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Dipole-dipole interactions and the origin of ferroelectric ordering in polar nematics

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ABSTRACT
A molecular origin of the ferroelectric ordering in the nematic phase is considered in detail considering a model based on electrostatic interaction between permanent molecular dipoles modulated by the anisotropic molecular shape. It is shown that a contribution to the total free energy of the long-range tail of the dipole-dipole interaction potential defines the total electrostatic energy of the system which depends on the sample shape and on the boundary conditions. This contribution may strongly affect the transition into the ferroelectric phase. However, the dipole-dipole interaction itself can hardly be responsible for the ferroelectric ordering in nematic liquid crystals for any reasonable values of the molecular dipole. A more promising model which combines dipole-dipole interaction and short-range orientational-translational correlations is also considered.

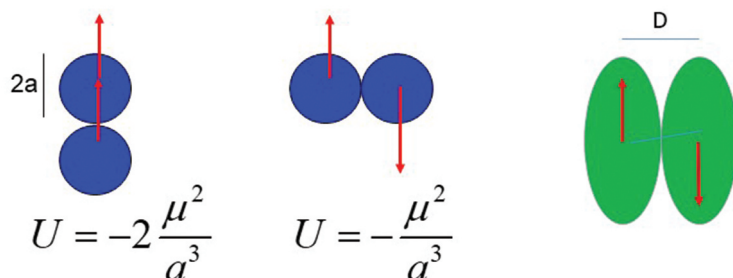Low energy configurations for dipolar spheres and ellipsoids.

$$U = -2\frac{\mu^2}{a^3} \qquad U = -\frac{\mu^2}{a^3}$$

1. Introduction

A possibility of proper ferroelectric ordering in nematic liquid crystals has been discussed for a long time assuming that in the case of sufficiently large molecular dipoles the dipole-dipole interaction may eventually result in the polar order. One notes, however, that the derivation of the contribution of the dipole-dipole interaction even to the simple mean-field free energy is not straightforward because the dipole-dipole interaction potential is strongly anisotropic and possesses the long range tail which results in the divergences of the corresponding integrals [2]. In particular, the dipole-dipole interaction potential vanishes after integration over all orientations of the unit intermolecular vector and the contribution of the dipole-dipole interaction to the total free energy depends on the shape of the sample [2].

These difficulties have been partially addressed in refs [3–5]. in the case of soft dipolar spheres the theory is only valid in the zero density approximation and thus it can hardly be applied to nematic liquid crystals. Moreover it has been shown by computer simulations [1,6–8] that at low densities strongly dipolar spheres tend to form chains rather then exhibiting the ferroelectric phase. The formation of chains is not taken into consideration in the mean field theory or in the low density approximations. A number of difficulties related to the long-range character of the dipole-dipole interaction arise also in the molecular theories of nematic liquid crystals composed of hard rod-like molecules with large permanent dipoles which are parallel to the molecular long axis [9–14]. Recently Sonnet and Virga have also considered the molecular model with a tilted

dipole [19]. It is interesting to note that no ferroelectric phase was found in [9–11] while the ferroelectric ordering has been predicted in [12,13]. It can be shown that the difference between these contradicting results is related to the way how the long range part of the dipole-dipole interaction potential is accounted for.

Recently the proper ferroelectric ordering has been discovered experimentally in the nematic phase exhibited by a number of materials composed of strongly polar molecules [15–18]. The temperature variation of the spontaneous polarisation, second harmonic generation and extremely large dielectric susceptibility have been studied experimentally [17–24]. One notes that in these strongly polar materials the total molecular dipole is composed of several dipoles located in different parts of the molecule and tilted with respect to the long molecular axis. In addition minor changes in the molecular structure may suppress the ferroelectric ordering regardless of the value of the total dipole [19,25–28]. Thus the polar interaction between such molecules can hardly be described using a model of a rod like molecule with the central dipole.

In this paper we consider the possible molecular origin of ferroelectric ordering in polar nematic liquid crystals (LCs) taking into consideration both the strong dipole-dipole interaction and the orientational-translational short range intermolecular correlations.

2. Can the dipole-dipole intermolecular interaction be responsible for the ferroelectric ordering in nematic liquid crystals

In the generalised molecular-field approximation the free energy of the polar nematic LC composed of uniaxial rigid molecules with single permanent dipoles can be written in the form:

$$F = F_0 \rho k_B T \int f_1(\mathbf{a} \cdot \mathbf{n}) log[4\pi f_1(\mathbf{a} \cdot \mathbf{n})] d^2\mathbf{a} d^3\mathbf{r}$$

$$- \frac{1}{2}\lambda(\rho) \int\int (\Theta(r_{12} - \xi(1,2)) - 1)f_1(\mathbf{a}_1 \cdot \mathbf{n})f_1(\mathbf{a}_2 \cdot \mathbf{n})d^3\mathbf{r}_1 d^3\mathbf{r}_{12}d^2\mathbf{a}_1 d^2\mathbf{a}_2$$

$$+ \frac{1}{2}\rho^2 \int\int \Theta(r_{12} - \xi(1,2))U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12})(f_1(\mathbf{a}_1 \cdot \mathbf{n})f_1(\mathbf{a}_2 \cdot \mathbf{n})d^3\mathbf{r}_1 d^3\mathbf{r}_{12}d^2\mathbf{a}_1 d^2\mathbf{a}_2 - \rho \int \mathbf{d} f_1(\mathbf{a} \cdot \mathbf{n})\mathbf{E}_0 d^2\mathbf{a}, \quad (1)$$

where the first term is the orientational entropy which depends on the orientational distribution function

$f_1(\mathbf{a} \cdot \mathbf{n})$ and the second term is the so-called packing entropy, where the coefficient $\lambda(\rho)$ is some function of the number density ρ which depends on a particular approximation, and $\Theta(r_{12} - \xi(1,2))$ is the steric cut off function which restricts the domain of integration to be $r_{12} > \xi(1,2)$ where $\xi(\mathbf{a}_1, \mathbf{a}_2, \mathbf{u}_{12})$ is the distance of minimum approach for the two interacting molecules. This domain is the whole region outside the excluded volume for the two molecules where the excludee volume is defined by the inequality $r_{12} < \xi(1,2)$. The third term in Equation() is a contribution from the pair intermolecular interaction potential $U(1,2) = U_0(1,2) + V_{dd}(1,2)$ which is a sum of the non-polar interaction potential $U_0(1,2)$ and the dipole-dipole interaction potential $V_{dd}(1,2)$ between the central molecular dipoles which is given by the well-known expression:

$$V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12}) = \frac{1}{r_{12}^3}((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12})),$$
$$(2)$$

where $\mathbf{d}_i$, $i = 1, 2$, is the dipole of the molecule i, $\mathbf{r}_{12}$ is the intermolecular vector and $\mathbf{u}_{12} = \mathbf{r}_{12}/r_{12}$ is the unit intermolecular vector.

One notes that the dipole-dipole interaction potential possesses opposite signs for different mutual orientation of the two dipoles. In addition, in the free enenrgy functional the dipole-dipole potential is modulated by the molecular shape. In the simplest case of spherical rigid molecules the lowest interaction energy $V_{dd} = -2d_1 d_2 R_{12}^{-3}$ corresponds to the configuration when $\mathbf{d}_1 = \mathbf{d}_2 = \mathbf{u}_{12}$ (see Figure 1). In contrast, the 'side by side' orientation of the two parallel dipoles corresponds to the positive energy $V_{dd} = +d_1 d_2 R_{12}^{-3}$. The antiparallel configuration also corresponds to the negative energy $V_{dd} = -d_1 d_2 R_{12}^{-3}$ which is two times higher than the energy of the parallel configuration. At the same time, for strongly anisotropic molecules the lowest energy configuration is the antiparallel one which does not promote the polar order.

In the simplest case one may assume that the molecular shape is non-polar and the ferroelectric ordering can only be promoted by the dipole-dipole interaction which makes the following contribution to the free energy:

$$\Delta F_{MF}^{(N)} = \frac{1}{2}\rho^2 \int d^2\mathbf{a}_1 d^2\mathbf{a}_2 \int_{r_{12} > \xi(1,2)} d^3\mathbf{r}_{12} V_{dd}(1,2)f_1(\mathbf{a}_1 \cdot \mathbf{n})f_1(\mathbf{a}_2 \cdot \mathbf{n})dr_1$$
$$(3)$$

One can readily see that this contribution contains the following volume integral of the dipole-dipole interaction potential:
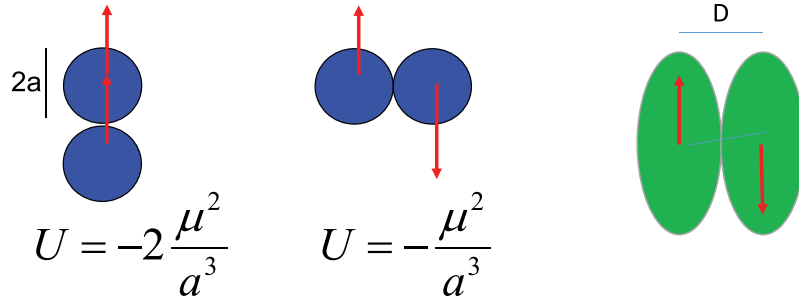
Figure 1. (Colour online) The lowest energy configurations for the two interacting dipolar spheres and dipolar ellipsoids.

$$\int_{r_{12}>\xi(1,2)} V_{dd}(1,2)d^3\mathbf{r}_{12}. \tag{4}$$

Taking into account that $\xi(1,2) < L$, where L is the length of the molecule, it is convenient to split the integral [1] into the two parts:

$$\int_{r_{12}>\xi(1,2)} V_{dd}(1,2)d^3\mathbf{r}_{12} = \int_{L>r_{12}>\xi(1,2)} V_{dd}(1,2)d^3\mathbf{r}_{12} + \int_{r_{12}>L} V_{dd}(1,2)d^3\mathbf{r}_{12}. \tag{5}$$

Here the second term in the right hand side of Equation (5). is the integral of the dipole-dipole potential over the whole sample outside the sphere of radius L while the first term is the integral over the region which is located inside the sphere of radius L outside the excluded volume for the two rod-like molecules.

Let us consider in more detail the second term in Equation (5). which can be written in the following explicit form:

$$\int_L^\infty r_{12}^2 dr_{12} \int d\mathbf{u}_{12} \frac{1}{r_{12}^3}((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12})). \tag{6}$$

From the molecular-statistical point of view an important property of the dipole-dipole interaction potential is the anomalous behaviour of its volume integral due to the long range character of the potential. Indeed, on the one hand the integral of the dipole-dipole potential over all orientations of the unit intermolecular vector u_{12} is equal to zero, i.e

$$\int \frac{1}{r_{12}^3}((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12}))d^2\mathbf{u}_{12} = 0. \tag{7}$$

On the other hand the integral over the intermolecular distance r_{12} diverges logarithmically at large r_{12}:

$$\int_D^\infty \frac{1}{r_{12}^3}((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12}))r_{12}^2 dr_{12} \to \infty. \tag{8}$$

In rigorous mathematical terms this means that the volume integral of the dipole-dipole potential is ill defined, i.e. the value of the integral depends on the order of integration. From the physics point of view this means that the integral of the dipole-dipole potential over the whole sample depends on the shape of the sample. This result has important consequences in the molecular theory of ferroelectric nematics. Indeed one can naively integrate the dipole-dipole potential over $\mathbf{u}_{12}$ and conclude that the dipole-dipole contribution to the free energy vanishes. However, this conclusion is incorrect because the volume integral of the dipole-dipole potential is ill defines as it diverges simultaneously after integration over r_{12}. Thus the whole contribution of the dipole-dipole potential to the free energy is also ill defined and cannot be evaluated in a straightforward way. This result illustrates some general difficulties arising in the statistical theory of systems with long range intermolecular interactions.

The difficulties related to the long-range character of the dipole-dipole interaction are well known in the theory of dielectric properties of solid crystals. The problem has been solved long ago using the method of lattice sums proposed by Ewald [29]. This method, however, cannot be directly applied to fluid ferroelectric materials because there is no positional order. On the other hand the general idea behind the Ewalds's theory is valid for any system with long range polar order including ferroelectric nematics. In the general case one has to separate the short range and long range contributions of the dipole-dipole potential to the total free energy of the ferroelectric phase and establish a relationship with the electric field in the system. This can be achieved by expressing the integral in Equation (8). into the following two parts:

$$\int_{r_{12}>L} V_{dd}(\mathbf{d}_1,\mathbf{d}_2,\mathbf{r}_{12})d^3\mathbf{r}_{12} = \int^{V_{dd}}(\mathbf{d}_1,\mathbf{d}_2,\mathbf{r}_{12})d^3\mathbf{r}_{12}$$
$$- \int_{r_{12}<L} V_{dd}(\mathbf{d}_1,\mathbf{d}_2,\mathbf{r}_{12})d^3\mathbf{r}_{12}, \quad (9)$$

where the first term in the right hand side of Equation (9). is the integral of the dipole-dipole potential over *the whole volume* of the sample and the second term is the integral of the potential over the sphere of radius L.

The second integral in Equation (9). over the sphere of radius L can be taken analytically [30] (pp. 139–43):

$$-\int_{r_{12}<L} V_{dd}(\mathbf{d}_1,\mathbf{d}_2,\mathbf{r}_{12})d^3\mathbf{r}_{12} = -\frac{4\pi}{3}(\mathbf{d}_1\cdot\mathbf{d}_2). \quad (10)$$

One notes that the result does not depend on the radius L.

The integral in the first term of Equation (5). has been evaluated numerically by Terentjev and Petschek for two ellipsoids of revolution [31], and the analytical interpolation formulae has also been obtained:

$$-\int_{\xi(1,2)<r_{12}<L} V_{dd}(\mathbf{d}_1,\mathbf{d}_2,\mathbf{r}_{12})d^3\mathbf{r}_{12} = -C_1(\mathbf{d}_1\cdot\mathbf{d}_2), \quad (11)$$

where

$$C_1 = -\frac{4\pi}{3}\left((1-\frac{D}{L})^{2/3} + \frac{2}{3}\frac{(D/L)(1-(D/L))}{(1-(D/L))^2+6(D/L)^2}\right) \quad (12)$$

For strongly anisometric molecules with $D/L \ll 1$ the constant C_1 can be estimated as

$$C_1 \approx -\frac{4\pi}{3}\left(1-\frac{4}{3}\frac{D}{L}\right). \quad (13)$$

Combining Equations (11) and (13), substituting them into Equation (1). and averaging with the orientational distribution functions one obtains the following contribution of the short range part of the dipole-dipole potential to the mean-field free energy density

$$\Delta F_{dd} = \frac{1}{2}\left(-\frac{4\pi}{3}-C_1\right)\mathbf{P}^2 \approx -\frac{1}{2}\frac{16\pi}{9}\mathbf{P}^2, \quad (14)$$

where the polarisation $\mathbf{P} = \rho<\mathbf{d}>$.

Now the polarisation dependent contribution from the orientational entropy (the first term in Equation (1)) can be obtained by expanding the orientational distribution function $f_1(\mathbf{a}\cdot\mathbf{n})$ in powers of the polar order parameter $\mathbf{p} = <\mathbf{a}>$:

$$f_1((\mathbf{a}\cdot\mathbf{n}),(\mathbf{a}\cdot\mathbf{P})) = f_0((\mathbf{a}\cdot\mathbf{n}))(1+\alpha(\mathbf{a}\cdot\mathbf{p})+\ldots), \quad (15)$$

where $\mathbf{p} = <\mathbf{a}>$ is the non-dimensional polar order parameter, $f_0((\mathbf{a}\cdot\mathbf{n}))$ is the non-polar orientational distribution function which describes the nematic ordering and $\alpha = 3/(2S+1)$ where S is the nematic order parameter. Here it has been assumed that the polarisation is parallel to the director $\mathbf{n}$.

Substituting Equation (15). into the first term of the free energy (1) and keeping only the quadratic term one obtains the following polarisation dependent contribution:

$$\Delta F_{ent} \approx \frac{\alpha kT}{\rho d^2}\mathbf{P}^2. \quad (16)$$

Finally the first term in Equation (9). can be averaged with the two orientational distribution functions (see Equation (3)) and integrated over the whole volume of the sample. Combining it with the last term in Equation (1). yields the following contribution to the total free energy which depends on the shape of the sample:

$$\Delta_{MF}^{(2)} = \frac{1}{2}\rho^2\int V_{dd}(\mathbf{d}_1,\mathbf{d}_2,\mathbf{r}_{12})f_1(\mathbf{a}_1\cdot\mathbf{n})$$
$$f_1(\mathbf{a}_2\cdot\mathbf{n})d^2\mathbf{a}_1 d^2\mathbf{a}_2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$
$$-\rho\int df_1(\mathbf{a}\cdot\mathbf{n})\mathbf{E}_0 d^2\mathbf{a}d^3\mathbf{r}, = -\frac{1}{2}\int\mathbf{P}(\mathbf{r}\cdot\mathbf{E}(\mathbf{r})d^3\mathbf{r}, \quad (17)$$

where we have taken into account that the actual macroscopic electric field $\mathbf{E}$ in the medium is expressed as (2)

$$\mathbf{E}(r) = \mathbf{E}_0 - \int\mathbf{T}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}')d^3\mathbf{r}', \quad (18)$$

and where $T_{\alpha\beta}$ is the dipole-dipole tensor:

$$T_{\alpha\beta}(\mathbf{R}) = \frac{1}{R^3}\left(\delta_{\alpha\beta}-3u_\alpha u_\beta\right), \quad (19)$$

and $\mathbf{u} = \mathbf{R}/R, \mathbf{R} = \mathbf{r}-\mathbf{r}'$.

Combining Equations (14,16). and (17) one obtains the final expression for the total mean-field total free energy of the ferroelectric nematic:

$$F = F_0 + \int d^3\mathbf{r}\left(\frac{\alpha kT}{\rho d^2}-\frac{8\pi}{9}\frac{D}{L}\right)\mathbf{P}^2(\mathbf{r})$$
$$+ (higher\ order\ terms\ in\ \mathbf{p})$$
$$-\frac{1}{2}\int\mathbf{P}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})d^3\mathbf{r}. \quad (20)$$

The last term in the free energy Equation (20) is the energy of the electric field in the volume of the sample which depends on the sample shape and on the boundary conditions, while the first integral in Equation (17). is the first term of the expansion of the short range contribution to the free energy in powers of the polarisation $\mathbf{P}$. The paraelectric nematic phase looses its

stability with respect to polarization when the coefficient in the P^2 term vanishes. As a result the second order transition temperature into the ferroelectric nematic phase is approximately given by:

$$kT_{Nf} = \frac{8\pi}{27}\frac{D}{L}(2S+1)\rho d^2. \qquad (21)$$

Thus one concludes that the transition into the ferroelectric nematic phase is in principle possible (at least in the mean-field approximation) but the transition temperature appears to be very low and is decreasing with the increasing of the molecular anisotropy. For typical values of the molecular dipoles the transition temperature is located deeply in the crystal phase. In order to obtain the transition at room temperatures the molecular dipole should be of the order of $20 Debye$ which seems to be too large. The interaction between such molecular dipoles at short separation is extremely strong, and it is reasonable to assume that the system will prefer to develop strong short-range orientational correlations promoting the antiparallel side by side low energy configurations which is a much more efficient way to reduce the free energy compared with the long range ferroelectric order.

Now let us discuss the role of the electrostatic energy of the whole sample, given by the last term in Equation (19), by considering for simplicity the homogeneous flat nematic cell with homogeneous spontaneous polarisation normal to the cell surface. There are two important limiting cases here. In the cell with short circuited electrodes, which corresponds to zero applied voltage, the macroscopic electric field $\mathbf{E} = 0$ and hence the electrostatic energy vanishes. In contract, in the same cell with disconnected electrodes (and no remaining charges on the electrodes) the displacement $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = 0$ and therefore $\mathbf{E} = -4\pi\mathbf{P}$. Substituting this into the last term in Equation (20). one concludes that the total electrostatic energy of such a cell is $2\pi V P^2$, where V is the sample volume. This contribution is quadratic in polarization and is positive w i.e. it destabilises the ferroelectric phase. One notes that the electrostatic energy is nonlocal and positive, and as a result the total free energy of the system is effectively reduced by splitting into domains with opposite polarisation or, generally, by creating an inhomogeneous polarisation profile. Thus the homogeneous ferroelectric ordering is more likely to be observed in the cell with zero applied voltage.

Recently a more realistic model based on electrostatic interaction between surface charge densities has been proposed by Madhusudana [32]. In this model ir is assumed that cylindrical rigid molecules possess uniaxial surface charge density specified by four density waves. Some parts of the surface are negatively charged while the adjacent parts are characterised by positive charge density. As a result there exists a nontrivial low energy configuration in which the two adjacent molecules are parallel but one of them is shifted with respect to another. In this configuration the negatively charged pars of one molecule are in contact with the positively charged parts of another molecule and the overall electrostatic enenrgy is negative. It has been shown [32] that for some values of the parameters this parallel configuration, which promotes the ferroelectric ordering, is more favourable then the antiparallel configuration without a shift. This is a very promising result, but, at the same time, it does not seem to be sufficient because it is important also to show that the contribution of such an interaction between charge densities makes a contribution to the free energy which is negative and sufficiently large to overcome the orientational entropy. In the mean-field approximation this contribution is given by the second term in Equation (1). where the dipole-dipole potential should be replaced by the corresponding interaction between surface charges. One notes that this contribution to the free energy is determined by the integral of the interaction energy between surface charge densities over the intermolecular vector r_{12}. This integral is an average over all configurations of the two molecules and not just over the two ones considered in [32]. Such an integral can only be evaluated numerically and this is a challenging task.

2.1. Short-range intermolecular correlations and the possible origin of ferroelectric ordering

As discussed above, in the framework of the man-field theory electrostatic dipole-dipole and charge-charge interactions between polar molecules. In particular, it is important to emphasise that dipole-dipole potential vanishes after integration over all orientations of the intermolecular unit vector which indicates that there is a delicate balance between parallel and antiparallel configurations which are characterised by positive and negative energies, respectively. At the same time this balance can be shifted by specific orientational-translational intermolecular correlations which may increase the statistical weight of some parallel configurations which promote the ferroelectric ordering. With these correlations taken into account the averaging of the dipole-dipole potential appears to be more complicated and one cannot use the mean-field approximation. The simplest way to take into consideration the polar interaction potential modulated by pair correlations is to use the second order thermodynamic perturbation theory. In the

framework of this perturbation theory the free energy of the polar nematic can be expressed as:

$$F = F_0 + \frac{1}{2}\rho^2 \int g_2(1,2) f_1((\mathbf{a}_1 \cdot \mathbf{n})) f_1((\mathbf{a}_2 \cdot \mathbf{n}))$$
$$\frac{1}{r_{12}^3}((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12})) d^3\mathbf{r}_{12} d\mathbf{a}_1 d\mathbf{a}_2, \quad (22)$$

where F_0 is the background free energy which does not depend on the dipole-dipole interaction. Here $g_2(1,2) = g_2(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2)$ is the pair correlation function in the non-polar nematic phase which depends on the relative orientation of the molecules 1 and 2. The correlation function can generally be expanded in the so-called spherical invariants:

$$g_2(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = \sum_{l,\lambda,L} J_{l\lambda L}(r_{12}) T^{l\lambda L}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2), \quad (23)$$

where the invariants $T^{l\lambda L}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2)$ contain the unit vector $\mathbf{a}_1$ to the power l, the vector $\mathbf{a}_2$ to the power L and the unit vector $\mathbf{u}_{12}$ to the power λ.

Taking into account first order terms which depend only on the two unit vectors, the pair correlation function can be approximated in the following simple way:

$$g_2(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) \approx g_{20}(r_{12}) + G(r_{12})\left((\mathbf{a}_1 \cdot \mathbf{u}_{12})^2 + (\mathbf{a}_2 \cdot \mathbf{u}_{12})^2\right)$$
$$+ N(r_{12})(\mathbf{a}_1 \cdot \mathbf{a}_2)^2 + \dots, \quad (24)$$

where the coefficients $g_{20}(r_{12})$, $G(r_{12})$ and $N(r_{12})$ are the decreasing functions of r_{12} because the correlations are assumed to be short-range.

Substituting Equation (24) into Equation (22). and assuming for simplicity that the nematic order is perfect one obtains the following contribution to the free energy:

$$\Delta F = -\frac{8\pi}{15} P^2 \int G(r_{12}) \frac{1}{r_{12}} dr_{12}, \quad (25)$$

where P is the polarisation. One notes that the integral $\int G(r_{12}) \frac{1}{r_{12}} dr_{12}$ is finite due to the rapid decrease of the function $G(r_{12})$.

The free energy contribution Equation (25). is negative and thus it promotes the ferroelectric ordering. However this conclusion crucially depends on the sign of the function $G(r_{12})$ which must be positive. It should be noted also that in this elementary theory it is sufficient to take into account just the interaction between single molecular dipoles, while the particular structure of the polar molecules, including the position and orientation of local dipoles, is supposed to effect the intermolecular correlations. For example, the maximum of the second term $G(r_{12})\left((\mathbf{a}_1 \cdot \mathbf{u}_{12})^2 + (\mathbf{a}_2 \cdot \mathbf{u}_{12})^2\right)$ in the expansion

of the correlation function corresponds to $\mathbf{u}_{12} \parallel \mathbf{a}$ if the function $G(r_{12})$ is positive. Thus this term promotes the slide of a molecule with respect to the neighboring one, i.e. it emphasises the parallel molecular configuration considered in the Madhusudana model [32].

3. Conclusions

In this paper we have considered a molecular origin of the ferroelectric ordering in the nematic phase taking into account mainly the dipole-dipole interactions and orientational-translational intermolecular correlations. It has been shown that the contribution of the dipole-dipole interaction to the free energy of the nematic phase can be evaluated consistently only by separation of the short-range and the long-range parts of the corresponding effective interaction potential modulated by the molecular shape. In particular, the contribution of the long-range tail of the dipole-dipole interaction to the total free energy of the ferroelectric nematic is equal to the total electrostatic energy and depends on the sample shape and boundary conditions.

It has also been shown that the electrostatic interaction between permanent longitudinal molecular dipoles can hardly be responsible for ferroelectric ordering for any reasonable values of the molecular dipole, at least in the mean-field approximation. A more realistic model of Madhusudana [32], based on electrostatic interaction between surface charge densities, seems to be more promising as it defines the additional parallel low energy configuration, in which the neighbouring molecules are shifted with respect to each other.

One may conclude that the molecular origin of ferroelectric ordering cannot be consistently described in the mean field approximation taking into account only electrostatic intermolecular interactions. It has been shown that the combination of the short-range orientational-transitional intermolecular correlations and the interaction between permanent dipoles results in the contribution to the free energy which promotes ferroelectricity. At the same time it should be noted that a consistent molecular-statistical theory of ferroelectric nematics, which takes into account the corresponding intermolecular correlations, has not been derived so far and is currently in progress.

Disclosure statement

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