

Long-range interactions and the pair-correlation function in dipolar main-chain nematic polymers

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A thermotropic nematic phase of dipolar mesogenic polymers with long-range interactions is considered. Using a graphical representation of the corresponding path integrals for the grand canonical ensemble, we derive a Dyson-type equation for the pair-correlation function. We calculate this correlation function in the random-phase approximation, accounting for anisotropic steric repulsion, dispersion, and dipole-dipole interactions between monomers. As an implication of the model, we calculate the (anisotropic) dielectric susceptibility of a dipolar nematic polymer, which shows a divergent behavior at some critical temperature.

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I. INTRODUCTION

Properties of the liquid-crystalline polymers have attracted considerable attention during the past decade from both theorists and experimentalists; this interest arises from the growing number of possible applications. These systems have unique macroscopic phenomena, not all of which have yet been well described. There is, however, a qualitative understanding that unusual properties of nematic polymers are caused by internal-chain degrees of freedom and by a competition between this internal-chain entropy and packing and dispersion forces in the system. Microscopic calculations of the properties of these materials facilitate understanding and controlling their behavior in various circumstances. This helps the search for new materials with desired macroscopic characteristics, because it relates the fundamental material parameters with the specific molecular structure. For main-chain polymers, the main molecular feature is, obviously, the great length of this chain, but one could expect the significant influence of other factors also.

The original analytical approach to the statistical description of a long semiflexible chain [1, 2] was developed by many authors to incorporate the orientational ordering and equilibrium properties of the low-temperature nematic phase [3, 4]. Further developments in the theory of nematic main-chain polymers include microscopic models for curvature elastic constants [5–7] and the analysis of the polar chain—when the mesogenic monomers possess an electric dipole moment and are anchored with a same direction along the chain [8–10]. Many interesting effects are predicted for this latter case of so-called dipolar nematic polymers; the most fascinating is the possibility of a proper ferroelectric phase in this system. The search for materials and conditions that would exhibit polar ordering in the absence of crystalline lattice is very active now. Different authors examine various systems and theoretical approaches to this problem: from computer experiments on dipolar liquids [11, 12] to phenomenological [8] and microscopic [10] treatment of polarized polymer

chains in the nematic phase. The possible ferroelectric phase transition, which we have predicted in the mean-field approximation, is an interesting and important phenomenon. This transition is governed by the long-range part of the pair-interaction potential, or in other words, by the conditions on the sample surface. This is a new type of ordering, stabilized globally by long-range forces in contrast with typical Ising-like systems with the neighbors interaction. Similar conclusions follow from Monte Carlo and molecular-dynamics simulations [11, 12].

This unusual situation requires a detailed investigation of pair correlations, both positional and orientational. The statistical averaging involves an integration over the whole sample volume of functions that essentially do not decay. Therefore, a microscopic theory using the mean-field approximation (i.e., ignoring long-range correlations) and any phenomenology based on this concept are insufficient to adequately describe polar ordering in liquids. Knowledge of the pair-correlation function is especially necessary in the case of polymers, where positions and orientations of (dipolar) monomers are, to a considerable extent, predefined by the chain interaction. One may expect certain alternations in the description and predictions even for nonpolar polymers with volume interactions (i.e., dispersion). Note that semiflexible chains at low temperatures are folded so that the persistent length becomes exponentially large [3]. This increase determines many practical effects in corresponding materials [4, 7] and it is essentially governed by pair correlations between monomers on the same chain. In all other aspects the cited papers are based on the mean-field approximation concept.

The purpose of this work is to investigate the complicated problem of positional and orientational correlations in a melt of semiflexible polymer chains, which exhibit nematic ordering. We develop a diagram technique, similar to the calculation of the Green's function in solids, and provide the partial summation in the limit of weak long-range interaction between monomers. We distinguish three basic situations: (i) nonpolar monomers

with a symmetric shape, interacting via dispersion forces; (ii) monomers with electric dipoles and the corresponding dipole-dipole interaction; and (iii) monomers possessing steric dipoles (asymmetry of shape), which affects the short-range packing correlations. In the general case polymer materials may have any combination of dispersion forces with the other two interactions; in theoretical models over the years all possible combinations of the above mentioned have been considered in the framework of the mean-field approximation. We obtain a general Dyson-like equation for the pair monomer-monomer correlation function $P_2(1,2)$ dependent on the separation of corresponding monomers, their orientations and locations of each on its corresponding chain. We use the concept of average probabilities, i.e., distribution functions independent on the monomer's number on its chain. In this approximation we obtain a compact expression for $P_2(1,2)$ in terms of spatial integrals and averages of the long-range interaction potential. At the end of this paper we illustrate the use of this pair-correlation function by calculating the dielectric susceptibility of a dipolar nematic polymer in paraelectric phase and compare it with previously obtained results.

II. DIAGRAM TECHNIQUE

We model our system as a melt of polymer chains, each having the same number N of mesogenic monomers, connected by semiflexible spacers with effective rigidity Ω . We will consider a bond probability [7] $P_B(i, i+1)$ —the conditional probability of subsequent monomers configuration in the absence of interactions other than bonding interactions between the monomers. Previously this has been concerned primarily with the relative orientation of monomers. Here we extend this to account for the relative positions as well. Thermotropic liquid-crystalline phases can appear only if the monomers are interacting with each other. We shall account for this pair interaction by means of the Mayer's function $f_{ik} = -1 + \exp[-\beta V(i, k)]$, where $V(i, k)$ is the total potential of interaction between each pair of monomers in the system; $\beta = 1/T$. In the next section we shall specify types of interactions considered in this paper: the anisotropic steric repulsion, isotropic and anisotropic dispersion attraction, and the dipole-dipole interaction (for this case we shall assume that monomers possess a permanent dipole moment, all pointed in the same direction along the chain).

We use the formalism of the grand canonical ensemble, in which it is more convenient to account for an arbitrary amount of chains in the system that eventually contributes only to the total system density. The grand partition function of our system takes the form (compare with [13])

$$\Xi = 1 + \sum_{\text{chains}} \int \prod_{j>k}^N (1 + f_{jk}) \Pi_{\alpha} e^{-\beta \mu_{\alpha}} \times \Pi_{i_{\alpha}} P_B(i_{\alpha}, i_{\alpha} + 1) \mathcal{D}\Gamma \quad (1)$$

where the index α specifies the different chains and ro-

man indices describe monomers, which belong either to the same chain (i_{α}) or to arbitrary chains. We denote by μ_{α} the (entropic) chemical potential of the chain α , which determines the macroscopic density of the system. The path integral in Eq. (1) is calculated over the whole configuration $\mathcal{D}\Gamma = \prod_{\alpha} \prod_{i_{\alpha}} d\mathbf{r}_{i_{\alpha}} d\mathbf{u}_{i_{\alpha}}$, i.e., positions and orientations of long axes of all monomers. The total pair probability of the configuration of monomers a and b is defined as

$$P(a, b) = \frac{1}{\Xi} \int \prod_{j>k} (1 + f_{jk}) \Pi_{\alpha} e^{-\beta \mu_{\alpha}} \Pi_{i_{\alpha}} P_B(i_{\alpha}, i_{\alpha} + 1) \times \delta(i_{\alpha} - a) \delta(i_{\alpha} - b) \mathcal{D}\Gamma \quad (2)$$

where the two δ functions symbolically remove the integration over the configuration of the two given monomers.

At this point we use the graphical representation of the path integrals above. Associate solid lines with the polymer chain itself, $e^{-\beta \mu_{\alpha}} \Pi_{i_{\alpha}} P_B(i_{\alpha}, i_{\alpha} + 1)$, on which open circles represent δ functions, specifying the configuration of the given monomers. Dashed lines will represent the pair interaction (the Mayer functions f_{jk}). Figure 1(a) shows the graphs to calculate the grand partition function, Eq. (1), in the limit of noninteracting chains. Figure 1(b) illustrates the approximate calculation of the single-particle probability of a given monomer orientation

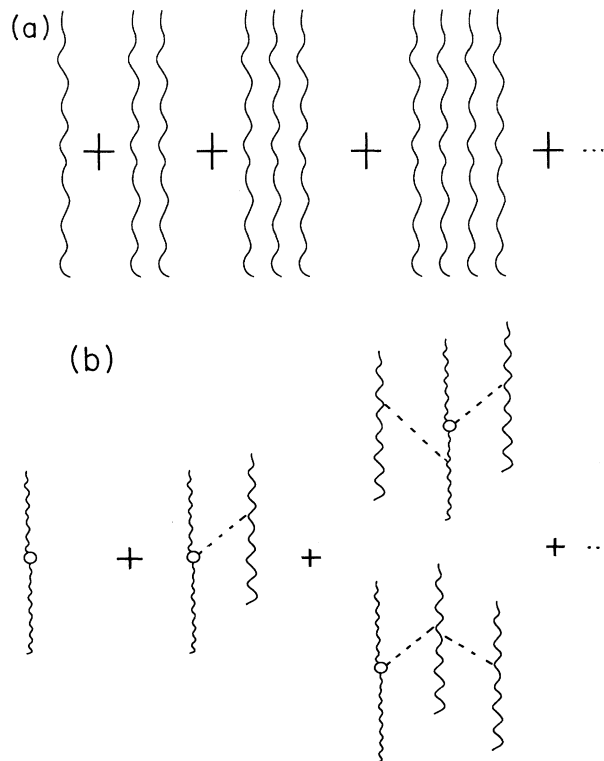


FIG. 1. Summation of graphs for (a) the grand partition function in the limit $f_{ik} = 0$, Eq. (1), and (b) the single-particle probability, Eq. (3).

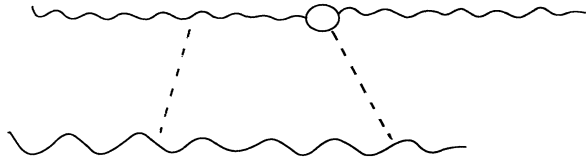


FIG. 2. The type of graph that we are not taking into account where the number of chains is less than or equal to the number of interactions between them.

\mathbf{u} , which is determined by a nematic mean-field potential $U(\mathbf{u})$ [4, 7]:

$$\begin{aligned} & \int e^{-\beta\mu_\alpha} \Pi_{i_\alpha} P_B(i_\alpha, i_\alpha + 1) \delta(i_\alpha - a) \mathcal{D}\Gamma_\alpha \\ & + \int e^{-\beta\mu_\beta} e^{-\beta\mu_\alpha} \Pi_{i_\alpha} \Pi_{j_\beta} f_{j_\beta i_\alpha} P_B(i_\alpha, i_\alpha + 1) \\ & \quad \times P_B(j_\beta, j_\beta + 1) \delta(i_\alpha - a) \mathcal{D}\Gamma_\alpha \mathcal{D}\Gamma_\beta + \dots \\ & \approx \int \Pi_i P_B(i, i + 1) e^{-\beta U(i)} \delta(i - a) \mathcal{D}\Gamma. \quad (3) \end{aligned}$$

The mean-field potential is determined by the system density and pair interactions of a given monomer with its surrounding

$$U(\mathbf{u}_i, \mathbf{r}_i) = \frac{T}{V} \sum_\alpha \sum_{j_\alpha} \int f_{ij_\alpha} G(i, j_\alpha) P(j_\alpha) d\mathbf{r}_{j_\alpha} d\mathbf{u}_{j_\alpha}$$

where $G(a, b)$ is the representation of the total pair probability Eq. (2): $P(a, b) = P(a)G(a, b)P(b)$.

The graph representation of Eq. (3), Fig. 1(b), does not account for “interaction loops,” when the two monomers on the same chain are indirectly interacting through the other chain, Fig. 2, omitting terms such as

$$\begin{aligned} & e^{-\beta\mu_\beta} e^{-\beta\mu_\alpha} \Pi_{i_\alpha} \Pi_{j_\beta} P_B(j_\beta, j_\beta + 1) f_{j_\beta i_\alpha} f_{j_\beta i'_\alpha} \\ & e^{-\beta\mu_\alpha} P_B(i_\alpha, i_\alpha + 1) \delta(i_\alpha - a) \mathcal{D}\Gamma_\alpha \mathcal{D}\Gamma_\beta \quad (4) \end{aligned}$$

corresponds to the widely accepted random-phase approximation (RPA) and gives only a small error in a dense system of long chains. We shall use this approximation throughout this paper.

In the presence of pair interaction between monomers the graph representation for the total pair probability in the system is shown in Fig. 3. The first row in this

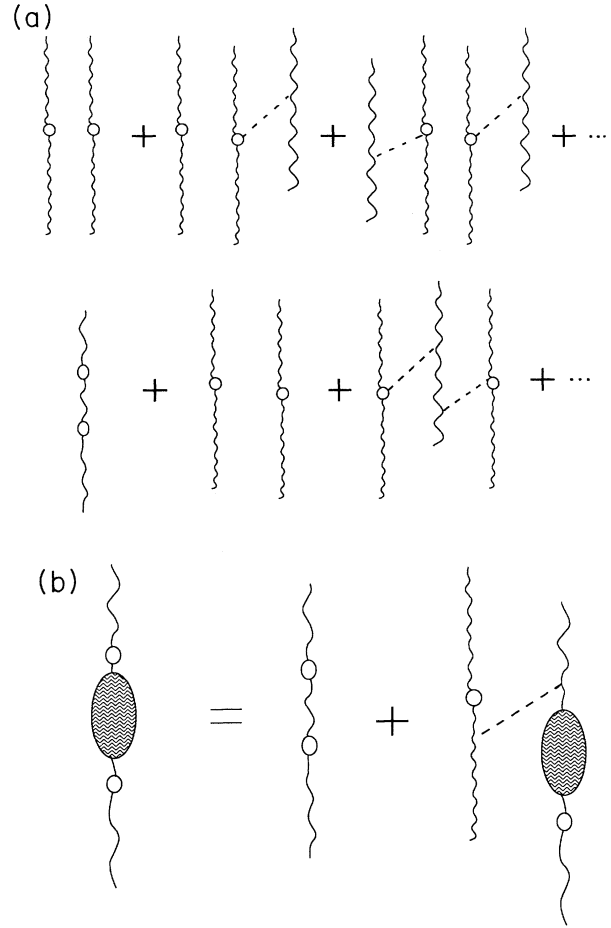


FIG. 3. (a) Summation of graphs for the two-particle probability $P(a, b)$; (b) the Dyson equation for the total pair-correlation function (shaded area represents the result of summation).

drawing gives, after summation, the “dressed” single-particle probabilities $P(a)P(b)$. The remaining graphs form (in the RPA approximation) the Dyson-like equation for the pair-correlation function, so that $P(a, b) = P(a)P(b)[1 + g_2(a, b)]$. Single-particle properties of the nematic polymer have been extensively examined elsewhere [3, 4, 7]; in this paper we concentrate on the correlational part of the total pair probability. It is convenient to write this equation in Fourier space, when it takes the form

$$\begin{aligned} P(a)P(b)g_2(a, b) = P_2(\mathbf{u}_a, \mathbf{u}_b; \mathbf{q}) = P_2^{(0)}(\mathbf{u}_a, \mathbf{u}_b; \mathbf{q}) + \rho \int P_2^{(0)}(\mathbf{u}_a, \mathbf{u}_i; \mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{R})} \left(-1 + \exp[-\beta V(\mathbf{u}_i, \mathbf{u}_k; \mathbf{R})] \right) \\ \times P_2(\mathbf{u}_k, \mathbf{u}_b; \mathbf{q}) d\mathbf{R} d\mathbf{u}_i d\mathbf{u}_k \quad (5) \end{aligned}$$

where ρ is the number density of monomers in the system and $\mathbf{R} = \mathbf{r}_i - \mathbf{r}_k$ is the separation of the two intermediate interacting particles. In the following two sections we shall calculate first the zero-order (single chain) pair probability $P_2^{(0)}$ and then the long-range pair-correlation function P_2 of interacting chains in the nematic phase.

III. ZERO-ORDER APPROXIMATION

The graph $P_2^{(0)}(a, b)$, which is zero order in interaction, defines the correlation between monomers on the same chain in the mean field. This is a so-called Green's function of the chain and its orientational properties have been obtained and examined previously [3, 4]. For our purposes, however, we need the combined positional and orientational dependence of this function. Therefore we extend the traditional calculation of this Green's function to incorporate relative positional coordinates of the monomers a and b .

The main recurrence equation for the partial partition function of k monomers on the chain M_k takes the form (we keep our notations [7, 10])

$$M_k(\mathbf{u}, \mathbf{r}) = \int P_B(\mathbf{u}, \mathbf{u}', \mathbf{r} - \mathbf{r}') M_{k-1}(\mathbf{u}', \mathbf{r}') \times e^{-U(\mathbf{u}')/T} d\mathbf{u}' d\mathbf{r}' \quad (6)$$

where $U(\mathbf{u})$ is the orientational mean-field potential in the nematic phase, which must be determined self-consistently. The initial condition for this recurrence sequence is $M_0 = 1$ (in the absence of any link) and the bond probability now is given by

$$P_B = \frac{\Omega}{\sinh \Omega} e^{\Omega(\mathbf{u} \cdot \mathbf{u}')} \delta(\mathbf{r}' - \mathbf{r} - \frac{1}{2}l(\mathbf{u} + \mathbf{u}')) . \quad (7)$$

In this expression Ω is the parameter of bare flexibility of the bond between the two subsequent mesogenic monomers ($\Omega \gg 1$ for semiflexible chains), and l is the length of the monomer. It is convenient to rewrite the recurrence equation in Fourier space

$$M_k(\mathbf{u}, \mathbf{q}) = \int \frac{\Omega}{\sinh \Omega} e^{\Omega(\mathbf{u} \cdot \mathbf{u}')} e^{-U(\mathbf{u}')/T} \times e^{-i(l/2)[(\mathbf{q} \cdot \mathbf{u}) + (\mathbf{q} \cdot \mathbf{u}')] } M_{k-1}(\mathbf{u}', \mathbf{q}) d\mathbf{u}' \quad (8)$$

and transform it to a differential equation, valid for $\Omega \gg 1$. In this equation there appears an effective \mathbf{q} -dependent mean field, which follows from Eq. (8). This equation for the propagator $g_0(1, 2)$ takes the form (compare with [4, 7])

$$\left[\frac{\partial}{\partial k / \Omega} - \nabla_{\mathbf{u}}^2 + \frac{\Omega U(\mathbf{u})}{T} + i\Omega l(\mathbf{q} \cdot \mathbf{u}) \right] g_0(\mathbf{u}, \mathbf{u}'; k, k') = \delta(\mathbf{u} - \mathbf{u}') \delta_{k, k'} \quad (9)$$

so that the pair probability for the chain $P_2^{(0)}(a, b)$ is

$$P_2^{(0)}(a, b) = \int g_0(1, a) g_0(a, b) g_0(b, N) d(1) d(N).$$

As it has been obtained and discussed elsewhere [4, 7], only the two lowest eigenstates of Eq.(9) are essential in the limit of long chains.

In this paper we are interested in the long-range effects, certainly of the length scale much larger than the monomer size l . Then the limit $ql \ll 1$ can be applied

throughout the calculations. In this case the terms with spatial (or wave vector) dependence play the role of perturbations in this equation (compare with the case of macroscopic elastic deformations [7, 10]) and the two first eigenfunctions take the form

$$W_0(\mathbf{u}, \mathbf{q}) = w_0(\mathbf{u}) - \frac{i\Omega l}{\Delta} (\mathbf{q} \cdot \mathbf{n}) w_1(\mathbf{u}) + \frac{\Omega^2 l^2}{2\Delta^2} (\mathbf{q} \cdot \mathbf{n})^2 w_0(\mathbf{u}) + \dots ,$$

$$W_1(\mathbf{u}, \mathbf{q}) = w_1(\mathbf{u}) + \frac{i\Omega l}{\Delta} (\mathbf{q} \cdot \mathbf{n}) w_0(\mathbf{u}) + \dots \quad (10)$$

where eigenfunctions w_0, w_1 of the position-independent theory [4] essentially are symmetric and antisymmetric combinations of $\exp[\frac{1}{2}\sqrt{\Omega J/T}(\mathbf{u} \cdot \mathbf{n})^2]$ in the two poles of the unit sphere of orientations \mathbf{u} ; parameter $\Delta = 32(\Omega J/T) \exp[-2\sqrt{\Omega J/T}] \ll 1$ is the splitting of the corresponding first two nonperturbed eigenvalues λ_0 and λ_1 . In these equations \mathbf{n} is the nematic director and J is the barrier height of the uniaxial mean-field orientational potential: $U \approx U_0 - J(\mathbf{u} \cdot \mathbf{n})^2$. Ground-state eigenvalues of the position dependent theory are

$$\Lambda_0(\mathbf{q}) = \lambda_0 + \Omega l^2 S(\mathbf{q} \cdot \mathbf{n})^2 + \Omega l^2 \frac{1-S}{3} q^2 + \frac{\Omega^2 l^2}{\Delta} (\mathbf{q} \cdot \mathbf{n})^2 + \dots ,$$

$$\Lambda_1(\mathbf{q}) - \Lambda_0(\mathbf{q}) = \Delta - 2 \frac{\Omega^2 l^2}{\Delta} (\mathbf{q} \cdot \mathbf{n})^2 + \dots \quad (11)$$

where $S \approx 1 - \frac{3}{2}\sqrt{T/\Omega J}$ is the nematic order parameter. Let us note here that these formulas are obtained in the limit of wave vectors, small enough that $\Omega l q / \Delta \ll 1$. Only, in this case, the magnitude of perturbation is small in comparison with the eigenvalues splitting and the conventional perturbation scheme is applicable. In the case of very strong nematic ordering and finite wave vectors q this inequality may no longer be valid (still at $ql \ll 1$) and Eqs. (10) and (11) will be different, determined by the version of perturbation theory for the two very close levels. This limit of the present theory corresponds to optical range, when the characteristic wavelength of external field is less than or comparable with the polymer persistence length $\Omega l q / \Delta \geq 1$. However, the long-range tail of the pair-correlation function, which we are mainly interested in, is defined by limitingly small wave vectors and we can safely use these equations.

In the limit of position independent theory, $q = 0$, the pair probability of the two monomers on the same chain is, as it has been obtained before [3, 4],

$$P_2^{(0)}(a, b) = w_0^2(\mathbf{u}_a) w_0^2(\mathbf{u}_b) + w_0(\mathbf{u}_a) w_1(\mathbf{u}_a) w_0(\mathbf{u}_b) w_1(\mathbf{u}_b) e^{-(\Delta/\Omega)(k_b - k_a)}, \quad (12)$$

which immediately leads to the expression for the single-particle probability $P(\mathbf{u}) \sim \exp[\sqrt{\Omega J/T}(\mathbf{u} \cdot \mathbf{n})^2]$ and the estimate for the chain persistence length L_{seg} along the

director, defined as $L_{\text{seg}} = l \sum_{k=1}^N \langle u_1^\alpha u_k^\beta \rangle n_\alpha n_\beta$:

$$L_{\text{seg}} = 2l \frac{\Omega}{\Delta} \left(1 - \frac{1 - e^{-\frac{\Delta}{\Omega} N}}{\Delta N / \Omega} \right), \quad (13)$$

where N is the total number of monomers on the chain (see also [3, 7, 14]).

In the general case, when both positions and orientations of subsequent monomers are accounted for, this same-chain pair probability acquires the following form:

$$P_2^{(0)}(a, b) = \frac{1}{Z_2} \left(w_0(\mathbf{u}_a) w_0(\mathbf{u}_b) W_0(a) W_0(b) + w_0(\mathbf{u}_a) w_0(\mathbf{u}_b) W_1(a) W_1(b) e^{-(\Delta/\Omega)(k_b - k_a) + 2[\Omega l^2 (\mathbf{q} \cdot \mathbf{n})^2 / \Delta](k_b - k_a)} \right), \quad (14)$$

where the normalization factor

$$Z_2 = 1 + \frac{\Omega^2 l^2 (\mathbf{q} \cdot \mathbf{n})^2}{\Delta^2} \times \left(1 - \exp \left[-\frac{\Delta}{\Omega} (k_b - k_a) + 2 \frac{\Omega l^2 (\mathbf{q} \cdot \mathbf{n})^2}{\Delta} (k_b - k_a) \right] \right)$$

and wave-vector-dependent eigenfunctions $W_0(\mathbf{u}, \mathbf{q})$ and $W_1(\mathbf{u}, \mathbf{q})$ are given by Eq. (10). It is important for the calculations below to note that all expressions for pair properties of monomers in the system are determined by symmetric and antisymmetric with respect to the $(\mathbf{u} \cdot \mathbf{n})$ sign reversal combinations of original nonperturbed eigenfunctions, namely $w_0^2(a)w_0^2(b)$, $[w_0(a)w_1(a)w_0^2(b) + w_0^2(a)w_0(b)w_1(b)]$, and $w_0(a)w_1(a)w_0(b)w_1(b)$. This fact, which is due to the large separation of next eigenvalues Λ_2, \dots and the large number of monomers N on chains, will greatly facilitate the solution of the Dyson equation for correlation functions in Sec. IV.

To complete this section we show that important expressions for the single-particle probability $P(\mathbf{u})$ and the longitudinal persistence length L_{seg} remain unchanged by the introduction of positional dependence in Eq. (14)

in this, zero-order, approximation:

$$P(\mathbf{u}) = \int P_2^{(0)}(\mathbf{u}, \mathbf{u}'; \mathbf{r} - \mathbf{r}') d\mathbf{u}' d\mathbf{r}' \\ = \int P_2^{(0)}(\mathbf{u}, \mathbf{u}'; \mathbf{q} = 0) d\mathbf{u}' ,$$

$$L_{\text{seg}} = l n_\alpha n_\beta \sum_{k=1}^N \int u_1^\alpha u_k^\beta P_2^{(0)}(\mathbf{u}_1, \mathbf{u}_k; \mathbf{q} = 0) d\mathbf{u}_1 d\mathbf{u}_k .$$

We also introduce here the average pair probability of the chain, which does not depend on numbers k and k' of the two monomers location on this chain. This average probability is an important characteristic of the long chain (see [3, 4] for single-particle properties) because the statistical correlation between monomers configuration is essentially absent after the persistence length $k' - k \gg L_{\text{seg}}/l$. For chains with $Nl \gg L_{\text{seg}}$ [which only fully satisfy the continuous limit in the main recurrence equation Eq. (9)] the majority of monomers are not directly correlated by the chain interactions and their relative configuration does not depend on their relative location $k' - k$. Therefore we define the function

$$\bar{P}_2^{(0)}(a, b) = \frac{2}{N(N+1)} \sum_{k_a=1}^N \sum_{k_b=1}^{k_a} P_2^{(0)}(a, b) \\ \approx \frac{1}{Z_2} \left[w_0(\mathbf{u}_a) w_0(\mathbf{u}_b) W_0(a) W_0(b) + \frac{2\Omega}{\Delta} \left(1 - \frac{1 - \exp[-\frac{\Delta}{\Omega} N + 2\frac{\Omega l^2}{\Delta} (\mathbf{q} \cdot \mathbf{n})^2 N]}{\Delta N / \Omega - 2\Omega l^2 (\mathbf{q} \cdot \mathbf{n})^2 N / \Delta} \right) w_0(\mathbf{u}_a) w_0(\mathbf{u}_b) W_1(a) W_1(b) \right], \quad (15)$$

so that the persistence length is still given by (13). In the following calculations we shall mainly use the average probabilities and correlation functions and will omit the bar distinguishing these functions.

IV. CALCULATION OF GRAPHS

The main equation for the consequent diagrams, derived in Sec. II, takes the form for average, site-independent, correlation functions:

$$P_2(a, b) = P_2^{(0)}(a, b) + \rho \int P_2^{(0)}(a, i) f_{ij} P_2(j, b) d(i) d(j) \\ \approx P_2^{(0)}(\mathbf{u}_a, \mathbf{u}_b, \mathbf{q}) - \rho \int_{\xi_{ij}} P_2^{(0)}(\mathbf{u}_a, \mathbf{u}_i, \mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{R})} \beta V(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}) P_2(\mathbf{u}_j, \mathbf{u}_b, \mathbf{q}) d\mathbf{u}_i d\mathbf{u}_j d\mathbf{R}$$

where ρ is the system number density, $\mathbf{R} = \mathbf{r}_j - \mathbf{r}_i$ is the monomer-monomer separation, and the Mayer's function f_{ij} is represented by two major parts: at large distances ($R > l$) $f_{ij} \approx -\beta V(i, j)$, while the steric repulsion determines an anisotropic cutoff of the integral in Eq. (16), $f_{ij} = 0$ at $R \leq \xi_{ij}$ [7]. In this framework the total potential of long-range interactions $V(i, j)$ between the corresponding monomers is considered as a perturbation over the reference system with only steric and chain interactions. As we discussed in the Introduction, we consider two parts in this long-range potential: the dispersion van der Waals forces and the dipole-dipole interaction between polar polarizable monomers. Note that, although the tensor of monomer's polarizability $\hat{\alpha}$ determines the leading effect in dispersion potential, it can be

neglected in the first approximation for dipolar interaction if monomers possess a large constant dipole moment \mathbf{m} . The third effect that influences the pair correlations, which we shall discuss in this paper, is an asymmetry of monomers shape. This steric effect belongs to the reference system, but it determines certain anisotropic effects when it is accounted for in the low-distance (steric) cutoff in integrals of long-range potentials.

As we discussed in Sec. III, all correlation functions in our approximations can be represented through symmetric and antisymmetric combinations of original non-perturbed eigenfunctions: $w_0^2(i)w_0^2(j)$, $[w_0(i)w_1(i)w_0^2(j) + w_0^2(i)w_0(j)w_1(j)]$, and $w_0(i)w_1(i)w_0(j)w_1(j)$. Hence we need only three matrix elements to define all coefficients in Eq. (16):

$$\begin{aligned} \mathcal{Q}_{00} &= \rho \int_{\xi_{ij}} w_0^2(i) e^{i(\mathbf{q} \cdot \mathbf{R}_{ij})} \beta V(i, j, \mathbf{R}_{ij}) w_0^2(j) d\mathbf{R}_{ij} d(i) d(j), \\ \mathcal{Q}_{01} &= \mathcal{Q}_{10} = \rho \int_{\xi_{ij}} w_0^2(i) e^{i(\mathbf{q} \cdot \mathbf{R}_{ij})} \beta V(i, j, \mathbf{R}_{ij}) w_0(j) w_1(j) d\mathbf{R}_{ij} d(i) d(j), \\ \mathcal{Q}_{11} &= \rho \int_{\xi_{ij}} w_0(i) w_1(i) e^{i(\mathbf{q} \cdot \mathbf{R}_{ij})} \beta V(i, j, \mathbf{R}_{ij}) w_0(j) w_1(j) d\mathbf{R}_{ij} d(i) d(j). \end{aligned} \quad (17)$$

This is a most general form for these matrix elements. We may consider possible simplifications that would be in accordance with the already made approximations. Basic perturbation equations for $P_2^{(0)}$ in Sec. III are written in the limit $ql\Omega/\Delta \ll 1$. Therefore, Fourier exponentials in \mathcal{Q}_{ab} can be expanded in powers of $qR \ll 1$ if the corresponding potential $V(\mathbf{R})$ decays at large distances between monomers. This evidently is the case for dispersion interaction ($V \sim 1/R^6$), whereas the dipole-dipole interaction ($V_{dd} \sim 1/R^3$) is not decaying quickly enough to justify such an expansion. Therefore, we shall use the expansion of the q -dependent exponential as the first step of calculating the above matrix elements in the case of van der Waals interaction between monomers (including possible polar steric effects)

$$\begin{aligned} \mathcal{I}_{ij} &= \frac{\rho}{T} \int \left(1 + iq_\alpha R_\alpha - \frac{1}{2} q_\alpha q_\beta R_\alpha R_\beta \right) \\ &\quad \times V_{vdw}(\mathbf{u}_i, \mathbf{u}_j, \mathbf{R}) \Theta(R - \xi_{ij}) d\mathbf{R} \end{aligned} \quad (18)$$

where the step function $\Theta(R - \xi_{ij})$ defines the steric cutoff on the distances less than the anisotropic form factor ξ_{ij} of monomers [15]. In the case of polar mesogenic monomers interacting via dipole-dipole potential, the full exponential $\exp[i(\mathbf{q} \cdot \mathbf{R})]$ must be accounted for and the integral \mathcal{I}_{ij} is a Fourier image of V_{dd} , calculated with the anisotropic steric cutoff $\Theta(R - \xi_{ij})$.

The result for the integral \mathcal{I}_{ij} is known for the case of anisotropic dispersion attraction between sterically symmetric (for example, spherocylindrical) monomers [7]: approximately $\mathcal{I}_{ij} = A + B(\mathbf{u}_i \cdot \mathbf{u}_j)^2 + \dots$ ($A \gg B$), so that the mean-field potential coupling constant from this

interaction is $\beta J = BS$. The actual dependence of \mathcal{I}_{ij} on the relative orientation of monomers long axes is much more sharp, but for the qualitative consideration of this paper the above expression through only the second Legendre polynomial is sufficient. Only the matrix element \mathcal{Q}_{00} is nonzero in this case, $\mathcal{Q}_{00} \approx \beta U_0 + \beta JS + \mathcal{Q}(q^2 l^2)$.

In the case when mesogenic monomers possess a steric dipole along monomers axes (with the magnitude s) [9] the integral \mathcal{I}_{ij} gets an additional, qualitatively different term $\frac{i}{12}(sl/d)[(\mathbf{q} \cdot \mathbf{u}_i) - (\mathbf{q} \cdot \mathbf{u}_j)]$. This contribution is asymmetric in one of the monomer unit vectors \mathbf{u}_i or \mathbf{u}_j and therefore the matrix element \mathcal{Q}_{01} becomes nonzero: $\mathcal{Q}_{01} \sim (i/12)\beta U_0(sl/d)(\mathbf{q} \cdot \mathbf{n})$. We just outline this possibility here, while the main effort we spend on the investigation of a more simple system without steric dipoles.

When dipole-dipole interaction is present in our system, the integral \mathcal{I}_{ij} is calculated differently from Eq. (18). This integration at finite wave vectors ($q \neq 0$) does not exhibit the usual difficulty with the divergence on the upper limit (the dependence on the sample shape) because of the Fourier exponential $e^{i(\mathbf{q} \cdot \mathbf{R})}$. The limit $q \rightarrow 0$ has been examined in our previous paper [10]. We assume a spherical shape of the sample and calculate all corresponding integrals consistently keeping this assumption (see also [16]) if the result of this calculation is a shape-independent material property. In this case, practical implications of these calculations, for example, the dielectric susceptibility, are not affected by the assumption about the system shape. Let us emphasize that it is not always so and the correlations in the system with dipole-dipole interaction should be treated carefully in each particular case.

Assuming the spherical sample shape we obtain, approximately

$$\mathcal{I}_{ij} \approx \frac{\rho}{T} \frac{(\mathbf{m}_i \cdot \mathbf{q})(\mathbf{m}_j \cdot \mathbf{q})}{q^2} - \frac{\rho}{T} \int_{\xi_{ij}} e^{i(\mathbf{q} \cdot \mathbf{R})} \left[\frac{(\mathbf{m}_i \cdot \mathbf{R})}{R^3} + i \frac{(\mathbf{m}_i \cdot \mathbf{q})}{R} \right] (\mathbf{m}_j \cdot d\mathbf{S}), \quad (19)$$

where \mathbf{m} is the electric dipole and the integral is calculated over the surface of the excluded volume for the relative positions of the two monomers—the low-distance anisotropic cutoff at $R = \xi_{ij} \approx d + \frac{1}{2}(l-d)[(\mathbf{u}_i \cdot \hat{\mathbf{R}}) + (\mathbf{u}_j \cdot \hat{\mathbf{R}})]$ (here d is the thickness of the mesogenic monomer $d/l \ll 1$). We assume that the long axis orientation of each monomer \mathbf{u} coincides with the orientation of its electric dipole. Then, for the spherical outer shape of the sample and in the limit $q \rightarrow 0$ we have the estimate [10]

$$P_2(a, b) = \mathcal{A}w_0^2(a)w_0^2(b) + \mathcal{B}[w_0^2(a)w_0(b)w_1(b) + w_0(a)w_1(a)w_0^2(b)] + \mathcal{C}w_0(a)w_1(a)w_0(b)w_1(b) \quad (20)$$

and we obtain for the coefficients \mathcal{A} , \mathcal{B} , and \mathcal{C} in the assumption that $\mathcal{Q}_{01} = 0$ (no steric dipoles):

$$\mathcal{A} = \frac{1 - iXY(1 + X^2Y)\mathcal{Q}_{11}\mathcal{B}}{1 + \mathcal{Q}_{00}}, \quad \mathcal{C} = \frac{(Y - iXY\mathcal{Q}_{00}\mathcal{B})(1 + X^2Y)}{1 + Y\mathcal{Q}_{11}(1 + X^2Y)} \quad (21)$$

and

$$\mathcal{B} = \frac{iXY(1 + X^2Y)}{(1 + \mathcal{Q}_{00})[1 + Y\mathcal{Q}_{11}(1 + X^2Y)] + X^2Y^2(1 + X^2Y)\mathcal{Q}_{00}\mathcal{Q}_{11}}.$$

In most cases there is a general simplification of these equations in the nematic polymer. Orientational ordering appears in the system only at sufficiently large mean-field potential and we always are within the limit $\mathcal{Q}_{00} \gg 1$; also $Y \gg 1$ and $X \ll 1$ (longest waves limit). We may then obtain the coefficients in the form of expansion, valid at $(\Omega/\Delta)ql \ll 1$:

$$\begin{aligned} \mathcal{A} &\approx \frac{1}{\mathcal{Q}_{00}} \left(1 - X^2 \frac{2Y^2\mathcal{Q}_{11}(Y\mathcal{Q}_{00}\mathcal{Q}_{11} - 1)}{\mathcal{Q}_{00}(Y\mathcal{Q}_{11} + 1)(\mathcal{Q}_{00} + Y\mathcal{Q}_{11})} \right), \\ \mathcal{B} &\approx -2iXY \frac{Y\mathcal{Q}_{00}\mathcal{Q}_{11} - 1}{\mathcal{Q}_{00}(Y\mathcal{Q}_{11} + 1)(\mathcal{Q}_{00} + Y\mathcal{Q}_{11})}, \\ \mathcal{C} &\approx \frac{Y}{Y\mathcal{Q}_{11} + 1} \left(1 - X^2 \frac{Y\mathcal{Q}_{00}(2Y\mathcal{Q}_{11} - 1)}{(Y\mathcal{Q}_{11} + 1)(\mathcal{Q}_{00} + Y\mathcal{Q}_{11})} \right). \end{aligned} \quad (22)$$

Equation (20), with Eqs. (22) [or Eqs. (21) in the detailed form] for coefficients, defines the long-range limit of the pair-correlation function in the nematic polymer with various interactions between monomers. The total pair probability of the two monomers configuration, averaged over their positions along their chains, is $P(a, b) = P(a)P(b) + P_2(a, b)$. We shall use this expression in Sec. V to calculate the dielectric susceptibility of a nematic polymer, as an example of implication of the general theory.

V. RESULTS AND DISCUSSION

Let us, first of all, discuss the expression for the pair-correlation function, Eq. (20), with coefficients in the

$\mathcal{I}_{ij} \approx \frac{4\pi}{3} \beta \rho m^2 (1-d/l)(\mathbf{u}_i \cdot \mathbf{u}_j)$. Hence the matrix element \mathcal{Q}_{11} becomes nonzero, $\mathcal{Q}_{11} \approx \beta \rho m^2 [\frac{4\pi}{3} - (\mathbf{q} \cdot \mathbf{n})^2/q^2 + \mathcal{O}(d/l; qd)]$.

Now we are in a position to solve the main equation for the pair-correlation function Eq. (16). Substitute expressions for the perturbed eigenfunctions Eq. (10) to it and introduce two dimensionless parameters that carry separately the dependence on the wave vector and on the chain contour length N : $X(\mathbf{q}) = (\Omega l/\Delta)(\mathbf{q} \cdot \mathbf{n})$ and $Y(N) = (2\Omega/\Delta)[1 - (1 - \exp[-N\Delta/\Omega])/(N\Delta/\Omega)]$. Note that, according to approximations we have made, $X \ll 1$; in the limit $X = 0$ we should recover the space-independent theory. In the limit of infinite chains we have $Y = 2\Omega/\Delta$; the case of very rigid chains without hairpins ($\Omega/N\Delta \gg 1$) corresponds to the dependence $Y \approx N$ —the length of extended chains. We are looking for the total correlation function in the form

small- \mathbf{q} limit, Eqs. (22). At the distances $R \rightarrow \infty$ ($X \rightarrow 0$) we have for these coefficients $\mathcal{A} \rightarrow 1/\mathcal{Q}_{00} \ll 1$, $\mathcal{B} \rightarrow 0$, and $\mathcal{C} \rightarrow Y/(1 + Y\mathcal{Q}_{11})$. This is essentially the mean-field limit, when $P(a, b) = P(a)P(b)$. At small but finite wave vectors, coefficients can be effectively written in a familiar form: $\mathcal{A} \sim 1/[1 + \mu^2(\mathbf{q} \cdot \mathbf{n})^2]$, etc. Note that at vanishing polar interaction ($\mathcal{Q}_{11} < \Delta/4\Omega \ll 1$) there is an anomaly in the behavior of the odd-odd coefficient \mathcal{C} . The even-even coefficient \mathcal{A} , which determines the average radial distribution function, shows an anomaly at even lower values of dipole-dipole interaction $\mathcal{Q}_{11} < \Delta/2\mathcal{Q}_{00}\Omega$. Both these anomalies are, probably, an artifact of simplifications made during the derivation of a compact form of coefficients Eqs. (22). The case $\mathcal{Q}_{11} \rightarrow 0$ requires a more subtle treatment, which would be beyond the scope of this paper.

When both averages of the long-range interaction, \mathcal{Q}_{00} and \mathcal{Q}_{11} , are noninfinitesimal Eqs. (22) remain reliable. In the opposite limit of a strong dipole-dipole interaction $\mathcal{Q}_{11} \gg (\Delta/\Omega)\mathcal{Q}_{00}$ one obtains a further simplification of the correlation length $\mu^2 \approx 4(\Omega/\Delta)^3 l^2$ and the radial distribution function of the two monomers separated by the distance \mathbf{r} along the director \mathbf{n} is

$$G_0^{\parallel}(r) \sim (\Delta/\Omega)^{3/2} e^{-r/\mu}, \quad \mu \sim (L_{\text{seg}})^{3/2} l^{-1/2}.$$

The positional correlations in the direction perpendicular to \mathbf{n} decay very rapidly on the length scale of the monomer size l . This means that the strong dipolar interaction enhances the anisotropy of the chain end-to-end distance in comparison with that obtained in the mean-

field approximation. It would be important in the future to investigate the properties of radial correlation functions for polar and quadrupolar order parameters [11], using the general form of the coefficients, Eqs. (21) and the realistic \mathbf{q} dependence of matrix elements Eqs. (17).

Let us illustrate the implications of the developed model on the example of dielectric properties of the polymer liquid crystal. Consider the case when mesogenic monomers do not possess a permanent dipole moment. In this case the long-range interaction between these monomers and the macroscopic dielectric susceptibility is determined by the molecular polarizability. We associate the microscopic, orientation-dependent tensor of polarizability $\hat{\alpha}(\mathbf{u})$ with each monomer in the system, $\hat{\alpha} = \alpha_{\perp} \hat{I} + (\alpha_{\parallel} - \alpha_{\perp}) \mathbf{u}\mathbf{u}$ for general uniaxial molecules. There is no direct dipole-dipole interaction between monomers and therefore we may not anticipate especially large correlation corrections. In this case it could be possible to use the expansion of the general dielectric constant in powers of an anisotropy of molecular (monomers) polarizability [17]:

$$\frac{\hat{\varepsilon} - \hat{I}}{\hat{\varepsilon} + \hat{2}} \approx \frac{4\pi}{3} \rho \left(\langle \hat{\alpha} \rangle - \rho \int P_2(i, j) \hat{\alpha}(i) \hat{K}(i, j) \hat{\alpha}(j) d(i) d(j) \right) \quad (23)$$

where $\hat{\varepsilon} = \hat{I} + 4\pi \hat{\chi}$, $\hat{K} = (\hat{I} + \rho \langle \hat{\alpha} \rangle \hat{I})^{-1} \hat{T}$, and the \hat{T} is the operator of dipole-dipole interaction $\hat{T} = (\hat{I} - 3\mathbf{u}\mathbf{u})/R^2$ at $ql \ll 1$ and $R > d$. Substituting expressions for $\hat{\alpha}(\mathbf{u})$ and P_2 , Eqs. (20) and (22) with only $\mathcal{Q}_{00} \neq 0$, and performing the integration with anisotropic lower limit ξ_{12} for the monomers separation, we obtain an estimate in the ($q \rightarrow 0$) limit for the static dielectric susceptibility of nonpolar nematic polymer. In the ($\alpha_{\parallel} \gg \alpha_{\perp}$) and ($S \rightarrow 1$) limits it takes the form

$$\begin{aligned} \hat{\chi} &= \chi_{\perp} \hat{I} + (\chi_{\parallel} - \chi_{\perp}) \mathbf{n}\mathbf{n}, \\ \chi_{\perp} &\approx \frac{\rho \alpha_{\perp}}{1 - \frac{4\pi}{3} \rho \alpha_{\perp}}, \\ \chi_{\parallel} &\approx \chi_{\perp} + \frac{(\rho \alpha_{\parallel} - \frac{4\pi}{3} \rho^2 \alpha_{\parallel}^2 \frac{2\Omega}{\Delta})(1 + \frac{4\pi}{3} \chi_{\perp})}{1 - \frac{4\pi}{3} \rho \alpha_{\perp} - \frac{4\pi}{3} \rho \alpha_{\parallel} + (\frac{4\pi}{3} \rho \alpha_{\parallel})^2 \frac{2\Omega}{\Delta}}. \end{aligned} \quad (24)$$

For typical mesogenic molecules $\rho \bar{\alpha} \sim 10^{-1}$; it is clear that the correlation correction is very large ($\Omega/\Delta \gg 1$) and, therefore, the expansion Eq. (23) [17] cannot be used for calculating dielectric properties of nonpolar nematic polymer. We are still unable to produce a reasonable theory for the liquid-crystalline polymers in the case, when the molecular polarizability is accounted for.

Now we return to the case of polar chains—when all mesogenic monomers possess a large permanent dipole moment $\mathbf{m} = m\mathbf{u}$, the direction of which is locked in the same direction along the chain. We neglect the effect of molecular polarizability $\hat{\alpha}(\mathbf{u})$, assuming that the main contribution to the macroscopic dielectric properties is determined by the permanent dipoles. In this case matrix element \mathcal{Q}_{11} is nonzero, along with \mathcal{Q}_{00} . For these qualitative arguments we can use the generalized Kirkwood-Fröhlich equation for the anisotropic liquid [18] together with approximation $\chi_{\parallel} \gg \chi_{\perp}$ (see [8, 10]). We have then

a simple relation between the components of the macroscopic susceptibility tensor and the correlator $\langle \mathbf{u}\mathbf{u} \rangle_0$ between pairs of monomers at zero external field:

$$\begin{aligned} \chi_{\perp} &\sim \beta \rho m^2 \langle u_{\mu}^{(a)} u_{\nu}^{(b)} \rangle_0 (\delta_{\mu\nu} - n_{\mu} n_{\nu}), \\ \chi_{\parallel} &\sim \frac{\beta \rho m^2 \langle u_{\mu}^{(a)} u_{\nu}^{(b)} \rangle_0 n_{\mu} n_{\nu}}{1 - 4\pi \beta \rho m^2 \langle u_{\mu}^{(a)} u_{\nu}^{(b)} \rangle_0 n_{\mu} n_{\nu}}. \end{aligned} \quad (25)$$

Using again Eq. (20) for the pair-correlation function and approximate expressions for matrix elements \mathcal{Q}_{00} and \mathcal{Q}_{11} in coefficients \mathcal{A} and \mathcal{C} , Eq. (22), we readily obtain the estimate for the macroscopic dielectric susceptibility of a polar nematic polymer. The component of susceptibility, which is perpendicular to the nematic director \mathbf{n} , is determined by the angular average of orientation of the same monomer, whereas the longitudinal component χ_{\parallel} has also a contribution from the different particles correlator:

$$\begin{aligned} \chi_{\perp} &\approx \frac{2}{3} \beta \rho m^2 (1 - S) \left[1 + \frac{16\pi}{3} \frac{\rho m^2 \Omega^4}{\beta U_0^2 \Delta^4} l^2 (\mathbf{q} \cdot \mathbf{n})^2 \right. \\ &\quad \left. \times \left(1 - \frac{3}{4\pi} \frac{(\mathbf{q} \cdot \mathbf{n})^2}{q^2} \right) \right] \\ &\sim \beta \rho m^2 \quad \text{at } q \rightarrow 0, \end{aligned} \quad (26)$$

$$\chi_{\parallel} \approx \frac{\beta \rho m^2 (1 + \mathcal{A} + \mathcal{C})}{1 - 4\pi \beta \rho m^2 (1 + \mathcal{A} + \mathcal{C})}, \quad (27)$$

where \mathcal{A} and \mathcal{C} are given by Eqs. (21), and $X \approx \frac{\Omega l}{\Delta} (\mathbf{q} \cdot \mathbf{n})$, $Y \sim \frac{2\Omega}{\Delta}$.

Let us recall that these expressions are obtained in the limit of very small wave vectors $ql\Omega/\Delta \ll 1$ [see Eqs. (10) and (11) and discussion therein] and essentially represent an expansion in powers of this wave vector. It is interesting to note that the main wave-vector dependence enters these equations in the form $(\mathbf{q} \cdot \mathbf{n})$ and it vanishes in the particular case, when $\mathbf{q} \perp \mathbf{n}$. In this case, the only non-locality of dielectric susceptibility in Eqs. (26) and (27) is a result of q dependence of matrix elements \mathcal{Q}_{00} and \mathcal{Q}_{11} , which is much weaker without a characteristic multiplier $\Omega/\Delta \gg 1$. In the uniform case ($q = 0$, $X = 0$) we recover the previously derived expression for longitudinal susceptibility [10] [with some numerical difference in denominator, which is due to a more accurate accounting for internal field effects in Eqs. (25)]

$$\chi_{\parallel} \approx \frac{\rho m^2 (2\Omega/\Delta)}{T - 4\pi \rho m^2 (2\Omega/\Delta)}, \quad (28)$$

or, qualitatively, $\chi_{\parallel} = \mathcal{C}/[T - T_c]$, where $T_c \sim 3 \times 10^{-1} \rho m^2 \Omega (1 - S)^2 \exp[\frac{3}{1-S}]$. This equation has set a basis of our arguments [10] about the possibility of a proper ferroelectric phase transition in a thermotropic nematic phase of dipolar main-chain polymers.

It is important to note that our consideration, based on the diffusion-equation approximation for the chain statistics and average, index-independent probabilities, is valid only for the case of essentially folded chains, when the majority of monomers do not have “memory” about the

configuration on the chain ends. This restriction sets a lower limit on the length of the chain, $N \gg \Omega/\Delta \gg 1$, in which our calculations are valid. Key equations for position- and orientation-dependent statistical properties of the polymer are written in the limit of very small wave vectors $\Omega l q/\Delta \ll 1$, when the ordinary perturbation scheme is applicable to the main equation (9) (see Sec. III and discussion therein). It is not difficult to extend the description to effects with a shorter characteristic wavelength, but it was beyond the scope of this paper and, therefore, all particular expressions for coefficients \mathcal{A} , \mathcal{B} , and \mathcal{C} , Eqs. (20) and (21), and dielectric susceptibility are given in the limit of most long wavelengths. We have employed several other approximations along the way, which are discussed in details in the text, in order to illustrate qualitative effects and derive analytical expressions. Note, however, that the general approach and

arguments of Sec. II, concerning the graph representation of the integrals in our grand canonical ensemble and the Dyson equation for the pair-correlation function, are valid independently on the above restrictions and may provide a useful apparatus for calculation of properties of main-chain liquid-crystalline polymers, in particular—their orientational and polar ordering.

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