameter which is biaxial in the general case.

Our approach is applicable both for uniaxial and biaxial liquid crystal as we remain within the one-constant approximation.

When we have N particles which is introduced in the paranematic phase the free energy for all system can be rewritten in the following form:

$$F = F_b + F_s. \quad (3)$$

We do not consider here the distribution entropy part of the free energy, because it does not have influence on the director distribution and does not have influence on the finding of the elastic interaction potential between the particles.

We can use the Fourier representation for the order parameter in the entire space, thereby considerably simplifying the problem. In the Fourier representation we have

$$Q_{ij}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3q \exp(-i\mathbf{q} \cdot \mathbf{r}) Q_{ij}(\mathbf{q}). \quad (4)$$

We substitute (4) in the bulk energy (1) to obtain

$$F_b = \frac{1}{2} \frac{1}{(2\pi)^3} \int d^3q (a + Lq^2) Q_{ij}(\mathbf{q}) Q_{ij}^*(\mathbf{q}). \quad (5)$$

Because we assume that the order parameter varies smoothly from point to point we can consider the director to have a given value inside the volume of the particle. This assumption is valid if the total volume of the suspended particles is much less than the entire volume of the system, i.e., the volume fraction of particles is small, $cv \ll 1$, where $c = N/V$ is the concentration, v is the volume of the particle (the ‘‘gas’’ approximation). As well we fix the local basis $(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$ associated with each particle. In this basis a scalar product of two arbitrary vectors can be written in the form $(\mathbf{a} \cdot \mathbf{b}) = (\mathbf{a} \cdot \mathbf{k}_s)(\mathbf{b} \cdot \mathbf{k}_s)$. The order parameter on the surface of the particle can therefore be expressed through the order parameter in the center of mass \mathbf{r}_p of the particle and its derivatives

$$Q_{ij}(\mathbf{r}_s) = Q_{ij}(\mathbf{r}_p) + (\rho \cdot \nabla) Q_{ij}(\mathbf{r}_p) + \frac{1}{2} (\rho \cdot \nabla)^2 Q_{ij}(\mathbf{r}_p), \quad (6)$$

where ρ is the vector drawn from the center of mass to the point \mathbf{s} on the surface. Surface energy density takes the form

$$f_s = \frac{1}{2} W Q_{ij}^0 Q_{ij}^0 - W Q_{ij}(\mathbf{r}_s) Q_{ij}^0 + \frac{1}{2} W Q_{ij}(\mathbf{r}_s) Q_{ij}(\mathbf{r}_s) \quad (7)$$

and the total surface energy $F_s = \sum_p \oint ds f_s^p$

It can be rewritten as

$$F_s = F_s^{(0)} + F_s^{lin} + F_s^{quad}, \quad (8)$$

$$F_s^{(0)} = (1/2) N W \sigma Q_{ij}^0 Q_{ij}^0, \quad (9)$$

$$F_s^{lin} = \sum_p -W \sigma Q_{ij}^0 Q_{ij}(\mathbf{r}_p) - Q_{ij}^0 \pi_s(\mathbf{k}_s \cdot \nabla) Q_{ij}(\mathbf{r}_p) - Q_{ij}^0 \chi_{st}(\mathbf{k}_s \cdot \nabla)(\mathbf{k}_t \cdot \nabla) Q_{ij}(\mathbf{r}_p), \quad (10)$$

where we have introduced such vector and tensor

$$\pi_l = \oint ds W \rho_l(\mathbf{s}),$$

$$\chi_{lm} = \oint ds W \rho_l(\mathbf{s}) \rho_m(\mathbf{s}), \quad (11)$$

where $\rho_l = (\rho \mathbf{k}_l)$, σ is an area of the surface of the particle. In the Fourier representation, we have

$$F_s^{lin} = \sum_p \frac{1}{2(2\pi)^3} \int d^3q [Q_{ij}(\mathbf{q}) A_{ij}^*(\mathbf{q}) + Q_{ij}^*(\mathbf{q}) A_{ij}(\mathbf{q})], \quad (12)$$

where

$$A_{ij}(\mathbf{q}) = -Q_{ij}^0 \sum_p [\sigma W / + i\pi_s(\mathbf{q} \cdot \mathbf{k}_s) - \chi_{st}(\mathbf{q} \cdot \mathbf{k}_s)(\mathbf{q} \cdot \mathbf{k}_t)] e^{i\mathbf{q} \cdot \mathbf{r}_p}.$$

Now we make similar operations with the quadratic term $\frac{1}{2} W Q_{ij}(\mathbf{r}_s) Q_{ij}(\mathbf{r}_s)$. But in this term we go to the continuum limit and replace the summation with the integration over the entire space, $\sum_p \Rightarrow c \int dV$, where $c = N/V$ is the concentration of particles, thus considering the interference of only long wave length distortions of the order parameter. This approximation leads to the very simple expression for F_s^{quad} in the Fourier representation

$$F_s^{quad} = \frac{c\sigma W}{2(2\pi)^3} \int d^3q Q_{ij}(\mathbf{q}) Q_{ij}^*(\mathbf{q}). \quad (13)$$

Then the total energy of the system takes the form (neglecting constant $F_s^{(0)}$)

$$F_{total} = F_b + F_s^{lin} + F_s^{quad}, \quad (14)$$

$$F_{total} = \sum_p \frac{1}{2(2\pi)^3} \int d^3q [a + cW\sigma + Lq^2] Q_{ij}(\mathbf{q}) Q_{ij}^*(\mathbf{q}) + Q_{ij}(\mathbf{q}) A_{ij}^*(\mathbf{q}) + Q_{ij}^*(\mathbf{q}) A_{ij}(\mathbf{q}). \quad (15)$$

A. Order parameter distribution in the doped paranematic liquid crystal

Having found the complete expression for the energy of the paranematic phase with particles, we can find the order parameter at any point of the system from the extremum condition

$$\frac{\delta}{\delta Q_{ij}^*(\mathbf{q})} F_{total} = [a + cW\sigma + Lq^2] Q_{ij}(\mathbf{q}) + A_{ij}(\mathbf{q}) = 0,$$

$$Q_{ij}(\mathbf{q}) = -\frac{A_{ij}(\mathbf{q})}{a + cW\sigma + Lq^2}. \quad (16)$$

This is solution in the Fourier representation—distribution of the order parameter.

B. The pair interaction potential between nanoparticles

Having found the order parameter field, we substitute (16) in (15) and obtain the energy of the system

$$F_{total} = -\frac{1}{2(2\pi)^3} \int d^3q \frac{A_{ij}(\mathbf{q})A_{ij}^*(\mathbf{q})}{a + cW\sigma + Lq^2} < 0. \quad (17)$$

The negative sign implies that the total free energy $E = F_s^{(0)} + F_{total}$ evaluated for solution (16) is less than the energy $E = F_s^{(0)}$ for the nondeformed order parameter field Q_{ij}^0 .

Let us introduce the operators

$$\hat{A} = \sigma W + \pi_s \partial_s + \chi_{st} \partial_s \partial_t, \quad (18)$$

where $\partial_s = (\nabla \mathbf{k}_s)$. Then the product $A_{ij}(\mathbf{q})A_{ij}^*(\mathbf{q})$ takes the simple form

$$A_{ij}(\mathbf{q})A_{ij}^*(\mathbf{q}) = Q_{ij}^0 Q_{ij}^0 \hat{A}_p \hat{A}_{p'} \sum_{pp'} e^{i\mathbf{q}(\mathbf{r}_p - \mathbf{r}_{p'})}. \quad (19)$$

The total energy F_{total} can be represented as the sum of the pair potentials between the two particles. The total energy F_{total} then takes the form

$$F_{total} = \frac{1}{2} \sum_{p,p'} U_{pp'}. \quad (20)$$

The subscript p indicates that we must substitute $\partial = \partial / \partial \mathbf{r}_p$ in the operator \hat{A}_p :

$$U_{pp'} = -\frac{Q_{ij}^0 Q_{ij}^0}{2(2\pi)^3} \hat{A}_p \hat{A}_{p'} \int d^3q \frac{e^{i\mathbf{q}(\mathbf{r}_p - \mathbf{r}_{p'})}}{a + cW\sigma + Lq^2}. \quad (21)$$

The expression $U_{pp'}$ has the meaning of the pair interaction potential between particles p and p' that is caused by long-range deformations of the order parameter field. This expression is valid for the particles of the ordinary shape and orientation. Having found the integral

$$\int d^3\mathbf{q} \frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{\lambda^2 + q^2} = \frac{2\pi^2 e^{-\lambda R}}{R}$$

we come to the following expression for interaction potential:

$$U_{pp'} = -\frac{Q_{ij}^0 Q_{ij}^0}{2\pi L} \hat{A}_p \hat{A}_{p'} \left(\frac{e^{-\lambda R}}{R} \right), \quad (22)$$

where $\mathbf{R} = \mathbf{r}_p - \mathbf{r}_{p'}$, $\lambda = \sqrt{(a + cW\sigma)/L}$.

Formula (22) represents the exact expression of the paranematic interaction between two ordinary nanoparticles embedded into the nematic liquid crystal in the isotropic phase [strictly speaking, for the case when $1/\lambda \gg r_0$, r_0 —the average size of the particle, so that series expansion (6) can be true].

We can simplify this formula for the case of symmetrical particles with three symmetry planes. In this case $\pi_s = 0$. Keeping only second derivatives on R we come to such expression of the interaction potential

$$U_{pp'} = -\frac{Q_{ij}^0 Q_{ij}^0}{2\pi L} \left[(\sigma W)^2 f(R) + \sigma W (\chi_{ss}^p + \chi_{ss}^{p'}) \frac{f'}{R} + \sigma W e_s e_t (\chi_{st}^p + \chi_{st}^{p'}) \left(f'' - \frac{f'}{R} \right) \right], \quad (23)$$

where $f(R) = e^{-\lambda R}/R$ and vector $\mathbf{e} = \mathbf{R}/R$ is the unit vector that is parallel to the radius vector \mathbf{R} between particles. As well the summation over repeating indices is made.

Thus we see, that paranematic interaction in a general case has isotropic and anisotropic parts of interaction

$$U_{pp'}(\mathbf{R}) = U_{isotropic}(R) + U_{anisotropic}(\mathbf{R}), \quad (24)$$

$$U_{isotropic}(R) = -\frac{Q_{ij}^0 Q_{ij}^0}{2\pi L} \left[(\sigma W)^2 f(R) + \sigma W (\chi_{ss}^p + \chi_{ss}^{p'}) \frac{f'}{R} \right], \quad (25)$$

$$U_{anisotropic}(\mathbf{R}) = -\frac{Q_{ij}^0 Q_{ij}^0}{2\pi L} \left[\sigma W e_s e_t (\chi_{st}^p + \chi_{st}^{p'}) \left(f'' - \frac{f'}{R} \right) \right]. \quad (26)$$

The origin of the anisotropic interaction is an anisotropy of the shape of particles. We see that results (22)–(26) do not depend on the uniaxiality or biaxiality of the liquid crystal, and it influences only on the renormalization constant.

In the uniaxial approximation the order parameter in the bulk and on the surface can be present in the form

$$Q_{ij}(\mathbf{R}) = S(\mathbf{R}) \left\{ n_i n_j - \frac{1}{3} \delta_{ij} \right\}, \quad Q_{ij}^0 = S_0 \left(v_i v_j - \frac{1}{3} \delta_{ij} \right), \quad (27)$$

where \mathbf{n} is the director and \vec{v} is the normal to surface, $S(\mathbf{R})$ represents the order parameter in the point \mathbf{R} and S_0 is constant. Then $Q_{ij}^0 Q_{ij}^0 = 2S_0^2/3$.

Let us apply these results for several types of particles embedded into the uniaxial phase on the nematic liquid crystal. Our approximation is valid only for very small size r_0 of particles $r_0 < 1/\lambda$. Actually this means that our approximation works only for nanoscale $r_0 = 10^{-3} - 10^{-2} \mu\text{m}$. Then for small spherical particles tensor $\chi_{st} = (4\pi/3) W r_0^4 \delta_{st}$ is symmetrical and potential of interaction is symmetrical too

$$U_{sphere-sphere}(R) = -\frac{(S_0 \sigma W)^2}{6\pi L} \left[1 + \frac{8}{3} (r_0 \lambda)^2 \right] \frac{e^{-\lambda R}}{R}, \quad (28)$$

here $\sigma = \pi r_0^2$, which is the area of the particle. Energy scale of this paranematic interaction is $U \sim 10$ kT for $S_0 = 0.4$, $r_0 = 10$ nm, $W = 10^{-4}$ J/m², $L = 10^{-11}$ N/m, $R \sim 10$ nm, $1/\lambda \sim 10$ nm. This result is clearly a Yukawa type potential. It differs from the Stark result which [16] $U \sim (e^{-\lambda R}/R) [1 + 6(\lambda/R) + 12(\lambda/R)^2]^2$ which is valid for *micron-size* scale $r_0 \geq 1/\lambda$, $r_0 \geq 0.1 \mu\text{m}$.

Now we find the interaction potential between two long cylinders with a radius smaller than the length $r_0 \ll l$ and with orientation along unit vectors ω_1 and ω_2 . We neglect terms of the order $O(r_0^3)$. Then the interaction potential is found to be

$$U_{cylinder-cylinder}(\mathbf{R}) = U_{isot,cyl-cyl}(R) + U_{anisot,cyl-cyl}(\mathbf{R}), \quad (29)$$

$$U_{isot,cyl-cyl}(R) = -\frac{(S_0\sigma W)^2}{6\pi L} \left[f(R) + \frac{l^2 f'}{6R} \right], \quad (30)$$

$$U_{anisot,cyl-cyl}(\mathbf{R}) = -\frac{(S_0\sigma W l)^2}{9\pi L} \left[f''(R) - \frac{f'}{R} \right] [(\mathbf{e}\omega_1)^2 + (\mathbf{e}\omega_2)^2], \quad (31)$$

$\mathbf{e}=\mathbf{R}/R$, $\sigma=2\pi r_0 l$ —area of the cylinder.

Such angular dependence of the anisotropic interaction $U \sim (\mathbf{e}\omega_1)^2 + (\mathbf{e}\omega_2)^2$ is typical for the interaction between nematogenic molecules (see Refs. [21–23]). It can lead to the orientational ordering of cylinders on the nanoscale like it works to create a nematic phase of the long nematogenic molecules. So we conclude that this anisotropic interaction may be responsible for the orientational ordering of long nanoparticles in the isotropic phase of nematic liquid crystals, i.e., paranematic phase.

III. CONCLUSIONS

We have proposed a general approach to the description of the long-ranged interaction between nanoparticles of ordinary shape in the paranematic phase, i.e., nematic liquid crystal in the isotropic phase. In general, the case interaction potential is of the Yukawa type with derivatives and is attractive. General formulas are found which define potential through tensorial characteristics of its form. Within the framework of one constant approximation the results are valid both for biaxial and uniaxial nematic liquid crystal in the isotropic state. Resultant interparticle interaction potential can be anisotropic despite the isotropy of the paranematic phase. The origin of such anisotropy is the shape of the nanoparticles. For example the anisotropic part of the potential between nanocylinders can lead to the orientational ordering of them in the isotropic phase of liquid crystals. This effect of orientational ordering can be important for the creation of a phase in the isotropic substances. For instance it is possible to use two nematic or smectic, with different temperatures of transition, to create an anisotropic phase of one component clusters within the isotropic phase of another component.

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