Ferroelectric instability in semiflexible liquid crystalline polymers of directed dipolar chains

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Abstract. A ferroelectric instability is predicted to occur in an experimentally accessible temperature range in a main-chain (semiflexible) liquid crystalline polymer with directed polar mesogenic segments. The long-range part of the dipole–dipole interaction is separated and its effect is completely accounted for in the average electric field. The remaining (local) free energy density is derived in the form of an expansion in powers of the spontaneous polarization. We derive simple expressions for the instability temperature and the polar mean-field coupling in a polar nematic polymer in terms of the molecular model parameters. Using simple estimates we show that ferroelectric ordering is more likely to occur in nematic polymers with directed polar segments than in low molecular weight nematic liquid crystals composed of polar molecules.

1. Introduction

It has long been understood that, in principle, a phase transition can take place in an isotropic liquid so that it spontaneously becomes polar. The continuum theory [1, 2] states that an isotropic liquid composed of polar molecules can undergo a second-order transition into a ferroelectric phase with symmetry $C_{\infty v}$. If the liquid is composed of chiral molecules, the transition is first order and the hypothetical ferroelectric phase is helicoidal.

In spite of these general arguments ferroelectric ordering in isotropic liquids has not yet been observed. This fact indicates that there are some strong microscopic effects that resist the appearance of polarization in a liquid, even when the permanent dipole moment of individual molecules is sufficiently large. Thus one has to look for some very specific systems to be able to expect a ferroelectric phase transition.

One direction is to search in a nematic liquid crystal phase which already has uniaxial symmetry. In such anisotropic liquids the molecular symmetry axes (long axes for rod-like particles and short ones for disk-like particles) are on average parallel and one can also expect polar ordering if the molecules possess large longitudinal dipoles. Several attempts have been made to include steric effects that would favour local polar alignment [3], in particular in a nematic of disk-like molecules. Regardless of the degree of success of these models, ferroelectric ordering phenomena in conventional nematic liquid crystals have not so far been observed.

From the microscopic point of view one finds immediately that the typical dipole–dipole interaction in a liquid is too weak to produce a thermodynamically stable local

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ordering. We can see this by introducing a dimensionless parameter $\rho m^2/k_B T$, where ρ is the number density and m is the molecular dipole. This parameter is the ratio of the average dipole–dipole interaction energy to the energy of thermal fluctuations. For typical molecular dipolar moments $|m| \sim 1$ D, and at typical densities and temperatures, one finds $\rho m^2/k_B T \sim 10^{-2}$, implying that the ferroelectric ordering must be destroyed by thermal molecular motion. On the other hand there exist nematic liquid crystals with very large molecular dipoles of about 5 D [4]. In this case the parameter $\rho m^2/k_B T \sim 1$. Unfortunately such nematic liquid crystals have a strong tendency to form dimers with antiparallel dipoles, while the appearance of a macroscopic polarization seems to be less favourable. However, these arguments remain qualitative and at the present time there is no consistent statistical theory which takes all these effects into consideration.

Recently the possibility of a ferroelectric phase transition in isotropic liquids and nematic liquid crystals has been supported by molecular dynamics [5] and Monte Carlo [6] simulations of polar ordering in simple dipolar liquids. However, in these simulations the polar ordering is sensitive to the boundary conditions, since the individual molecular dipoles interact with the reaction field from the surrounding dielectric. This field gives a negative contribution to the free energy of the form $-aT_c|P|^2$, which may produce an instability if the dielectric susceptibility of the medium surrounding the sample is sufficiently large. It is important that this kind of transition is stabilized *globally* by long-range dipolar forces. This is different from usual phase transitions where the order parameter appears as a result of a *local* instability and is determined by the short-range part of the interaction potential. When the susceptibility of the surrounding medium is small there is no transition and we do not know what will happen when this susceptibility is equal to that of the sample liquid itself (i.e. for the case of an infinite sample).

Dipolar nematic polymers are among the most promising materials in which to obtain polar ordering because the individual monomers' dipole moments m_k are already strongly correlated and consistently aligned along the chain. (This correlation becomes greatly enhanced in the nematic phase [7, 8].) Preparation of such materials requires sequential polymerization of asymmetric (polar) monomers [9] and is briefly discussed at the end of section 5. Recently Lam and Wang [10] have presented a simple mean-field theory to describe the ferroelectric transition in such polymer systems. These authors have assumed a polar form of the mean-field potential, acting on each monomer, $U \sim g(m_k \cdot P)$, and expressed the spontaneous polarization and the phase transition temperature in terms of the mean-field coupling constant. However, this theory may be considered as a semi-phenomenological one since it does not permit the transition temperature to be expressed in terms of molecular model parameters. Thus one cannot estimate the transition temperature for real nematic polymers and also cannot answer the question why these materials, rather than conventional nematics, are more likely to be polar.

Dipolar nematic polymers are known to possess a large dielectric susceptibility [7, 8] which is determined by the cooperative responce of all polar momomers within a semi-rigid segment of the chain. Such a system will therefore be very sensitive to polarization fluctuations. As a result, the polar interaction between chains can cause ferroelectric ordering at reasonable temperatures and dipole strengths. Recently, Terentjev and Petcheck [12] calculated the dielectric susceptibility of a dipolar nematic polymer taking into account interchain interaction. In this theory it is shown that the susceptibility can diverge at a critical temperature which is a function of the dipole strength and the nematic order parameter. However, it is necessary to go further to construct a consistent theory of a ferroelectric phase transition in a nematic polymer. In particular, one must calculate the free energy as a function of the spontaneous polarization and take account, in a consistent

way, of contributions from the long-range part of the monomer dipole–dipole interaction.

In this paper we shall consider in detail the possibility of a ferroelectric phase transition in nematic polymer melts using the density functional approach. We shall derive the Landau-type expansion of the corresponding free energy in powers of the macroscopic polarization P and discuss the ferroelectric instability which manifests itself in the sign inversion of the familiar quadratic term $a(T - T_c)P^2$. However, we shall not analyse the actual equilibrium structure of the low-temperature ferroelectric phase, although we shall return to this important question in the discussion. We shall show that the ferroelectric instability temperature T_c is roughly proportional to the persistence length of the polymer L_{segm} which rapidly increases with the growth of the nematic order parameter. As a result, the estimated values of the instability temperature may be in an experimentally accessible range for realistic values of the dipole strength. This explains why dipolar nematic polymers seem more likely to be ferroelectric than low molecular weight nematic liquid crystals. Indeed, in conventional nematics the corresponding instability temperature is of the order of $(d/L)\rho d^2/k_B$, where d is the molecular diameter, while in nematic polymers the temperature T_c is proportional to the additional factor $L_{segm}/L \gg 1$, where L is the monomer length.

This paper is arranged as follows. In section 2 we discuss the density functional of the polymer melt in the mean-field approximation including the free energy of a single chain and the interaction between different chains. We also present a simple method for substracting the long-range part of the dipole–dipole interaction, which is then absorbed in the energy of the average electric field in the medium. In section 3 we consider a perturbation theory for the configurational entropy of the polymer chain in a polar mean field and derive an expression for the free energy as a function of the average polarization. In section 4 we derive explicit expressions for the polar mean field and for the ferroelectric instability temperature. Finally, in section 5 we summarize our conclusions and compare the possibilities of observing a ferroelectric instability in nematic polymers and low molecular weight nematics.

2. Density functional of the polar nematic polymer

2.1. Interaction energy of polar monomers on the polymer chain

We consider a system of N_{ch} interacting semiflexible chains, consisting of polar monomers with dipole moments $m_i = mu_i$ along the chain (the monomer's index i runs from 1 to N for each chain, u is the tangential unit vector—the long axis of a monomer). The Hamiltonian for this system can be written in the form $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int}$, where $\mathcal{H}_0$ describes the penalty for bending the individual chains and $\mathcal{H}_{int}$ includes all relevant pair interactions:

$$\beta\mathcal{H}_0 = -\sum_{\alpha}^{N_{ch}}\sum_{i}^{N}\Omega(u_i^\alpha \cdot u_{i+1}^\alpha) \sim \frac{1}{2}\Omega\sum_{\alpha}^{N_{ch}}\int_0^N ds \left(\frac{\partial u_\alpha}{\partial s}\right)^2$$

$$\mathcal{H}_{int} = \frac{1}{2}\sum_{\alpha,\beta}^{N_{ch}}\sum_{i,j}^{N}\mathcal{V}(i_\alpha, j_\beta)$$

(1)

where $\beta = 1/k_BT$, the last expression for $\mathcal{H}_0$ corresponds to the worm-like chain model [13], and s is the continuous representation of the integer index i. The molecular field approximation applied to such a polymer system can be interpreted as a substitution of $\mathcal{H}_{int}$ by a mean-field potential acting on each given monomer:

$$U^{MF}(u_{i_\alpha}) = \rho \int \mathcal{V}_{eff}(i_\alpha, j_\beta) f(j_\beta)\, d\{j_\beta\}$$

(2)

where ρ is the number density, $f(j_\beta)$ is the proper one-particle distribution function and $d\{j_\beta\}$ represents integration over all degrees of freedom of the corresponding monomer with its index j located on the chain indexed β. The free energy of the system of N_{ch} chains can then be written in the form

$$\mathcal{F} = -N_{ch}k_B T \ln \mathcal{Z}_N - \frac{1}{2}\rho^2 \int \mathcal{V}_{eff}(1,2)f(1)f(2)\,d\{1\}\,d\{2\} \tag{3}$$

where $\mathcal{Z}_N$ is the partition function of an individual chain in the mean field and the second term contains the average energy of the pair interaction between two arbitrary monomers '1' and '2' in the system. The effective pair potential $\mathcal{V}_{eff}$ is usually determined by an expansion of the Mayer's function, $f_{12} = k_B T\,(-1 + \exp[-\beta\mathcal{V}(1,2)])$ in powers of the soft attraction potential

$$\mathcal{V}_{eff}(1,2) \approx \mathcal{V}_{att}(1,2)e^{-\beta V_{rep}(1,2)} - k_B T\left[e^{-\beta V_{rep}(1,2)} - 1\right] \tag{4}$$

where V_{rep} is a hard-core (singular) repulsion potential. In the absence of long-range attraction forces this expression reduces naturally to the standard excluded volume interaction (isotropic, or anisotropic) [14]. In a molecular theory of polar polymers one has to take into account the dipole–dipole interaction between monomers.

$$\mathcal{V}_{dd}^{eff}(1,2) = m_1 \cdot \widehat{T}(r_{12}) \cdot m_2\,\Theta(\xi_{12} - r_{12}) \tag{5}$$

with the standart dipole–dipole operator $\widehat{T}_{ij}(r) = r^{-3}(\delta_{ij} - 3\hat{x}_i\hat{x}_j)$, where i, j are the Cartesian coordinate indices; the unit vector $\hat{x} = r/r$. The steric cut-off is represented here by a step function: $\exp[-\beta V_{rep}(i,j)] \rightarrow \Theta(\xi_{ij} - r_{ij})$, where $r_{ij} = |r_i - r_j|$ and ξ_{ij} is an (anisotropic) form factor—the minimal distance of approach of the two monomers i and j. This step function is equal to unity outside the restricted regions where the hard cores of the two monomers penetrate into each other, and is equal to zero inside (see [15] for more details). Assume, for generality, that there is an external electric field, E_0, also present in the system, which interacts with dipolar monomers via an additional potential $-(m \cdot E_0)$.

However, one cannot simply substitute the dipole–dipole potential (5) into the free energy (3) since the second term in (3) diverges after integration over r_{12}. This is the well known property of long-range dipole–dipole interactions, which must be treated with caution in the statistical theory of condensed matter. In fact one first has to separate the long- and short-range parts of the total potential.

The long-range part of the total interaction potential can be extracted by distinguishing between the average and fluctuating parts of the electric field which acts on a given molecule [16]. It is the interaction between the molecular dipoles and the average electric field in the media that appears to be long range. The average of this long-range part of the interaction is simply the energy of the electromagnetic field in the volume of the sample and can be considered within the context of continuum theory. The rest of the interaction (fluctuating part) appears to be short-range and can be treated by a statistical theory in the usual way. It should be noted that this is a standard procedure of the regularization of potentially divergent forces, first applied long ago by Ewald [17] in the theory of dielectrics. Below we consider in some detail the separation between the short- and long-range parts of the effective dipole–dipole interaction using the simple model of a classical fluid composed of non-polarizable molecules with permanent dipoles.

2.2. Long-range part of the dipole–dipole interaction

In the molecular field approximation the average interaction between permanent dipoles in a molecular liquid can be written as

$$U_d = \tfrac{1}{2}\rho^2 \int \mathcal{V}_{dd}(1,2) e^{-\beta V_{rep}(1,2)} f(1) f(2)\, d\{1\}\, d\{2\} - \rho \int (E_0 \cdot m) f(1)\, d\{1\} \tag{6}$$

where $\mathcal{V}_{dd}$ is the usual dipole–dipole interaction potential and $\mathcal{V}_{rep}$ is the energy of steric repulsion, which is equal to infinity when molecules '1' and '2' penetrate into each other and is equal to zero otherwise. The second term in (6) represents interaction with the external field E_0 produced by charges outside the dielectric. The integration is performed, as usual, over the translational and orientational degrees of freedom, $d\{1\} = dr_1\, du_1$.

At large separations r_{12} the integral in (6) diverges, while at short distances the effective interaction potential in (6) vanishes due to the steric cut-off. The divergence can be more conveniently eliminated if one also considers the average of the 'pure' dipole–dipole interaction potential, without the cut-off at small r_{12}. If we add and subtract such a term from equation (6), the latter can be rewritten as

$$U_d = \tfrac{1}{2}\rho^2 \int \mathcal{V}_{dd}(1,2)[\Theta(\xi_{12} - r_{12}) - 1] f(1) f(2)\, d\{1\}\, d\{2\}$$

$$+ \tfrac{1}{2}\rho^2 \int \mathcal{V}_{dd}(1,2) f(1) f(2)\, d\{1\}\, d\{2\} - \rho \int (E_0 \cdot m) f(1)\, d\{1\} \tag{7}$$

where $\Theta(\xi_{12} - r_{12})$ is the step function introduced in equation (5). Now the effective potential in the first term in (7), $\mathcal{V}_{dd}(1,2)[\Theta(\xi_{12} - r_{12}) - 1]$, is different from zero only at small intermolecular separations, $r_{12} < \xi_{12}^{max} = l$. The long-range dipole–dipole interaction is now contained in the second term in equation (7).

Now we are going to show that the last two terms in (7) represent the energy of the electromagnetic field in the medium and can be explicitly expressed in terms of the macroscopic (average) electric field $E(r)$ and the polarization $P(r)$. In the uniform system we can write

$$P = \rho \langle m \rangle = \rho \int m f(1)\, d\{1\}. \tag{8}$$

The average electric field now takes the form

$$E(r) = E_0 - \int \widehat{\mathsf{T}}(r - r') \cdot P(r')\, dr'. \tag{9}$$

Using equations (8) and (9) we can represent the average dipole–dipole interaction potential in the form

$$\tfrac{1}{2}\rho^2 \int\int \mathcal{V}_{dd}(1,2) f(1) f(2)\, d\{1\}\, d\{2\} - \rho \int (E_0 \cdot m) f(1)\, d\{1\}$$

$$= \frac{1}{8\pi} \int E^2(r)\, dr - \frac{1}{8\pi} \int E_0^2(r)\, dr - \int (P(r) \cdot E(r))\, dr + \text{surface terms}. \tag{10}$$

In a similar way one can separate the short- and long-range parts of the mean-field potential U^{MF}, expressing them in terms of the effective short-range dipole–dipole potential $\mathcal{V}_{dd}(1,2)[\Theta(\xi_{12} - r_{12}) - 1]$ and the average electric field in the medium, E:

$$U^{MF} = U_0^{MF} + U_{dd}^{MF} - (P \cdot E) \tag{11}$$

with

$$U_{dd}^{MF}(1) = \rho \int \mathcal{V}_{dd}(1,2)[\Theta(\xi_{12} - r_{12}) - 1]f(2)\,d\{2\} \tag{12}$$

where U_0^{MF} is the part of molecular field (2) determined by non-polar interactions, and the long-range effects are contained in the last term. We note that the free energy of a nematic polymer (3) depends on the average dipole–dipole potential (7) and the mean field (2). Taking into account (10)–(12) we conclude that the free energy of the polar nematic polymer can be expressed in terms of the effective short-range dipole–dipole potential $\mathcal{V}_{dd}(i,j)[\Theta(\xi_{ij} - r_{ij}) - 1]$, while all the long-range effects are accumulated in the energy of the average electric field in the medium, $E(r)$.

It is important to note here that this average electric field is determined by boundary conditions and there often is an experimental possibility of ensuring that E vanishes in the sample. This is the case, for example, when the sample is placed between shortened condenser plates. In the rest of this paper we shall set $E = 0$ since we are concerned with the appearance of local spontaneous polarization, which is not induced by any external field.

2.3. Free energy of a single polymer chain

The free energy of a single polymer chain is given by the first term in equation (3), where the configurational partition function $\mathcal{Z}_N$ is a functional of the one-particle distribution function $f(i)$ through the expression (2) for the mean-field U^{MF}

$$\mathcal{Z}_N = \int \mathcal{D}r\mathcal{D}u \, \exp\left[\sum_i^N \Omega(u_i \cdot u_{i+1}) - \beta U^{MF}(u_i)\right]$$

$$\times \prod_i \delta\left(r_{i+1} - r_i - \frac{l}{2}[u_{i+1} + u_i]\right)\delta(u_k^2 - 1) \tag{13}$$

where l is the monomer length.

According to the general density functional approach to the theory of anisotropic liquids [18] the free energy of the system can be represented as a functional of the average one-particle distribution function, $f(r, u)$, which depends both on the position and on the orientation of the particle (monomer in our case). The general structure of this functional is not known, of course, but the functional derivatives of the free energy *are* known and are related to the direct correlation functions of the medium.

In equation (3) the second term already has the form of a functional of $f(r, u)$. The problem is to derive the density functional for the individual chain in an external field U^{MF}—the first term in the free energy (3). Various approximations of this functional exist. Historically, the first one is the Edwards' expression for the excluded volume screening [14], which produced terms $\sim [\nabla\rho(r)]^2$ in the free energy. Lifshits [19] has proposed another method of converting to collective variables, obtaining the chain configuration entropy in the form $\sim [\nabla\rho(r)]^2/4\rho(r)$. Other versions for the density functional for this individual chain free energy have been obtained either by the development of these two models, or combining them in some way [20]. The situation is more complicated when both the orientational and translational distribution functions are non-uniform. In this case the proper density functional must combine gradients $\partial/\partial r$ and $\partial/\partial u$ of the one-particle density $f(r, u) = \sum_k \delta[r - r_k]\delta[u - u_k]$. Grosberg and Khokhlov [21] have written the expression, based on the same idea of the ground-state dominance [19], as

$$\beta F \approx N_{ch} \int ds\, f^{1/2}\left[l(u \cdot \nabla_r) - \nabla_u^2 + \frac{\partial}{\partial s}\right]f^{1/2}\,dr\,du \tag{14}$$

which is suitable when the number density of monomers is uniform and there are no external fields breaking the uniaxial non-polar symmetry of the system.

The derivation of a complete density functional free energy for the semiflexible chain, allowing for variations of both orientational distribution function and the number density, is a separate theoretical task. In this paper we can avoid this problem by either using equation (14) when the conditions for its validity are satisfied, or by keeping this first term in the free energy (3) in the form of a path integral, understanding that it does represent the functional of $f(i)$ through the definition of mean field. This one-particle distribution function, in turn, must correspond to a minimum of the free-energy functional (3). Therefore, since we are looking for terms proportional to $|P|^2$ in the free energy, only linear corrections $f - f_0 \sim P$ should be kept in the distribution function of the low-symmetry state.

3. Perturbation theory for configurational entropy

The general expression for the individual chain free energy functional in a nematic phase with polarization (we take for definiteness that the direction of P coincides with the uniaxial anisotropy direction n) can be obtained from equation (13) by introducing a delta-function constraint at

$$P = \sum_i (m_i \cdot n)\delta(r - r_i) = \frac{m}{V}\sum_i (u_i \cdot n) \tag{15}$$

(the last equality is valid only for a uniform system). Note that for a directed dipolar chain polarization P is proportional to the end-to-end distance $R = l\sum_i u_i$. Exponentiating this constraint and assuming a spatially uniform system we obtain

$$\mathcal{Z}_N = \int \mathcal{D}\lambda\, \mathcal{D}u\, e^{i\lambda P} \prod_i \exp\left(\Omega(u_i \cdot u_{i+1}) - \beta U^{MF}(u_i) - i\lambda\frac{m}{V}(n \cdot u_i)\right)$$

$$= \int \mathcal{D}\lambda\, du\, du'\, e^{i\lambda P} G(u, u', N; [\lambda]) \tag{16}$$

where λ is the auxiliary field associated with fixed polarization which acts as an external field in (16). The integral over the configurations $\{u_i\}$ is expressed through the propagator $G(u, u', N; [\lambda])$ of the chain in this external potential $\sim \lambda(n \cdot u_i)$. $G(u, u', N; [\lambda])$ satisfies the orientational diffusion equation with perturbation

$$\left[\frac{\partial}{\partial N} - \frac{1}{\Omega}\nabla_u^2 + \frac{1}{k_B T}U^{MF}(u) + i\lambda\frac{m}{V}(n \cdot u)\right] G(u, u', N; [\lambda]) = \delta(N)\delta(u - u'). \tag{17}$$

In this equation, as in (14), ∇_u^2 is the angular part of the Laplace operator. The mean-field potential U^{MF} in the non-polar nematic phase has two deep wells around the poles of the unit sphere of orientations u, along the nematic director $n = -n$, and the barrier of the height J on its equator, penalizing the deviations of u from n. Qualitatively, in the polar phase, $U^{MF} \sim J_1(n \cdot u) - J(n \cdot u)^2$. In the main order the mean-field potential barrier J is proportional to the nematic order parameter S and the polar coupling constant J_1 is proportional to polarization, $J_1 = J_1^0 P$. This polar portion of the molecular field can be readily accomodated into the main equation (17) by renormalizing the auxiliary field, viz $\lambda' = \lambda - iV(J_1^0/m k_B T)P$.

There are several ways to solve equation (17). The most convenient and well developed route is by expressing its eigenfunctions through spheroidal functions Sp_n [22]. The solution of the corresponding eigenproblem with the polar perturbation $\sim (n \cdot u)$ is described in detail by Terentjev and Petschek [12, 23]. Here we merely apply that solution assuming, as

in [12], that nematic ordering is sufficiently strong (there are many experimental, as well as theoretical, indications that even at the transition to isotropic phase, the order parameter of the main-chain polymer melt remains sufficiently high, $S \sim 0.5$).

A small, but important, technical point is relevant here. One has to be careful with the estimate of the relative magnitude of the 'perturbation potential' λ in equation (17) and the splitting of the eigenvalues of the initial problem. This splitting may be exponentially small in the hairpin regime of the nematic phase [7, 8, 12]: $\Lambda_1 - \Lambda_0 = \Delta \sim \beta\Omega J \exp\left[-2\sqrt{\beta\Omega J}\right] \ll 1$. In many cases it is safe to assume the perturbation to be infinitesimal, but here our final purpose will be to perform integration $\int \mathcal{D}\lambda$ in (16) and it is necessary to keep the value of λ unbound. Therefore, generally it might be better to use the generalized form of perturbation theory, which gives the 'standard' version and the degenerate version for 'close levels' in its limiting cases. However, in this paper we seek an expansion of the final free energy in powers of P—the field conjugate to λ—keeping only the leading term. Accordingly, the optimal value of λ can be taken limitingly small and corrections at large λ neglected.

The chain propagator for the initial system (at $\lambda = 0$) is expressed through the spheroidal eigenfunctions of the non-perturbed equation (17), taking the form [8]

$$G_0(u, u', N) = \sum_{n=0}^{\infty} \left(\frac{2n+1}{2}\right) Sp_n(u) Sp_n(u') e^{-\Lambda_n N/\Omega} \tag{18}$$

where eigenfunctions of the even order are symmetric with respect to $u \to -u$ change (they are expressed in terms of even-order Legendre polynomials) and odd eigenfunctions are antisymmetric. At high order parameter the corresponding eigenvalues coalesce in pairs

$$\Lambda_0 \approx 2\sqrt{\beta\Omega J} \qquad \Lambda_1 - \Lambda_0 = \Delta \approx 32\beta\Omega J \exp\left[-2\sqrt{\beta\Omega J}\right] \ll 1 \tag{19}$$

(higher-order eigenvalues are much larger, $\Lambda_{2n} \sim 2(2n+1)\sqrt{\beta\Omega J}$, and are irrelevant at sufficiently large N). The spheroidal functions $Sp_0(u)$ and $Sp_1(u)$, being the eigenfunctions of equation (17) at $\lambda = 0$, at high order parameter essentially become symmetric and antisymmetric combinations of $\exp\left[\frac{1}{2}\sqrt{\beta\Omega J}(n \cdot u)^2\right]$ on the two poles of the unit sphere of orientations of u, normalized by the condition $\int \left(\frac{2n+1}{2}\right) Sp_n(u) Sp_m(u) \, du = \delta_{nm}$ (see [22] for more details).

Therefore the relevant correction to the individual chain propagator in the presence of perturbation λ' is obtained from equation (17) by recursion as

$$G(u, u'N; [\lambda]) = G_0(u, u', N)$$

$$- \left(i\lambda'\frac{\Omega m}{V}\right) \int_0^N ds_1 \int du_1 \, G_0(u, u_1, N - s_1)(n \cdot u_1) G_0(u_1, u', s_1)$$

$$+ \left(-\lambda'^2\frac{\Omega^2 m^2}{2V^2}\right) \int_0^N ds_1 \int_0^{s_1} ds_2 \int du_1 \, du_2 \, G_0(u, u_1, N - s_1)(n \cdot u_1)$$

$$\times G_0(u_1, u_2, s_1 - s_2)(n \cdot u_2) G_0(u_2, u_1, s_2) + \cdots . \tag{20}$$

Using the symmetry properties of spheroidal functions and integrating over the chain contour length to obtain the Debye function of $\left(\frac{N\Delta}{\Omega}\right)$ in the last term, we have

$$G(u, u', N; [\lambda]) \approx \frac{1}{2} Sp_0(u) Sp_0(u') e^{-\Lambda_0 N/\Omega}$$

$$\times \left(1 - \frac{3}{8}\lambda'^2 \Omega^2 \left(\frac{m}{V}\right)^2 \left[\int du_1 \, Sp_0(u_1)(n \cdot u_1) Sp_1(u_1)\right]^2\right)$$

$$\times \int_0^N \mathrm{d}s_1 \int_0^{s_1} \mathrm{d}s_2 \, \mathrm{e}^{-\Delta|s_1 - s_2|/\Omega} \Bigg)$$

$$\approx \tfrac{1}{2} S p_0(u) S p_0(u') \mathrm{e}^{-\Lambda_0 N/\Omega}$$

$$\times \left(1 - \tfrac{1}{4}\lambda'^2\Omega^2 \left(\frac{m}{V}\right)^2 \frac{\Omega N}{\Delta}\left[1 - \frac{\Omega}{N\Delta}(1 - \mathrm{e}^{-N\Delta/\Omega})\right]\right). \tag{21}$$

Integrating (21) over u and u' and lifting the term with λ'^2 in the exponent, we can perform the final (Gaussian) integration over $\mathcal{D}\lambda$ in equation (16). Changing the variables from λ to λ' in the limit of very long chains ($N \to \infty$) we obtain

$$\mathcal{Z}_N \approx \tfrac{1}{2}\left(\int S p_0(u) \, \mathrm{d}u\right)^2 \mathrm{e}^{-\Lambda_0 N/\Omega} \int \mathcal{D}\lambda \, \exp\left[\mathrm{i}\lambda' P - \frac{1}{4}\lambda'^2 \frac{\Omega^3}{\Delta} \frac{Nm^2}{V^2}\right] \exp\left[-\frac{V}{m}\frac{J_1^0}{k_B T} P^2\right]$$

$$= \mathcal{Z}_N^0 \exp\left[-\frac{V^2\Delta}{\Omega^3 Nm^2} P^2 - \frac{V}{m}\frac{J_1^0}{k_B T} P^2\right]. \tag{22}$$

Accordingly, the free-energy density is expanded in powers of the system polarization as

$$F_0(P) \approx F_0(0) + k_B T \frac{\Delta}{\Omega^3 \rho m^2} P^2 + \frac{J_1^0}{m} P^2 + \cdots \tag{23}$$

where, as before, $\rho = N/V$ is the number density of polar monomers and we have put $E = 0$.

4. Polar molecular field in a ferroelectric polymer

The free energy of a nematic polymer is given by equation (3). In the previous section we obtained an expression for the first term of this expression (configurational entropy) in terms of the spontaneous polarization P. One of the coefficients of the expansion (23) depends on the coupling constant J_1^0 which determines the polar part of the molecular field that acts on a monomer in a ferroelectric polymer. The parameter J_1^0 can be obtained using the general expression (12) for the polar molecular field and the expression for the effective short-range dipole–dipole interaction potential

$$U_{\mathrm{dd}}^{\mathrm{MF}}(1) = \rho \int \mathcal{V}_{\mathrm{dd}}(1,2)[\Theta(\xi_{12} - r_{12}) - 1]f(2)\,\mathrm{d}\{2\} = J_1^0 P\,(n \cdot u_1). \tag{24}$$

The second term of the free energy (3) also contains the average of the effective dipole–dipole potential: interaction between monomers throughout the system independent of their assignment to a specific chain, modulated at short distances by steric repulsion. This contribution can be written as a purely orientational average in the form

$$-\tfrac{1}{2}\rho^2 \langle V_{\mathrm{dd}}^{\mathrm{eff}}\rangle = -\tfrac{1}{2}N\rho \int \mathbf{U}(u_1, u_2)f(u_1)f(u_2)\,\mathrm{d}u_1\,\mathrm{d}u_2 \tag{25}$$

where the positional integration has been performed to define the function $\mathbf{U}$. Such integration is effectively performed over the anisotropic excluded volume domain $r_{12} = |r_2 - r_1| < \xi_{12}$

$$\mathbf{U}(u_1, u_2) = \int \mathcal{V}_{\mathrm{dd}}(1,2)[\Theta(\xi_{12} - r_{12}) - 1]\,\mathrm{d}r_{12}. \tag{26}$$

The measure of integration in (26) is $\mathrm{d}r_{12} = r_{12}^2\,\mathrm{d}r_{12}\,\mathrm{d}\hat{x}_{12}$, where the unit vector $\hat{x}_{12}$ describes the orientation of r_{12}, the separation of centres of mass of the two monomers. It

is well known that the uniform orientational average of dipole–dipole potential $\mathcal{V}_{dd}(1, 2)$, i.e. the result of its integration over $d\hat{x}_{12}$ on a sphere, gives zero. Therefore we may separate the integration domain in (26) into the isotropic (spherical) part $r_{12} < d$ ($\xi_{12}^{min} = d$, the monomer thickness) and the anisotropic part, $d < r_{12} < \xi_{12}$. The first integral contains a singularity at $r_{12} = 0$, which has been discussed by Mazur and Mandel [24], for example. This term determines the depolarization factor of the sphere and is equal to

$$\int_0^d \left[(m_1 \cdot m_2) - 3(m_1 \cdot \hat{x}_{12})(m_2 \cdot \hat{x}_{12}) \right] \frac{dr_{12}}{r_{12}^3} = -\frac{4\pi}{3} m^2 (u_1 \cdot u_2) . \quad (27)$$

The second integral over the anisotropic part of an excluded volume integration domain takes the form

$$\int_d^{\xi_{12}} \mathcal{V}_{dd}(1, 2)\, dr_{12} = \int \left[(m_1 \cdot m_2) - 3(m_1 \cdot \hat{x}_{12})(m_2 \cdot \hat{x}_{12}) \right] \left(\ln \xi_{12}(\hat{x}) - \ln d \right)\, d\hat{x}_{12}$$

$$= m^2 \mathcal{K}\{u_1, u_2\}(u_1 \cdot u_2) . \quad (28)$$

The procedure of such integration over an anisotropic excluded volume for two spherocylinders has been described by Gelbart and Ben-Shaul [15], and the particular integral with dipole–dipole interaction potential over an external volume ($\xi_{12} < r_{12} < \infty$) has been calculated numerically in [12]. That result is equal to (28) with the opposite sign, so we can use its interpolated formula

$$\mathcal{K}\{u_1, u_2\} \approx \frac{4\pi}{3} \left(1 - \frac{d}{l} \right)^{2/3} - \frac{8\pi}{9} \frac{d/l\,(1 - d/l)}{(1 - d/l)^2 + 6(d/l)^2} \left[1 - P_2(u_1 \cdot u_2) \right] \quad (29)$$

where $P_2(u_1 \cdot u_2)$ is the second Legendre polynomial of the scala product $(u_1 \cdot u_2)$. Interpolation (29) does not deviate for more than 5% from the numerical result in the whole region of variation of d/l ($0 < d/l < 1$).

Finally, collecting all contributions (27) and (28) to the average effective dipole–dipole potential and performing the orientational averaging with probability distributions $f(u)$, we obtain

$$-\tfrac{1}{2}\rho^2 \langle \mathcal{V}_{dd}^{eff} \rangle \approx \frac{2\pi}{3} P^2 \left[1 - \left(1 - \frac{d}{l} \right)^{2/3} + \frac{2}{3} \frac{d/l\,(1 - d/l)}{(1 - d/l)^2 + 6(d/l)^2}(1 - S) \right]$$

$$\approx \frac{8\pi}{9} \frac{d}{l}(1 - S/2)P^2 \qquad \text{for } d/l \ll 1 \quad (30)$$

where $S = \langle P_2(u_1 \cdot u_2) \rangle$ is the nematic order parameter of the system. The polar correction to the molecular field potential U^{MF} (cf equation (12)) is given by

$$U_{dd}^{MF} \approx -\frac{4\pi}{3} mP(n \cdot u_1) \left[1 - \left(1 - \frac{d}{l} \right)^{2/3} + \frac{2}{3} \frac{d/l\,(1 - d/l)}{(1 - d/l)^2 + 6(d/l)^2}(1 - S) \right]$$

$$\approx -\frac{16\pi}{9} \frac{d}{l}(1 - S/2)mP\,(n \cdot u_1) \qquad \text{for } d/l \ll 1 . \quad (31)$$

Equation (31) defines the value of the coupling constant J_1^0

$$J_1^0 \approx -\frac{16\pi}{9} \frac{d}{l}(1 - S/2)m \qquad \text{for } d/l \ll 1 . \quad (32)$$

5. Results and discussion

The total free energy density of a dipolar nematic polymer melt is given by two terms in equation (3). This expression has been transformed into an expansion in powers of the uniform average polarization in the system (which is assumed to be along the principal axis of anisotropy n)

$$F \approx F_0 + k_B T \frac{\Delta}{\rho m^2 \Omega^3} P^2 - \frac{8\pi}{9} \frac{d}{l} (1 - S/2) P^2 = F_0 + a(T - T_c) P^2 \quad (33)$$

where the instability temperature is given by

$$k_B T_c = \frac{8\pi}{9} \frac{d}{l} \frac{\rho m^2 \Omega^3}{\Delta} (1 - S/2) \quad (34)$$

and where F_0 is the free energy of a non-polar phase. The expansion (33) indicates that at some temperature $T = T_c$ there must be a polarization instability in a dipolar nematic polymer. In fact, at $T < T_c$ the long-wavelength fluctuations of polarization are growing and the polymer can become ferroelectric.

It is interesting to note that the instability temperature T_c is inversely proportional to the geometric anisotropy of a single chain segment l/d. Thus $T_c \to 0$ at $l/d \to \infty$. This tendency can be readily understood if one takes into account the fact that two long parallel polar rods always have a positive dipole–dipole interaction energy except for the rare case when the intermolecular radius vector r_{12} is almost parallel to the long axes. However, this tendency of decreasing T_c is overcomed by the rapid growth of the parameter Δ^{-1} in equation (34). We note that the parameter Δ is related to the persistence length of the semiflexible polymer chain in the direction parallel to the nematic director, $L_{seg} \sim 1/\Delta$. At the same time the parameter Δ determines a large longitudinal dielectric susceptibility of a nematic polymer, $\chi_{\parallel}^0 \approx \rho m^2 \Omega / k_B T \Delta \sim \exp[\frac{1}{2}\sqrt{\Omega J/k_B T}]$ [11]. Using this simple expression for the susceptibility of the nematic polymer one can rewrite the instability criterion (34) as

$$1 = \frac{8\pi}{9} \frac{d}{l} \Omega^2 \chi_{\parallel}^0 . \quad (35)$$

Now one can readily see that the possibility for the ferroelectric ordering in dipolar nematic polymer is related to large values of the longitudinal chain susceptibility.

It is interesting to compare equation (35) with the corresponding expression for low molecular weight nematic composed of polar molecules. One can qualitatively perform the calculation, similar to this paper, also for the case of conventional nematic. The only (but important) difference will be in the configurational entropy, which has a particularly simple form in this case, $\sim f(u) \ln f(u)$. As a result one can write the following expression for the free-energy density of a polar nematic

$$F \approx F_0 + \frac{1}{2\chi_{\parallel}} P^2 + \langle\langle \mathcal{V}_{dd}^{eff} \rangle\rangle$$

where the susceptibility $\chi_{\parallel} \sim \rho m^2 / k_B T$ and the average of the effective dipole–dipole interaction potential has essentially the same form as in the polymer case (see the third term in equation (33)). Now the hypothetical instability temperature T_c' for a conventional nematic can be estimated as $k_B T_c' \sim (d/l) \rho m^2$. We note that this expression is very similar to equation (34). However, the value of the susceptibility $\chi_{\parallel}$ (and hence the value of the instability temperature) is much lower than in the case of a semiflexible nematic polymer.

Let us assume that the longitudinal dipole moment $m \sim 1$ D (in fact it can be several times larger for strongly polar mesogenic molecules). Taking the number density

$\rho \sim 2 \times 10^{21}$ cm^{-3} we arrive at the estimate of the polarizational instability temperature for low molecular weight nematic, namely $T_c' \sim 3(d/l)$ K. Therefore, for typical axial ratios of mesogenic molecules, the temperature T_c' must be less than 1 K. The estimates, presented here, are obviously very crude. However, they can be considered as an indication that the corresponding instability is not practically accessible in a system like a rod-like nematic liquid crystal.

By contrast, in the case of nematic polymers the longitudinal susceptibility $\chi_\parallel$ is much larger and grows exponentially when the nematic order parameter S is increased. Thus one can hope that the instability criterion (35) can be satisfied for reasonable values of the dipole moment m and temperature T_c. Indeed, the parameter Δ can be estimated as $\Delta \approx 32(\Omega J/k_B T)\exp\left[-2\sqrt{\Omega J/k_B T}\right]$ and the nematic order parameter $S \approx 1 - \frac{3}{2}\sqrt{k_B T/\Omega J}$ in the case of $\Delta \ll 1$ (section 3). The equation (34) can be rewritten as

$$k_B T_c \sim \frac{1}{27}(d/l)\,\rho m^2 \Omega^3 (1-S)^2 e^{3/(1-S)} \qquad \text{for } (1-S) \ll 1 \qquad (36)$$

i.e. this expression is asymptotically valid at large nematic order parameter. The rapid, exponential rise of the instability temperature is due to effecitve chain elongation and the cooperative effect of the dipoles on its persistent segments.

A typical value for the effective rigidity Ω of an alkyl chain with 6–8 carbon atoms is $\Omega \sim 3$–5. Taking $S = 0.75$ we arrive at the estimate $T_c \sim (d/l) \times 10^4$ K. This is a very high transition temperature. We note, however, that the estimate strongly depends on the value of nematic order parameter and, for example, for $S = 0.7$ one obtains $T_c \sim (d/l) \times 30$ K. Therefore a ferroelectric instability can occur in strongly ordered semiflexible nematic polymers composed of polar mesogenic segments.

It is important to note that dipolar nematic main-chain polymers have been synthesized recently [25, 26] in the search for new nonlinear optical materials. In [26], asymmetrically disubstituted cyanostilbene monomers have been polymerized with alkyl spacers of 7 to 12 CH$_2$ units. It has been demonstrated that these polymers have high first- and second-order dielectric susceptibilities in the nematic phase. Therefore, the initial conditions for the application of our theory are satisfied and further investigation of these, or similar, materials would be desirable.

In conclusion we would like to stress that the results of this paper only give some indication of the possible polarizational instability. This does not mean that we will necessarily find a homogeneously polarized polymer sample at lower temperatures. In fact, the analysis of [1, 2] shows that a homogeneously polarized fluid must be unstable and the equilibrium structure can be rather complex.

Acknowledgments

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