On the origin of the ferroelectric ordering in nematic liquid crystals and the electrostatic properties of ferroelectric nematic materials.

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Abstract

Possible molecular origin of ferroelectricity in the nematic phase is discussed in detail considering a number of models based on direct dipole-dipole interaction and electrostatic interaction between surface charge densities. A more model which combines dipole-dipole interaction and short-range orientational-translational correlations is also considered . In particular we derive a contribution to the total free energy of the long-range tail of the dipole-dipole interaction potential and show that this contribution depends on the sample shape and on the boundary conditions. As a result this shape dependent contribution may strongly effect the transition into the ferroelectric phase depending on the actual boundary conditions maintained experimentally.

We also consider two conjugated thermodynamic potentials which depend on the electric field in the medium and on the displacement field, respectively. It is shown that the actual polarization corresponds to the minimum of one of these potentials depending on the boundary conditions which may have significant experimental consequences. In the framework of the general Landau de Gennes theory, which employs both potentials, the ferroelectric properties of different nematic cells are considered including the ones with fixed applied voltage and free cells with disconnected electrodes.

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I.   INTRODUCTION

A possibility of proper ferroelectric ordering in isotropic fluids and nematic liquid crystals in particular was attracting a significant attention during several decades. Such a possibility was initially supported by a simple idea that the interaction between sufficiently large molecular dipoles sooner or later will result in a long range polar order. This idea was indeed supported by early computer simulations [1–6] of the system of soft and hard dipolar spheres at low densities. In addition, the ferroelectric phase in the system of dipolar spheres has also been predicted theoretically using the density functional theory at low densities [5] It should be noted, however,that the theoretical analyses of the dipole-dipole interaction in the framework of a molecular-statistical theory is not straightforward due to its strong anisotropy and the long range character. In particular, the dipole-dipole interaction potential vanishes after integration over all orientations of the unit intermolecular vector which makes it difficult to account for this interaction in the standard molecular-field approximation. Another difficulty is related to the fact that the contribution of the dipole-dipole interaction to the total free energy depends on the shape of the sample [7] due to the long-range tail of the potential. These difficulties have been partially addressed in refs. [8–10], where the ferroelectric ordering of soft spheres has also been predicted, but it is important to note that the theory is only valid in the zero density approximation and thus it can hardly be applied to realistic dipolar fluids.

Later it has been realised that the elementary description cannot be valid even in the case of very low densities. Indeed, more detailed computer simulations indicate [4, 11–13] that spheres with sufficiently large dipoles tend to form chains rather then exhibiting the ferroelectric phase. The formation of chains is not taken into consideration neither in the mean field theory nor in the low density approximation based on virial expansion and thus the early molecular theories cannot describe the results of these simulations. The formation of chains and their equilibrium distribution at low densities can be described using the theory of living polymers [14–16] but at higher densities such an approach is again not valid as at the computer simulation indicate that at high densities there are no individual chains and also no long range polar order [12]. Thus the formation of the ferroelectric phase in the system of dipolar spheres seems to be highly unlikely which, in fact, corresponds to the existing experimental data as no ferroelectric phase has been observed so far in low

molecular isotropic fluids composed of weakly anisotropic molecules regardless of the value of the molecular dipole. Similar difficulties arise also in the molecular theories of nematic liquid crystals composed of strongly polar molecules [17–22] which employ the model of the ellipsoid of revolution or the sphere cylinder with the permanent dipole which is parallel to the molecular axis and located either at the molecular centre [17–21] or anywhere on the molecular axis. The model with tilted dipoles has also been analysed recently by Bisi, Sonnet and Virga [22]. No ferroelectric phase was found in [17–19] while the theories presented in [20, 21] predict the ferroelectric ordering. The difference between these contradicting results is mainly related to the way how the long range part of the dipole-dipole interaction potential is accounted for in the molecular-statistical theory as discussed in Section 2.

Very recently the proper ferroelectric nematic phase has finally been discovered in few liquid crystal materials composed of strongly polar molecules [23–26], and the spontaneous polarization, second harmonic generation and giant dielectric susceptibility have been studied experimentally by several groups [25–32, 37]. It should be noted that the molecular structure of these ferroelectric materials is very specific. The total molecular dipoles are very large but they are composed of several smaller dipoles which are located in different parts of the molecule and tilted with respect to the primary molecular axis. In addition such molecules possess a significant lateral group. It has also been shown that minor changes in the molecular structure may result in the loss of the ferroelectric phase even when the total molecular dipole remains approximately the same [27, 33–36]. A review of ferroelectric nematic materials has been published recently by R.Mandle [34]. Thus one may conclude that the polar interaction between such mesogenic molecules appears to be rather complex and the system can hardly be described using a simple model of the ellipsoid or a sphere cylinder with the central dipole.

In this review we critically analyse the possible molecular origin of ferroelectric ordering in strongly polar nematic liquid crystals (LCs) as well as in isotropic dipolar fluids in simple and qualitative way without considering the formal aspects of the corresponding molecular-statistical theories. We first consider the role of strong dipole-dipole interaction in isotropic fluids composed of dipolar hard spheres and then use the results to analyse a number of more realistic molecular models for ferroelectric nematics with a special emphasis on the role of short range intermolecular correlations combined with electrostatic interactions between different molecular fragments.

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II.   CAN DIPOLE-DIPOLE INTERACTION PROMOTE FERROELECTRICITY IN FLUIDS?

In the general case the proper ferroelectric ordering (i.e. the ferroelectric phase where the spontaneous polarization is the primary order parameter) should be determined by some polar intermolecular interaction. However, it is not obvious that the electrostatic dipole-dipole interaction is always the primary microscopic cause of the ferroelectric ordering. The dipole-dipole interaction is indeed responsible for the emergence of the ferroelectric phase in some crystals but it is not clear yet if it can promote ferroelectricity in dipolar fluids without positional order. In this section we discuss the properties of the dipole-dipole interaction and its contribution to the free energy of the system of dipolar spheres which is the simplest fluid system capable of exhibiting the ferroelectric phase, at least in principle. Our conclusions will then be applied also to the ferroelectric nematics.

A.   Anisotropy of the dipole-dipole electrostatic interactions

The dipole-dipole electrostatic interaction potential is given by the following well known expression

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

where $\mathbf{d}_i$, $i = 1, 2$, is the permanent 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 is not only strongly anisotropic but it also possesses opposite signs for different mutual orientation of the two dipoles. As shown in Fig.1, the lowest interaction energy $V_{dd} = -2d_1 d_2 R_{12}^{-3}$ corresponds to "nose to tail" configuration when $\mathbf{d}_1 = \mathbf{d}_2 = \mathbf{u}_{12}$. 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 of the two side by side dipoles also corresponds to the negative energy $V_{dd} = -d_1 d_2 R_{12}^{-3}$ but it is higher than the energy of the parallel "head to tail" configuration. From the molecular point of view one of the most important properties of the dipole-dipole interaction potential is the anomalous behaviour of its volume integral. Indeed the volume integral of the potential can be expressed as the following double integral:

$$\int_V V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12}) dV = \int \int \frac{1}{r_{12}^3} \left((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12}) \right) r_{12}^2 dr_{12} d^2 \mathbf{u}_{12}. \tag{2}$$
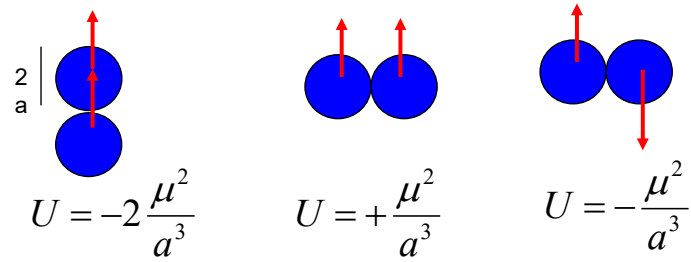
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FIG. 1: —The lowest and the highest energy configurations of the two interacting dipoles.

One notes that the integral of the dipole-dipole potential over all orientations of the unit intermolecular vector $\mathbf{u}_{12}$ vanishes identically, i.e

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

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

$$\int_D^\infty \frac{1}{r_{12}^3} \left((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12}) \right) r_{12}^2 dr_{12} \to \infty. \tag{4}$$

From the rigorous mathematical point of view 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. The important physical consequence of this is that the integral of the dipole-dipole potential over the finite sample depends on the shape of the sample due to the long range character of the potential. This property is particularly important for the correct

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account of the dipole-dipole interaction in the molecular theory as discussed in the next subsection.

B. Dipole-dipole interaction and the possibility of ferroelctric order in the system of dipolar spheres.

Let us assume that the system of hard spheres with sufficiently large dipoles may exhibit the orientationally ordered ferroelectric phase promoted by the dipole-dipole interaction. Then in the mean field approximation the contribution of the dipole-dipole interaction potential to the free energy density of the homogeneous polar phase is expressed as:

$$\Delta F_{MF} = \frac{1}{2}\rho^2 \int \int \Theta(r_{12} - D)\frac{1}{r_{12}^3} \left((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12})\right) f_1(\mathbf{a}_1 \cdot \mathbf{n}) f_1(\mathbf{a}_2 \cdot \mathbf{n}) \times$$

$$r_{12}^2 dr_{12} d^2\mathbf{u}_{12} d^2\mathbf{a}_1 d^2\mathbf{a}_2 - \rho\mathbf{E}_0 \int \mathbf{d} f_1(\mathbf{a} \cdot \mathbf{n}) d^2\mathbf{a}, \tag{5}$$

where ρ is the number density, the unit vectors $\mathbf{a}_1, \mathbf{a}_2$ are in the direction of the permanent dipoles $\mathbf{d}_1, \mathbf{d}_2$, respectively and $f_1(\mathbf{a}_1 \cdot \mathbf{n})$ is the orientational distribution function of the polar phase which depends on the coupling between the molecular axis $\mathbf{a}_1$ and the director $\mathbf{n}$. Here $\Theta(r_{12} - D)$ is the step function, $\Theta(r_{12} - D) = 0$ if the two spheres penetrate each other and $\Theta(r_{12} - D) = 1$ if they do not. This function describes the steric cut off which means that the centres of the two spheres cannot bc closer then D. Finally the last term is a contribution from a coupling between the molecular dipole and the external electric field $\mathbf{E}_0$.

Eq.(5) contains the multiple integral over $r_{12}, \mathbf{u}_{12}, \mathbf{a}_1$ and $\mathbf{a}_2$ and 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 for the reasons discussed in the previous subsection. Indeed, the dipole-dipole contribution Eq.(5) can be expressed in terms of the volume integral of the dipole-dipole interaction potential:

$$\Delta F_{MF}/V = \frac{1}{2}\rho^2 \int \left(\int_V \Theta(r_{12} - D)V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12})dV\right) f_1(\mathbf{a}_1 \cdot \mathbf{n}) f_1(\mathbf{a}_2 \cdot \mathbf{n}) d^2\mathbf{a}_1 d^2\mathbf{a}_2. \tag{6}$$

As discussed in the previous subsection, the volume integral of the dipole-dipole potential is ill defined as it depends on the order of integration. The integral vanishes is the integration over $\mathbf{u}_{12}$ is performed first and it diverges if one begins with the integration over r_{12}. This

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result is not effected by the fact that the integration is performed in the range $r_{12} > D$ (due to the steric cut off) as the divergence occurs when $r_{12} \to \infty$. 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. One notes also that these difficulties are not related to the mean-field approximation and remain in any molecular-statistical theory. For example, in the second virial approximation which is valid at very small densities, the free energy density of the orientationally ordered system of dipolar hard spheres can be written in the well known form:

$$F/V = \rho K_B T \int f_1(\mathbf{a} \cdot \mathbf{n}) log[4\pi f_1(\mathbf{a} \cdot \mathbf{n})] d^2\mathbf{a}$$

$$-\frac{1}{2} k_B T \rho^2 \int f_1(\mathbf{a}_1 \cdot \mathbf{n}) f_1(\mathbf{a}_2 \cdot \mathbf{n}) \int_{r_{12}>D} \left(\exp(-\beta V_{dd}(1,2)) - 1 \right) d^3\mathbf{r}_{12} d^2\mathbf{a}_1 d^2\mathbf{a}_2, \qquad (7)$$

where $\beta = 1/k_B T$.

The integral over the Maier function $\exp(-\beta V_{dd}(1,2)) - 1$ in Eq.(7) is complicated but at large distance r_{12} between the interacting dipoles the dipole-dipole potential is small , and hence the nondimensional parameter $\beta V_{dd}(1,2) \ll 1$. As a result, for sufficiently large r_{12}, the Maier function $\exp(-\beta V_{dd}(1,2)) - 1 \approx -\beta V_{dd}(1,2))$ and hence for large r_{12} one arrives at the same ill defined integral of the dipole-dipole potential as in the mean-field approximation.

It should be noted that the difficulties related to the long-range tail of the dipole-dipole interaction are well known in the theory of dielectric properties of solid crystals. The problem has been generally solved long ago using the method of lattice sums proposed by Ewald [38]. The method of lattice sums, 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 also valid for any system with spontaneous polarization including ferroelectric nematic LCs. In fact one has to separate the short range and long range contributions to the total free energy of the ferroelectric phase and establish a relationship with the average electric field in the system. This can be achieved by splitting the integral in Eq.(4) into two different parts.

According to Eq.(4) the contribution of the dipole-dipole interaction to the mean-field

free energy contains the following volume integral of the potential:

$$\int_V \Theta(r_{12} - D)V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12})dV = \int_{r_{12}>D} V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12})d^3\mathbf{r}_{12}. \tag{8}$$

This integral can be expressed as a difference to the following terms:

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

where the first term in the right hand side of Eq.(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 excluded volume (see Fig.2) of the two spheres. The excluded volume is a sphere with the diameter of $2D$ and with the centre located at the centre of one of the spheres. The centre of the second sphere cannot be located inside the excluded volume because the spheres cannot penetrate each other.

The second integral in Eq.(9) over the spherical excluded volume can be taken analytically [39] (pp. 139-43):

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

One notes that the result does not depend on the sphere diameter D.

The contribution of the integral (10) to the total free energy is determined by the corresponding average of (10) with the orientational distribution functions according to Eq.(7):

$$\Delta F_{MF}^{(1)}/V = \frac{1}{2}\rho^2 \int \left(-\frac{4\pi}{3}(\mathbf{d}_1 \cdot \mathbf{d}_2)\right) f_1(\mathbf{a}_1 \cdot \mathbf{n})f_1(\mathbf{a}_2 \cdot \mathbf{n})d^2\mathbf{a}_1 d^2\mathbf{a}_2 = -\frac{2\pi}{3}\mathbf{P}^2, \tag{11}$$

where the polarization $\mathbf{P}$ is the average molecular dipole $\mathbf{P} = \rho \int \mathbf{d}f_1(\mathbf{a} \cdot \mathbf{n})$.

The first term in Eq.(9) together with the last term in Eq.(6) give rise to the following contribution:

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

$$-\rho \int \mathbf{d}f_1(\mathbf{a} \cdot \mathbf{n})\mathbf{E}_0 d^2\mathbf{a} d^3\mathbf{r}, = -\frac{1}{2}\int \mathbf{P}(\mathbf{r} \cdot \mathbf{E}(\mathbf{r})d^3\mathbf{r}, \tag{12}$$

where we have taken into account that the actual macroscopic electric field $\mathbf{E}$ in the medium is expressed as [7]

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 - \int \mathbf{T}(\mathbf{r} - \mathbf{r}')\mathbf{P}(\mathbf{r}')d^3\mathbf{r}', \tag{13}$$

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

$$T_{\alpha\beta}(\mathbf{R}) = \frac{1}{R^3}\left(\delta_{\alpha\beta} - 3u_\alpha u_\beta\right), \tag{14}$$
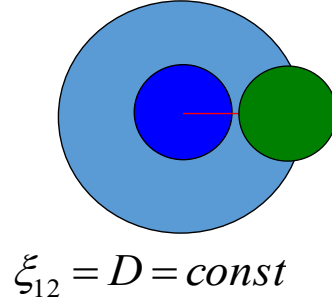
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$$\xi_{12} = D = const$$

FIG. 2: excluded volume for two hard spheres.

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

Combining Eqs.(11) and (12) one obtains the final expression for the contribution of the dipole-dipole interaction to the total free energy:

$$\Delta F_{MF} = \frac{1}{2} \int \left(-\frac{4\pi}{3} \mathbf{P}^2(\mathbf{r}) - \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) \right) d^3\mathbf{r}. \tag{15}$$

Thus one concludes that the total contribution of the dipole-dipole interaction is composed of two different terms. The first term is negative and is proportional to the square of the spontaneous polarization $\mathbf{P}$. Hence it promotes the ferroelectric ordering in the system of strongly polar spheres.

In contrast, the second term in Eq.(15) is the contribution from the long range part of the dipole-dipole interaction and appears to be the energy of the electrostatic field in the volume of the sample. This contribution depends on the shape of the sample and on the boundary
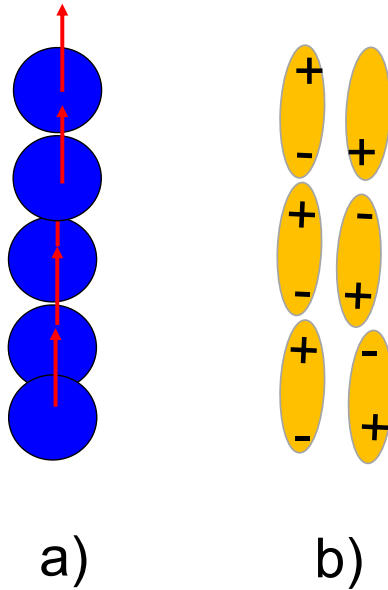
FIG. 3: Chains formed at low densities by dipolar hard spheres (a) or by anisometric hard particles with opposite charges at the two ends.

conditions. For example, in the spherical or the infinite flat sample both the spontaneous polarization and the macroscopic electric field are homogeneous. If such samples are surrounded by the conducting medium (for example, if the flat sample is sandwiched between short circuited conducting electrodes) the macroscopic electric field vanishes everywhere in the sample and hence the second term in Eq.(15) also vanishes. In contrast, in the spontaneously polarized spherical sample in vacuum the macroscopic electric field $\mathbf{E} = -4\pi\mathbf{P}/3$ and hence the whole free energy contribution (15) vanishes. In this case the dipole-dipole interaction does not promote ferroelectricity. In a similar way, in the infinite flat sample in vacuum the electric field $\mathbf{E} = -4\pi\mathbf{P}$ and the total contribution to the free energy density is positive, i.e. $+4\pi P^2$ which opposes the ferroelectric ordering.

One notes that some of these results have also been obtained in [8–10] and the conclusion

has been made that at sufficiently large value of the permanent dipole the system of dipolar spheres should undergo a transition into the ferroelectric phase, at least at low densities. This simple conclusion, however, does not seem to be correct and is not supported by advanced computer simulations. Indeed, the detailed simulations [4, 11–13] indicate that spheres with sufficiently large dipoles prefer to form polar flexible chains rather then exhibit the long range ferroelectric order (see Fig.3 a). In other words it is more energetically favorable for two dipolar spheres to occupy the head -to-tail configuration, which corresponds to the lowest energy, rather then to maintain the long-range polar order. At higher densities the individual chains are no longer observed but at the same time the ferroelectric ordering is also not observed. The formation of polar chains is a correlation phenomenon and it cannot be described in the mean-field or low density approximation. Thus one may concludes that also at liquid densities the dipolar order cannot be described in the mean-field approximation and a very sophisticated molecular statical theory is required which takes into consideration strong short-range orientational-translational correlations.

We have considered the possibility of the ferroelectric order in the system of dipolar spheres in much detail here because a very similar approach can also be used in the theory of nematic liquid crystals composed of elongated rigid molecules with central dipoles. We will see in the next section that the main conclusions which we have arrived at so far are also valid for such model polar nematics.

III. MOLECULAR MODELS FOR FERROELECTRIC NEMATICS.

A. Rigid molecules with central dipoles.

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:

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

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

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

$$(16)$$

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 defined after eq.(6). The third term in Eq.(16) 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 nonpolar interaction potential $U_0(1,2)$ and the dipole-dipole interaction potential $V_{dd}(1,2)$ given by eq.(1). Here the steric cut-off function 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 between the centres of the two rigid molecules. This function depends on the molecular shape. Finally the last term is a coupling between the molecular dipoles and the external electric field.

Assuming that the molecular shape is nonpolar and there are no other polar intermolecular interactions, the ferroelectric ordering can only be promoted by the dipole-dipole interaction which makes the following contribution to the free energy:

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

$$-\rho \int \mathbf{d} f_1(\mathbf{a} \cdot \mathbf{n}) \mathbf{E}_0 d^2\mathbf{a}. \tag{17}$$

Similar to the case of dipolar spheres considered in the previous section the contribution (17) contains the integral of the dipole-dipole interaction potential outside the excluded volume defined by the condition $r_{12} > \xi(1,2)$:

$$\int_{r_{12}>\xi(1,2)} V_{dd}(1,2) d^3\mathbf{r}_{12}. \tag{18}$$

As discussed above this volume integral is ill defined as it depends on the order of integration. Indeed, the integral vanishes if the integration over $\mathbf{u}_{12}$ is performed first, and the integral diverges after integration over r_{12}. It should be noted that this result does not depend on the molecular shape or the shape of the excluded volume as the divergence occurs at large r_{12} due to the long range tail of the dipole-dipole potential. Now the integral (18) can be expressed as a difference of the two terms similar to Eq.(9):

$$\int_{r_{12}>\xi(1,2)} V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12}) d^3\mathbf{r}_{12} = \int V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12}) d^3\mathbf{r}_{12} - \int_{r_{12}<\xi(1,2)} V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12}) d^3\mathbf{r}_{12}.$$

$$\tag{19}$$

Here the first term is the integral of the dipole-dipole potential over the whole sample which is exactly the same as in the case of dipolar spheres (see the first term in Eq.(9)). Thus it can be expressed in terms of the macroscopic electric field $\mathbf{E}$ in the medium and together with the last term in Eq.(7) yields the following contribution to the total free energy which is the same as Eq.(12):

$$\Delta F_{MF}^{(2)} = -\frac{1}{2} \int \mathbf{P}(\mathbf{r} \cdot \mathbf{E}(\mathbf{r}) d^3\mathbf{r}. \tag{20}$$

The second term in Eq.(19) gives rise to the following contribution to the free energy density which depends on the macroscopic polarization $\mathbf{P}$:

$$\Delta F_{MF}^{(1)}/V = \frac{1}{2}\rho^2 \int \int_{r_{12}<\xi(1,2)} V_{dd}(\mathbf{d}_1, \mathbf{d}_2, \mathbf{r}_{12}) d^3\mathbf{r}_{12} f_1(\mathbf{a}_1 \cdot \mathbf{n}) f_1(\mathbf{a}_2 \cdot \mathbf{n}) d^2\mathbf{a}_1 d^2\mathbf{a}_2. \tag{21}$$

Here the function $\xi(1,2)$ depends on the relative orientation of the two rigid molecules and it cannot be evaluated analytically even for simple shapes like ellipsoids of revolution of spherocylinders. As a result Eq.(21) cannot be significantly simplified in the general case. At the same time it is possible to expand Eq.(21) in powers of the polarization $\mathbf{P}$ keeping only the quadratic term which determines the transition temperature into the ferroelectric phase. In the case of small polarization the orientational distribution function can be expanded keeping the first linear term:

$$f_1((\mathbf{a} \cdot \mathbf{n}), (\mathbf{a} \cdot \mathbf{P})) = (4\pi)^{-1} \left(1 + 3(\mathbf{a} \cdot \mathbf{p}) + ...\right). \tag{22}$$

where $\mathbf{p}$ is the nondimensional polar order parameter, $\mathbf{p} = \mathbf{P}/\rho d$. Substituting Eq.(22) into Eq.(21) one obtains the following quadratic contribution to the free energy:

$$\Delta F_{MF}^{(1)}/V = C_1 \mathbf{P}^2, \tag{23}$$

where

$$C_1 = \frac{9}{2} \int_{r_{12}<\xi_{12}} d^3\mathbf{r}_{12} \frac{1}{r_{12}^3} \left((\mathbf{a}_1 \cdot \mathbf{a}_2) - 3(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{a}_2 \cdot \mathbf{u}_{12})\right)(\mathbf{a}_1 \cdot \mathbf{a}_2)\frac{d^2\mathbf{a}_1}{4\pi}\frac{d^2\mathbf{a}_2}{4\pi}, \tag{24}$$

where we have assumed that the molecular dipole is parallel to the primary molecular axis, i.e. $\mathbf{d} = \mathbf{a}d$.

The integral (24) over the excluded volume has been evaluated numerically by Terentjev and Petschek for two ellipsoids of revolution [40], and the following interpolation formulae has been obtained:

$$C_1 = -\frac{2\pi}{3}\left(1 - (1 - \frac{D}{L})^{2/3}\right) + \frac{2}{3}\frac{(D/L)(1 - (D/L))}{(1 - (D/L))^2 + 6(D/L)^2} \tag{25}$$

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where L is the molecular length and D is the molecular diameter.

A simple estimate for the constant C_1 can be obtained for strongly anisometric molecules when $D \ll L$:

$$C_1 \approx \frac{8\pi}{9} \frac{D}{L}. \tag{26}$$

One notes that in this limiting case the constant C_1 is positive. Moreover, according to Eq.(25) the constant C_1 is positive for all $L > 2D$ and hence for any reasonable anisometry of the mesogenic molecules the electrostatic interaction between central dipoles, which are parallel to the long molecular axis, does not promote the ferroelectric ordering for any value of the dipole.. This qualitative result is also valid if the dipole is located anywhere on the molecular axis [42]. It should be noted also that our conclusions are formerly valid in the molecular-field approximation. However, using the analogy with the system of dipolar spheres one expects that at low densities short-range correlations between elongated molecules with large dipoles will result in the formation of chains with adjacent molecules in side by side antiparallel configuration. Such correlations are expected to be important also at liquid densities, and they will most probably suppress long range ferroelectric order. Thus the simple model of a rigid molecule with large permanent dipole cannot be used to explain the ferroelectric ordering in polar nematics and more sophisticated models are required. This is not surprising from the experimental point of view as it is well known that small changes in the location and orientation os some molecular dipoles may lead the loss of the ferroelectric phase despite the fact that the total dipole remains approximately the same.

B. Models based on polarized charge distribution

Existing ferroelectric nematic LCs are composed of strongly polar molecules with several dipoles located in various parts of the molecular structures. In this case it may be more reasonable to to consider a model with a certain charge distribution on the molecular surface with some areas positively charged and other areas with negative charge density. The simplest model of this kind is the rigid elongated molecule with effective positive charge $+Q$ at one end and the corresponding negative charge $-Q$ at another end (see Fig.4). The electrostatic interaction energy between such molecules is the sum of all charge-charge
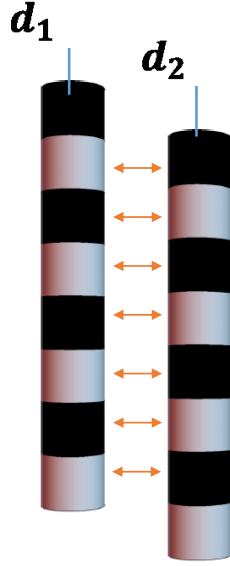
14

FIG. 4: Low energy configuration for two mutually shifted rod-like molecules with modulated surface charge density.

interaction potentials:

$$U_{QQ}(1,2) = \frac{Q^2}{R_{++}} + \frac{Q^2}{R_{--}} - \frac{Q^2}{R_{+-}} - \frac{Q^2}{R_{-+}}, \tag{27}$$

where R_{ij} is the distance between the charge i in the molecules 1 and the charge j in the molecule 2 which depends on the relative orientation of the two molecules, $i, j = (+, -)$.

The contribution of this charge-charge interaction to the mean-field free energy is given by the same Eq.(17) where the dipole-dipole interaction potential is replaced by the potential (27). The free energy contribution contains a similar volume integral of the charge-charge potential:

$$\int_{r_{12}>\xi(1,2)} U_{QQ}(1,2)d^3\mathbf{r}_{12}. \tag{28}$$

One can readily see that if the distance l between the charge and the end of the molecule

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is sufficiently small, the integral (28) is dominated by the parallel head to tail configuration which corresponds to the lowest energy. In this configuration the predominant term in the potential (27) is the interaction energy between the positive charge of one molecule and the neighboring negative charge of the second molecule: $-Q^2/R_{+-} \sin -Q^2/2l$. One notes that this term is negative and hence the corresponding contribution to the free energy is also negative, and one can make a premature conclusion that the charge-charge interaction may promote ferroelectric ordering. This conclusion, however, is incorrect for the same reason as the corresponding conclusion in the case of dipolar hard spheres. Similar to the system of dipolar spheres the lowest energy corresponds to parallel head to tail configuration and hence, at low densities, it is more energetically favorable for the system of elongated molecules with two opposite charges to form chains rather then to exhibit the nematic ferroelectric phase (See Fig.3 b).

In the high density nematic phase there are no individual chains but there should be strong head to tail parallel correlations. At the same time one expects that equally strong antiparallel side by side correlations should exist in all directions perpendicular to the long molecular axis (see Fig.4). These correlations cannot be taken into account in the molecular-field approximation and at present there is no theory which can account for them. Thus it is reasonable to assume that charge-charge interactions in the this simple model cannot be responsible for the ferroelectric ordering in the nematic phase.

A more sophisticated model based on electrostatic interaction has been proposed by Madhusudana [41]. Mahusudana has considered a cylindrical rigid molecule with uniaxial surface charge density specified by four density waves (see Fig.5) of the same wavelength and different amplitudes and phases. As a result some parts of the surface are negatively charged while the adjacent parts are characterised by positive charge density. One can readily see that the parallel side by side configuration with full overlap is energetically unfavorable because all neighboring parts of the two molecules possess the charge densities of the same sign and hence the molecules repel each other in this configuration. In contrast, in the antiparallel side by side configuration with full overlap the molecules attract each other and thus the antiparallel orientation of the adjacent molecules is more favorable. It has been shown in [41], however, that for some values of the parameters the minimum of the interaction energy is achieved when the adjacent molecules are parallel but one of them is shifted with respect to another in such a way that the negatively charged pars of the

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molecular surface are in contact with the positively charged ones. This conclusion has also been supported by considering a cluster of parallel molecules with molecular cross sections located on the hexagonal lattice [41]. This is an indication that the electrostatic interaction, proposed by Madhusudana, may be responsible for ferroelectric ordering in nematic LCs.

At the same time this result does not seem to be sufficient because one has to show that the contribution of this electrostatic interaction to the free energy is negative and sufficiently large to overcome the orientational entropy. Only in this case the interaction can drive the transition into the ferroelectric phase. In the mean-field approximation such a contribution is given by Eq.(6) where the dipole-dipole potential is replaced by the corresponding interaction between surface charges. In the simple case of parallel molecules the contribution to the free energy density is determined by the integral of the potential over the intermolecular vector $\mathbf{r}_{12}$. This integral is an average over all configurations of the two molecules and not just over the two ones considered in [41]. Taking into account that the the potential itself is a four fold integral over the surface densities of the two molecules, the final free energy contribution contains the seven fold integral which is difficult to evaluate even numerically.

C. Orientational-positional correlations and the origin of ferroelectric ordering.

We have seen in the previous two subsections that various dipole-dipole and charge-charge interactions between rod-like polar molecules can hardly be responsible for the ferroelectric ordering in nematic LCs, at least in the framework of simple models. This is partially related to the fact that dipole-dipole potential vanishes after integration over all intermolecular unit vectors which means that there is a delicate balance between negative and positive energies of parallel and antiparallel configurations, respectively. On the other hand, there exists the nonchiral LC phase where the simple dipole-dipole may indeed drive the transition into the ferroelectric phase which has been observed experimentally. This is the ferroelectric smectic A phase exhibited by bent-core molecules with large transverse dipoles [45–47]. In the case of perfect smectic order the centres of bent-core molecules are located in the smectic planes. Then it is reasonable to assume in the first approximation that the interaction of molecules within one smectic layer is significantly stronger than the interaction between different layers. In this case it is sufficient to average the dipole-dipole interaction over the intermolecular vector $\mathbf{r}_{12}$ assuming that $\mathbf{r}_{12}$ is parallel to the smectic plane. As a result one obtains the

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following 2D integral:

$$< V_{dd}(1,2) >_{2D} = \int \int_{r_{12}>D} \frac{1}{r_{12}^3} \left((\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{u}_{12})(\mathbf{d}_2 \cdot \mathbf{u}_{12}) \right) r_{12} dr_{12} d\mathbf{u}_{12}, \qquad (29)$$

where $\mathbf{u}_{12}$ is the 2D unit intermolecular vector which is also parallel to the smectic plane.

It is interesting to note that, in contrast to the 3D case, the integral (29) is not ill defined. Indeed, the integral does not vanish after the integration over the 2D unit vector $\mathbf{u}_{12}$ and it does not diverge when $r_{12} \to \infty$. As a result the integral (29) can easily be evaluated analytically:

$$< V_{dd}(1,2) >_{2D} = -\frac{1}{2} D^{-1}(\mathbf{d}_1 \cdot \mathbf{d}_2). \qquad (30)$$

One can readily see from Eq.(30) that in the 2D case the averaged dipole-dipole interaction potential is negative and is increasing proportionally to the square of the dipole moment. Thus for sufficiently large dipoles the negative contribution of the dipole-dipole interaction to the free energy, which promotes the ferroelectric ordering, can overcome the positive contribution from the orientational entropy which promotes the disordered phase. A detailed molecular-statistical theory based on these ideas together with phase diagrams is presented in [48].

Simple estimates presented above cannot be directly applied to nematic LCs because they do not possess any translational order. However, similar results can also be obtained by taking into account orientational-translational intermolecular correlations. The existence of such correlations indicates that different relative orientations of the two molecules have different probability and hence the averaging of the dipole-dipole potential appears to be more complicated. From this point of view the strong smectic order corresponds to very strong positional correlations when the two adjacent molecules are located either in the same smectic layer or in adjacent layers, while all intermediate configurations have very low probability. In order to take these correlations into account one has to go beyond the mean-field approximation. The corresponding correlation statistical theories of anisotropic fluids are very complex but at the same time there exists the second order thermodynamic perturbation theory which enables one to estimate the contribution of a certain part of the pair interaction potential mediated by pair correlations.

In the second order thermodynamic perturbation theory [43] the free energy of the polar

nematic can be written in the form:

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

(31)

where F_0 is the ground state free energy which does not depend on the dipole-dipole inter-
action. Here $g_2(1,2) = g_2(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2)$ is the pair correlation function in the nonpolar 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:

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

(32)

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 only few first order terms which depend only on two unit vectors,
the pair correlation function can be approximated in the following elementary way:

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

(33)

where the coefficients $g_{20}(r_{12}), G(r_{12})$ and $N(r_{12})$ rapidly decay with the increasing r_{12} as
the correlations are short-range.

Substituting Eq.(33) into Eq.(31) one obtains the following contribution to the free energy
in the case of perfect orientational order:

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

(34)

where $P = \rho d$ is the polarization. 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 Eq.(34) obviously promotes the ferroelectric ordering but
this conclusion crucially depends on the sign of the function $G(r_{12})$ which must be positive.
It should be noted also that elementary calculations presented in this subsection are based
on the interaction between total effective molecular dipoles, i.e the particular structure of the
polar molecules does not seem to be important here. However, the last conclusion is incorrect
because in this model the ferroelectric ordering is impossible without strong intermolecular
correlations of the particular type. Such correlations are expected to be strongly effected by
location and orientation of permanent dipoles within the molecular structure or, equivalently,
by the charge distribution at the molecular surface.

Indeed, let us consider 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. If the function $G(r_{12})$ is positive the maximum of the correlation function corresponds to $\mathbf{u}_{12} \parallel \mathbf{a}$ i.e. it promotes the slide of a molecule with respect to the neighboring one. It is interesting to note that in the Madhusudana model [41] the minimum energy configuration of the two neighboring molecules is the one where a molecule is shifted with respect to the second one.

In conclusion we would like to emphasise that a consistent molecular-statistical theory of ferroelectric nematics, which takes into account intermolecular correlations, should also include a calculation of the correlation function itself. This kind of theory is not available at present and the corresponding formalism is in progress.

IV.   ELECTROSTATICS OF THE FERROELECTRIC NEMATIC PHASE.

A.   Two conjugated thermodynamic potentials.

Electrostatic properties of dielectric materials are conventionally described using the two thermodynamic potentials which depend on the macroscopic electric field in the medium $\mathbf{E}$ or on the electric induction vector $\mathbf{D}$, respectively. In the case of ferroelectric materials one also employs the so called conditional thermodynamic potentials which also depend on the polarization $\mathbf{P}$ and which are used in the Landau theory of phase transitions. The derivation and the detailed discussion of these potentials can found, for example, in the seminal book of Landau and Lifschits "Electrodynamics of continuum media [44].

In the general case it is possible to introduce the thermodynamic potential $F(T, \mathbf{E})$ which determines the dielectric properties of the material at fixed electric field $\mathbf{E}$, and the potential $G(T, \mathbf{D})$ which is defined at fixed $\mathbf{D}$. The electric field at fixed $\mathbf{D}$ is determined by the partial derivative of the potential $G(T, \mathbf{D})$:

$$\mathbf{E} = 4\pi \frac{\partial G(T, \mathbf{D})}{\partial \mathbf{D}}\Big|_T, \tag{35}$$

while the induction $\mathbf{D}$ at fixed $\mathbf{E}$ is determined as the derivative of $F(T, \mathbf{E})$:

$$\mathbf{D} = -4\pi \frac{\partial F(T, \mathbf{E})}{\partial \mathbf{E}}\Big|_T. \tag{36}$$

These potentials are often called conjugated as they are related by the Legendre transfor-

mation, i.e.

$$F(T, \mathbf{E}) = G(T, \mathbf{D}) - \frac{1}{4\pi} \mathbf{E} \cdot \mathbf{D}. \tag{37}$$

Recall a similar relationship between the Gibbs potential $\Phi(T, V)$ which depends on the system volume V and the Helmholz potential $H(T, P)$ which depend on pressure P:

$$\Phi(T, V) = H(T, P) - PV, \tag{38}$$

where P and V are also conjugated thermodynamic variables.

In the description of the ferroelectric phase it is convenient to introduce the so called conditional thermodynamic potentials $\tilde{G}(T, \mathbf{P}, \mathbf{E})$ and $\tilde{F}(T, \mathbf{P}, \mathbf{D})$ [44] which also depend on the macroscopic polarization $\mathbf{P}$. Here the polarization is determined by minimization of these potential with respect to $\mathbf{P}$ at fixed $\mathbf{E}$ or $\mathbf{D}$, respectively:

$$\frac{\partial F(T, \mathbf{P}, \mathbf{E})}{\partial \mathbf{P}}\bigg|_{T, \mathbf{E}} = 0, \tag{39}$$

or

$$\frac{\partial G(T, \mathbf{P}, \mathbf{D})}{\partial \mathbf{P}}\bigg|_{T, \mathbf{D}} = 0, \tag{40}$$

where we have dropped the tilde over the conventional thermodynamic potentials for simplicity.

Integrating the equation

$$4\pi \frac{\partial F(T, \mathbf{P}, \mathbf{E})}{\partial \mathbf{E}}\bigg|_T = -\mathbf{D} = -\mathbf{E} - 4\pi \mathbf{P}, \tag{41}$$

over $\mathbf{E}$ at fixed polarization $\mathbf{P}$ one obtains the following expression for the potential $F(T, \mathbf{P}, \mathbf{E})$:

$$F(T, \mathbf{P}, \mathbf{E}) = F_0(\mathbf{P}, T) - (\mathbf{P} \cdot \mathbf{E}) - \frac{E^2}{8\pi}, \tag{42}$$

where the potential $F_0(\mathbf{P}, T)$ depends only on polarization $\mathbf{P}$. Here we ignore the dependence of the potential on density and other thermodynamic variables which are not relevant for this simple consideration.

According to the well known Landau theory the potential $F_0(\mathbf{P}, T)$ can be expanded in powers of polarization P if P is relatively small:

$$F_0(\mathbf{P}, T) = \frac{1}{2}\alpha \left(T - T_c\right) P^2 + \frac{1}{4}bP^4 + ..., \tag{43}$$

where T_c is the temperature of the second order transition into the ferroelectric phase.

The potential $F(\mathbf{P}, \mathbf{E}, T)$ is defined at fixed macroscopic electric field $\mathbf{E}$. Experimentally it is possible to control the voltage V applied to the flat nematic LC cell and hence only the average electric field $\mathbf{E}_0 = V/l$ where l is the cell thickness. Thus simple expressions presented in this section are formally valid only in the case of the homogeneous electric field and polarization. The thermodynamic potentials for inhomogeneous ferroelectric nematics are more complex and are briefly discussed below.

In the case of fixed electric field minimization of the potential $F(\mathbf{P}, \mathbf{E}, T)$ together with Eq.(42) with respect to $\mathbf{P}$ yields the following well known expression for the polarization:

$$\alpha \left(T - T_c\right) P + bP^3 = E. \tag{44}$$

Differentiating both sides of Eq.(44) with respect to $\mathbf{E}$ one obtains

$$\left(\alpha \left(T - T_c\right) + 3bP^2\right) \frac{dP}{dE} = 1. \tag{45}$$

Hence the expression for the polarizability $\chi = dP/dE|_{E=0}$ of the ferroelectric material is obtained from Eq.(45):

$$\chi = \frac{dP}{dE} = \frac{1}{\alpha \left(T - T_c\right) + 3bP^2}. \tag{46}$$

In the paraelectric phase $P = 0$ and hence the polarizability obeys the Curie-Weiss law:

$$\chi_p = \frac{1}{\alpha \left(T - T_c\right)}. \tag{47}$$

In contrast, in the ferroelectric phase it follows from Eq.(44) at $E = 0$ that $bP^2 = -\alpha \left(T - T_c\right)$. Substituting this into Eq.(46) one obtains:

$$\chi_f = \frac{1}{2\alpha \left(T_c - T\right)}. \tag{48}$$

Thus the dielectric susceptibility of the ferroelectric phase is two times smaller than that of the paraelectric phase which is also a well known result [44].

Substituting Eqs.(43) into Eq.(37) one obtains also the expression for the second potential $G(T, \mathbf{P}, \mathbf{D})$:

$$G(T, \mathbf{P}, \mathbf{D}) = F_0(\mathbf{P}, T) + \frac{1}{8\pi} \left(D - 4\pi P\right)^2$$
$$= \frac{1}{2}\alpha \left(T - T_c\right) P^2 + \frac{1}{4}bP^4 + 2\pi P^2 - (\mathbf{D} \cdot \mathbf{P}) + \frac{1}{8\pi}D^2. \tag{49}$$

One notes that the potential $G(T, \mathbf{P}, \mathbf{D})$ contains the term $2\pi P^2$ which does not enter the expression for $F(T, \mathbf{P}, \mathbf{E})$. This term is often called "self energy" and is related to the

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electrostatic energy of the sample. This term is quadratic in polarization P and hence it shifts the transition temperature into the ferroelectric phase which is now expressed as $T_c' = T_c - 4\pi/\alpha$.

B.   Coupling between the polarization and the nematic order parameter.

The standard description presented in the previous subsection is oversimplified as it does not take into account the role of the nematic order parameter. In the ferroelectric nematic phase the thermodynamic potentials F and G depend also on the nematic tensor order parameter $Q_{ij} = S(n_i n_j - (1/3)\delta_{ij})$ which is again determined by minimization of the corresponding potential. The lowest order coupling term between the polarization and the nematic tensor has the form $-(1/2)BP_i Q_{ij} P_j$. Neglecting the higher order coupling terms, the potential F is approximately expressed as:

$$F(T, \mathbf{P}, \mathbf{E}) = \frac{1}{2}\alpha \left(T - T_c \right) P^2 - \frac{1}{2}BP_i Q_{ij} P_j + \frac{1}{4}bP^4 - (\mathbf{P} \cdot \mathbf{E}) - \frac{E^2}{8\pi}, \tag{50}$$

Assuming that the spontaneous polarization P_0 at zero electric field is parallel to the director $\mathbf{n}$ (i.e. $B > 0$)one obtains by minimization of the potential (50):

$$P_0 = \frac{\alpha}{b} \left(T_{c,\parallel} - T \right)^{1/2}, \tag{51}$$

where $T_{c,\parallel} = T_c + 2SB/3\alpha$. Thus the nematic LC undergoes the transition into the ferroelectric nematic phase at $T = T_{c,\parallel}$.

In the case of nonzero electric field the total polarization can be expressed as a sum of two contributions, $\mathbf{P} = \mathbf{P}_\parallel + \mathbf{P}_\perp$, where $\mathbf{P}_\parallel$ is parallel to the director $\mathbf{n}$ while $\mathbf{P}_\perp$ is normal to the director. Minimization of the potential (50) yields the two independent equations for $P_\parallel$ and $P_\perp$ in the paraelectric nematic phase:

$$\alpha \left(T - T_c \right) P_\parallel - \frac{2}{3}BSP_\parallel = E_\parallel,$$

$$\alpha \left(T - T_c \right) P_\perp + \frac{1}{3}BSP_\perp = E_\perp. \tag{52}$$

Thus the longitudinal and the transverse dielectric polarizability of the paraelectric nematic phase are given by the following expressions:

$$\chi_\parallel = \frac{1}{\alpha \left(T - T_{c,\parallel} \right)}, \tag{53}$$

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and

$$\chi_\perp = \frac{1}{\alpha \left(T - T_{c,\perp}\right)},\tag{54}$$

where $T_{c,\perp} = T_c - SB/3\alpha$.

It should be noted that only the polarizabiity $\chi_\|$ diverges at the second order transition temperature $T_{c,\|}$ into the ferroelectric phase while transverse polarizability $\chi_\perp$ remains finite.

C. Different thermodynamic potentials for different boundary conditions and experimental consequences

As discussed above, there exist two conjugated thermodynamic potentials for ferroelectric nematics which depend either on the macroscopic electric field $\mathbf{E}$ or on the electric induction $\mathbf{D}$. Thus the equilibrium state of the ferroelectric nematic corresponds to the minimum of one of these potentials. The correct potential, which should be used in every particular case, is determined by the boundary conditions.

Let us consider for simplicity the flat nematic LC cell with conducting electrodes on the two parallel surfaces. It is well known that the electric field in the LC medium can be controlled experimentally by applying the voltage V. Assuming that the electric field and the polarization are homogeneous one concludes that the macroscopic electric field $E = V/l$, where l is the cell thickness, and $\mathbf{E}$ is parallel to the z axis which is normal to the cell surface. In this case one has to use the potential $F(T, \mathbf{P}, \mathbf{E})$ which depends on the electric field and which is given by Eq.(50). Minimization of this potential yields the following equation for the equilibrium polarization:

$$\alpha \left(T - T_c\right)\mathbf{P} - \frac{1}{3}BS\left(2\mathbf{P}(\mathbf{P}\cdot\mathbf{n})\right) + bP^2\mathbf{P} = \mathbf{E}.\tag{55}$$

One notes that in the absence of the electric field the minimum of the potential corresponds to $\mathbf{P} \parallel \mathbf{n}$ if $B > 0$ while in the case of nonzero field the total polarization deviates slightly from $\mathbf{n}$.

The important particular case here corresponds to the LC cell with short circuited electrodes. In this case the applied voltage $V = 0$ and hence the average electric field in the LC medium vanishes. Then the spontaneous polarization is determined by Eq.(51) and it is parallel to the director $\mathbf{n}$.

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Now let us consider the nematic LC cell with disconnected electrodes. In such a system the electric field cannot be controlled experimentally while the electric induction $\mathbf{D}$ can be specified by fixing the density σ of the external charges at the electrodes because the normal component $D_z = 4\pi\sigma$. One notes that only the component D_z can be controlled experimentally in such a cell. Thus the properties of such a system should be described by minimization of the potential $G(T, \mathbf{P}, D_z)$ which is defined as a function of D_z. The most important particular case of a system with disconnected electrodes is the so called free sample without any external charges. In this case the normal component of $\mathbf{D}$ vanishes, i.e. $D_z = P_z + E = 0$ and therefore the electric field in the nematic medium $E = -P_z$. This means that in the nematic materials with high spontaneous polarization the macroscopic electric field in the free cell with disconnected electrodes is also very large. As a result the electrostatic energy density in the system is also very large and this state is globally unstable. It is well known that in solid ferroelectrics the positive electrostatic energy is reduced by splitting into domains. However, in ferroelectric nematics the situation is more complicated because sharp domain boundaries in a fluid are also unstable. Instead it is more likely that the ferroelectric nematic cell with disconnected electrodes will exhibit some kind of a striped structure with inhomogeneous director distribution.

The free energy density $G(T, \mathbf{P}, D_z)$ for the homogeneous flat ferroelectric nematic cell is generally given by the expression $G(T, \mathbf{P}, D_z) = F(T, \mathbf{P}, E_z) + E_z D_z / 4\pi$ where we have taken into account that the electric field in such a cell is always parallel to the z-axis which is normal to the surfaces. Here $F(T, \mathbf{P}, E_z)$ is given by Eq.(50) with $E = E_z$ and hence:

$$G(T, \mathbf{P}, D_z) = \frac{1}{2}\alpha\left(T - T_c\right)P^2 - \frac{1}{2}BP_iQ_{ij}P_j + \frac{1}{4}bP^4 - P_zE_z - \frac{E_z^2}{8\pi} + E_zD_z/4\pi$$

$$= \frac{1}{2}\alpha\left(T - T_c\right)P^2 - \frac{1}{2}BP_iQ_{ij}P_j + \frac{1}{4}bP^4 + 2\pi P_z^2 - P_zD_z + \frac{1}{8\pi}D_z^2. \qquad (56)$$

It should be noted that here the "self energy" $2\pi P_z^2$ depends only on the z component of the polarization which contributes to the z component of $\mathbf{D}$.

It is reasonable to assume that in ferroelectric nematics with large spontaneous polarization the magnitude of the polarization is approximately constant while the orientation of the polarization in the fluid may easily change, at least in the bulk. In the free cell without external charges at the electrodes, which correspond to $D_z = 0$, the positive "self-energy" term is minimized when $P_z = 0$ i.e. the polarization is parallel to the surface of the cell. However, one should also take into account that the spontaneous polarization is strongly

coupled with the director because it is defined as the average of the transverse molecular dipole. Thus in a cell with strong homeotropic anchoring there is a balance between the electrostatic self energy and the anchoring energy of the director at the surface. As a result the polarization may tilt with respect to the surface normal. In the case of infinitely strong anchoring the polarization remains normal to the surface at the surface but may tilt in the bulk creating an inhomogeneous polarization profile.

The general results presented in this subsection may have significant experimental consequences. In particular, it should be taken into consideration that both the magnitude and the orientation of the polarization may be different in ferroelectric nematic cells with applied voltage or with disconnected electrodes, respectively, because the equilibrium state of the system in these two cases correspond to the minimum of two different thermodynamic potentials. For example, if the ferroelectric nematic cell is prepared with disconnected electrodes and then the voltage if applied, the orientation of the polarization or the polarization profile may change even when the applied voltage is small. The thing is that in the free cell wit disconnected electrodes the macroscopic electric field in the nematic medium is very large if the spontaneous polarization is large. As discussed above, in this case the electric field $E_z = -4\pi P_z$, i.e. it is of the same order as the spontaneous polarization. In contrast, in the case of small applied voltage the average macroscopic electric field in the ferroelectric nematic is also small, i.e. $E = V/l$. Thus applying the voltage (or simply connecting the electrodes which corresponds to zero applied voltage)results in a dramatic reduction of the electric filed in the nematic medium which may effect the ferroelectric properties. In a similar way, disconnecting the electrodes after electro-optical measurements under applied voltage will result in the strong increase of the electric filed which may change the spontaneous polarization and thus effect the results, obtained using other experimental techniques (for example, the optical measurements) which do not require any applied voltage. Also, if the electrodes are disconnected too fast, some nonzero charge density may be left at the electrodes, and this will result in nonzero D_z which is coupled with polarization according to Eq.(56) and which may also effect the ferroelectric properties.

D.   Inhomogeneous polarization and the inhomogeneous electric field

So far we have considered the idealised ferroelectric nematic cell with homogeneous polarization and homogeneous macroscopic electric field.However, it is very much possible that in real ferroelectric nematics the spontaneous polarization follows some spacial pattern (like in the splay nematic phase) or, at least, there exist a boundary region where the orientation or the magnitude of the polarization changes from the boundary to the bulk value. It follows from the general principles of thermodynamics that in such inhomogeneous systems the equilibrium polarization profile should also correspond to a minimum of some thermodynamic potential. At the same time the derivation of such a potential is not straightforward. Indeed, on the first sight it may be possible to introduce the conditional potentials $F(T, \mathbf{P}, \mathbf{E})$ and $G(T, \mathbf{P}, \mathbf{D})$ where all fields $\mathbf{P}, \mathbf{E}, \mathbf{D}$ are inhomogeneous, and to use expressions for the potentials obtained in the previous subsections. It should be emphasised, however, that both the derivation and even the very definition of these potentials are inconsistent because the inhomogeneous polarization $\mathbf{P}(\mathbf{r})$ and the inhomogeneous electric field $\mathbf{E}(\mathbf{r})$ in the medium are not independent.

Indeed, let again consider the homogeneous (in x, y directions) nematic Lc cell where $F(T, \mathbf{P}$ and $\mathbf{E})$ may only depend on z. It follows then from the equation $div\mathbf{D} = 0$ in the bulk that the component $D_z = const$ across the cell. At the same time $D_z = 4\pi P_z(z) + E(z) = const$. Integrating this equation over z from 0 to l one also obtains:

$$E_{av} + 4\pi P_{av} = 4\pi P_z(z) + E(z) = const, \tag{57}$$

where $P_{av} = (1/l) \int_0^l P_z(z)dz$ and $E_{av} = (1/l) \int_0^l E(z)dz$ are the average polarization and the average electric field , respectively.

Now the polarization and the electric field can be expressed as a sum of the homogeneous and inhomogeneous parts, i.e. $E(z) = E_{av} + \delta E(z)$ and $P_z(z) = P_{av} + \delta P_z(z)$. Substituting these expressions into Eq.(57) one obtains that $\delta E(z) = -4\pi \delta P_z(z)$ which means that the inhomogeneous part of the polarization is linearly related to the inhomogeneous part of the macroscopic electric field. Thus it is impossible to minimise the thermodynamic potential with respect to the inhomogeneous polarization keeping the inhomogeneous electric field fixed because fixing the inhomogeneous part of the electric field means that the corresponding part of the spontaneous polarization is also fixed. In a similar way it is also impossible to integrate over $E(z)$ at fixed $P(z)$ which is required in Eq.(41). Thus one concludes that

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the potential F can only depend on the average macroscopic electric field E_{av} which is independent from the polarization $P_z(z)$ .Differentiating the potential $F(T, E_{av}, P_z(z))$ with respect to to E_{av} one obtains:

$$\frac{\partial F}{\partial E_{av}} = -D_z = -E_{av} - 4\pi P_{z,av}. \tag{58}$$

Now Eq.(58) can be integrated over E_{av} at fixed full polarization $\mathbf{P}$ yielding the following expression

$$F(T, E_{av}, P_z(z)) = F_0(T, \mathbf{P}) - E_{av} P_{z,av} - \frac{1}{2} E_{av}^2. \tag{59}$$

Here the potential $F_0(T, \mathbf{P})$ depends on the inhomogeneous polarization and hence one should include the gradient term into the expansion Eq.(56):

$$F_0(T, \mathbf{P}) = \frac{1}{2}\alpha\left(T - T_c\right) P^2 - \frac{1}{2} B P_i Q_{ij} P_j + \frac{1}{4} b P^4 + \kappa(\nabla \mathbf{P})^2 + ..., \tag{60}$$

where $(\nabla \mathbf{P})^2 = \nabla_i P_j \nabla_i P_j$.

V. CONCLUSIONS

In this review we have considered the possible molecular origin of the ferroelectric ordering in strongly polar nematic LCs taking into consideration various polar interactions and orientational-translational correlations. We have seen that electrostatic interaction between permanent longitudinal molecular dipoles can hardly be responsible for ferroelectric ordering regardless the value of the dipole or its location within the molecular volume, at least in the mean-field approximation. In addition, the contribution of the dipole-dipole interaction to the total free energy of the ferroelectric nematic depends on the sample shape and boundary conditions. This is related to the long-range character of the dipole-dipole interaction.

Another class of models is based on electrostatic interaction between molecular charge densities. Such models, in principle, can better reflect the actual polar molecular structure although simple models can hardly be successful as well. For example, the simplest possible interaction between the pairs of opposite charges located at the two ends of the molecule also cannot be responsible for the ferroelectric ordering. This interaction promotes ferroelectricity in the mean-field approximation but at least at low densities the free energy is more effectively reduced by formation of polar chains similar to the system of strongly dipolar spheres. At liquid densities typical for nematic LCs individual chains can no longer

be stable but there should be strong head to tail parallel correlations counterbalanced by equally strong antiparallel side by side correlations which are expected to supress the long range dipolar order.

A more sophisticated model of Madhusudana [41] , based on electrostatic interaction between surface charge densities is more promising. In this model the molecular surface is characterised by charge density of alternating sign, and for some values of the parameters the minimum of the interaction energy between parallel adjacent molecules is achieved when one molecule is shifted with respect to another in such a way that the negatively charged parts of the molecular surface are in contact with the positively charged ones. The interaction energy in this configuration is lower then that of the antiparallel configuration which is an indication that such interaction may promote the ferroelectric ordering. At the same time these results are incomplete because it is important to show that the corresponding intermolecular interaction makes a contribution to the free energy density of the proper sign. This contribution contains the integral of the potential over the intermolecular vector $\mathbf{r}_{12}$ which is an average over all configurations of the two molecules beyond the two ones which correspond to the minimum energy. Numerical evaluation of this integral is a challenging task and has not been undertaken so far.

The third model combines the effect of the dipole-dipole interaction with that of the short-range orientational-transitional pair correlations. These correlations give additional statistical weight to some relative configurations of the two adjacent molecules and as a result even the interaction between permanent molecular dipoles results in the contribution to the free energy which promotes ferroelectricity. It should be noted that this model is also incomplete because in principle the corresponding relevant terms in the expansion of the correlation function should be calculated in the framework of the same molecular-statistical theory which has not been achieved so far.

The consideration of different molecular models for ferroelectric nematics has been supplemented by the discussion of the general theory of dielectric properties of ferroelectric nematic LCs based on the two conjugated thermodynamic potentials. The first potential $F(T, \mathbf{P}, \mathbf{E})$ depends on the macroscopic electric field $\mathbf{E}$ in the nematic medium and on the polarization $\mathbf{P}$ which is determined by the minimization of this potential. The second potential $G(T, \mathbf{P}, \mathbf{D})$ depends on the electric displacement $\mathbf{D}$ and the polarization $\mathbf{P}$ which is also determined by minimization. The potential F defines the equilibrium state of the

system at fixed macroscopic electric field while the potential G specifies the equilibrium state at fixed $\mathbf{D}$ which is related to the density of external charges at the sample surface. From the experimental point of view the potential F describes the properties of the nematic LC cell with applied voltage while the potential G corresponds to the same LC cell with disconnected electrodes. In the latter case the normal component of $\mathbf{D}$ is proportional to the remaining density of external charges at the electrodes (which is equal to zero in the simplest case of free sample). The most important conclusion here is that the absolute value and the orientation of the spontaneous polarization corresponds to the minimum of one of these potentials depending on boundary conditions, i.e they may be different in the same cell with fixed applied voltage or the density of external charges at the electrodes.

In addition to the general theoretical significance this results in a number of experimental consequences. For example, if the voltage is applied to the ferroelectic nematic cell which has been originally prepared with disconnected electrodes,the magnitude and the orientation of the polarization may change even when the applied voltage is small. This is determined by the fact that application of a small voltage results in a dramatic reduction of the electric filed in the nematic medium which may effect the ferroelectric properties. In a similar way, disconnecting the electrodes after some measurements under applied voltage will result in the strong increase of the electric field which may change the spontaneous polarization and thus effect the results obtained applying other experimental techniques to the free cell.

Finally one notes that the properties of ferroelectric nematic liquid crystals are rather different from the properties of solid ferroelectrics mainly because the spontaneous polarization may easily rotate in the fluid medium. As a result there are many interesting particular cases which have not been studied theoretically so far and thus both the molecular and the continuum theory of ferroelectric nematics is still in progress.

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