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Uniaxial ordering and rotator phase of ribbonlike polymers

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The phase transition in bended and twisted ribbonlike polymer systems is described in meanfield approximation by use of the lattice model with directed self-correlated walks. This phase transition can be of either first or second order depending on the ratio of the constants in the effective energy of interaction of a polymer with the environment. For the first-order phase transition it is found, in particular, that the phase transition temperature depends on polymer length, decreasing linearly with reciprocal length for lengths exceeding 100 monomer units. On the other hand, the jump of the specific entropy is independent of the polymer length for the molecules containing more than 30 monomers. The obtained results are in full agreement with the existing experimental data.

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I. INTRODUCTION

The polymers consisting of macromolecules with anisotropic bending rigidity and rotational degrees of freedom show a number of very interesting properties, for example, when cooled, liquid alkanes convert firstly into the so-called rotator phase and thereafter into a crystalline state [1]. As was shown experimentally [2–6], the rotator phase of normal alkanes can be observed only for rather short macromolecules consisting of 10-100 monomer units. This rotator phase is characterized by a nematic chain ordering while the rotational degrees of freedom remain disordered, thereby increasing the entropy of the system. It transpires that there are five types of rotator phases that differ in packing of oriented chains; however, all of them have the monomolecular layered structure.

Usually, the formation of a rotator phase is described as nematic ordering [7] in the framework of the nematic polymer theory [8–12]. The first theoretical model of orientational self-organization in polymer systems was given by Onsager [8], who considered the lyotropic transition of a dilute solution of long rigid rods into a nematic phase. The Onsager model was generalized later on to the case of concentrated systems of long semiflexible polymer molecules [9]. At the same time, the phenomenological mean-field approximation describing nematic ordering in polymer systems was developed [7,10,11]. The latter was based on the Kratky-Porod model [12], which allows only small bends of a macromolecule due to thermal fluctuations; i.e., the persistent mechanism of polymer flexibility. Note that in the theories based on the Kratky-Porod model, the two important circumstances are omitted. First, the persistent mechanism of chain flexibility excludes the possibility of large local bends of the macromolecule. Second, in the framework of the nematic theory, the rotational degree of freedom has no effect on the formation of a rotator phase. The first restriction is essential only for rather short wormlike chains, while the second presumption, in our opinion, should be revised. Indeed, the rotational symmetry in the rotator phase is broken and weak correlations in the distribution of the rotational degree of freedom can arise, although integrally the rotational degree of freedom remains disordered.

Both abovementioned circumstances can be taken into account in the context of the discrete semiphenomenological model of *directed self-correlated walks* on the regular lattice (DSCW) [13–15]. The model has been applied to the description of conformational statistics of polymer chains with arbitrary rigidity and length [16–21]. The modification of this model allows one to consider the local bending anisotropy of a macromolecule and to describe the conformational statistics of the ribbonlike polymers possessing a rotational degree of freedom [22]. Moreover, this modification also enables one to analyze the influence of all these macromolecular properties on the formation of the rotator phase and serves as a base for the following consideration.

II. MODEL OF THE SYSTEM

The anisotropic bending rigidity and rotational degrees of freedom of polymer molecules that can form the rotator phase are related to their anisotropic cross sections. Indeed, each monomer of such molecules is to be thought of as a three-axial ellipsoid but not as a cylinder, and the conformational state of the molecules, being anisotropic in cross sections, is determined by relative orientations of axes of the neighboring monomers. Thus, the possibilities of the bends of a molecule in the directions of the second and third axes are not equivalent and, in addition, a new degree of freedom, which is connected with the relative orientation of the neighboring monomers of the chain in the plane perpendicular to molecule contour, is to be taken into account. This degree of freedom corresponds to the internal twist of a macromolecule and is called a rotational one. If the anisotropy of macromolecules is strong enough, these polymers are referred to as ribbonlike polymers. These polymers are the object of our analysis.

The local feature of ribbonlike macromolecules can be taken into account by considering each monomer as an elementary object characterized by an additional parameter called "polarization," which corresponds to the rotational degree of freedom and determines the local anisotropy of stiffness. The change of polarization (without a bend) corresponds to the twist of a chain. At the same time, depending on polarization, the bending of a chain can be realized as follows: bending from the direction x only in the direction y, from the direction y only in the direction z, and from the direction z only in the direction x; i.e., according to a cycle of the right-hand triple of vectors: $x \to y \to z$. Another possible direction of bending is the left-hand triple of vectors, $x \to z \to y$; i.e., from the direction x only in the direction z, from the direction z only in the direction y, and from the direction y only in the direction x. We name these two types of polarization as right-hand and left-hand polarizations, respectively. Note that at each bending of a chain, the chain polarization changes to the opposite one[1].

Let us consider random walks of a "particle" on a regular cubic lattice. The probability of a direction choice at each following jump depends both on the jump direction and on polarization "of the walking particle" of the previous step. Such random walks correspond to DSCW. The pathways of the particle that performs such a random motion corresponds to the conformation of a ribbon-like chain of arbitrary rigidity.

Let $\mathbf{e}(n)$ be the vector depending on the jump at the nth step of a random walk, which means the position of the nth monomer of the chain. The stiffness and polarization of a macromolecule are specified by distribution of conditional probabilities of the direction and polarization at step $(n+1)$, $\mathbf{e}(n+1)$, at the given direction and polarization of the previous step, $\mathbf{e}(n)$. The possibilities are as follows: a particle may maintain the direction [with probability $(1-\beta)$] or move in a perpendicular direction that is allowed by polarization (with probability β). Analogously, let the probability to maintain a given polarization be $(1-\omega)$ and the probability to change polarization be ω.

Assuming that bending and twisting (polarization change) are thermally activated processes the appropriable probabilities are given as follows:

$$\beta(T) = \frac{\exp(-E_\beta/T)}{1+\exp(-E_\beta/T)}, \quad \omega(T) = \frac{\exp(-E_\omega/T)}{1+\exp(-E_\omega/T)}, \tag{1}$$

where E_β and E_ω are the activation energies for bending and twisting, respectively.

The state of the nth monomer of the chain is determined by the column vector of the probability distribution of directions and polarizations of the nth step of the walk. Since we are interested only in the phenomenon of orientational self-organization of polymer chains, each monomer of these chains can be considered as a directional line but not as a vector, and the appropriate column vector of the probability distribution can be expressed as a direct product of two column vectors:

$$|P(n)\rangle = |p^{(\omega)}(n)\rangle \otimes |p^{(c)}(n)\rangle, \tag{2}$$

where the index ω corresponds to "polarization" and the index c corresponds to the three directions of the coordinate axes x, y, z.

The column vectors of the probability distribution at nth and $(n+1)$th steps are connected by the transfer matrix $\hat{\mathbf{T}}$:

$$|P(n+1)\rangle = \hat{\mathbf{T}}|P(n)\rangle. \tag{3}$$

The 6×6 transfer matrix $\hat{\mathbf{T}}$ can be represented as the sum of direct products:

$$\hat{\mathbf{T}} = (1-\beta)\omega \otimes \mathbf{I}^{(c)} + \beta(\omega_+ \otimes \mathbf{U} + \omega_- \otimes \mathbf{U}^{-1}), \tag{4}$$

where $\mathbf{I}^{(c)}$ is the unit 3×3 matrix and

$$\mathbf{U} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \omega = \begin{pmatrix} 1-\omega & \omega \\ \omega & 1-\omega \end{pmatrix}, \quad \omega_+ = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad \omega_- = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}.$$

The distribution function of orientation and polarization of monomers is expressed through the powers of the matrix $\hat{\mathbf{T}}$ [20,21]. The matrix blocks ω and $\omega_\pm$ do not commute and, therefore, the problem of the calculation of the distribution function is reduced to the diagonalization of the 6×6 matrix; i.e., to the solution of an algebraic equation of the sixth order which, in general, has no analytical solution. One can apply instead the method of the generating function that is commonly used for the study of systems with a varying number of particles.

The generating function

$$\hat{\mathbf{G}}(\xi) = \sum_{n=0}^{\infty} \xi^n \hat{\mathbf{T}}^n \tag{5}$$

can be represented as the 2×2 block matrix, the indexes of which correspond to the polarization, and each block is a 3×3 matrix.

Depending on the polarizations of monomers located at the ends of a chain, denoted by "+" and "−," corresponding equations for the matrix elements of the generating function have the following form (see Appendix A):

$$\begin{aligned} \mathbf{G}^{+,+}(\xi) = \mathbf{G}^{-,-}(\xi) = {} & \frac{1-\xi(1-\beta)(1-\omega)}{6[\beta+(1-\beta)\omega]} \\ & \times \left(\frac{1}{\xi-\xi_3} - \frac{1}{\xi-1}\right) \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \\ & - \frac{1-\xi(1-\beta)(1-\omega)}{3\sqrt{\beta^2-\beta(1-\beta)\omega+[(1-\beta)\omega]^2}} \\ & \times \left(\frac{1}{\xi-\xi_1} - \frac{1}{\xi-\xi_2}\right) \begin{pmatrix} -1 & 1/2 & 1/2 \\ 1/2 & -1 & 1/2 \\ 1/2 & 1/2 & -1 \end{pmatrix}, \end{aligned} \tag{6}$$

$$\mathbf{G}^{\pm,\mp}(\xi) = \xi D(\xi)\mathbf{B}^{\mp}\mathbf{G}^{+,+}(\xi), \tag{7}$$

where

$$D(\xi) = [1-\xi(1-\beta)(1-\omega)]^{-1}, \quad \mathbf{B}^{\pm} = (1-\beta)\omega\mathbf{I} + \beta\mathbf{U}^{\pm 1},$$

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[1] Such a description of ribbon-like macromolecules is quite reasonable from a physical point of view. At the same time its rigorous substantiation is beyond the framework of this paper and was given in previous work [22]

$$\xi_{1,2} = \frac{1}{(1-\beta)(1-\omega) \pm \sqrt{\beta^2 - \beta(1-\beta)\omega + [(1-\beta)\omega]^2}}, \quad \xi_3 = \frac{1}{2(1-\beta)(1-\omega) - 1}. \tag{8}$$

The use of this method allows one to analyze the orientational self-ordering of the system of ribbonlike polymer chains by taking into account both bending and rotational degrees of freedom.

III. ORIENTATION ORDERING OF CHAINS WITH A TWIST DEGREE OF FREEDOM

Since we are interested in the self-ordering of a nematic type, we have to indicate a preferential direction along which a chain will be oriented after the spontaneous symmetry breaking. Let this preferential direction be the z-axis. The extent of ordering can be described by order parameter η which can be defined in the following way:

$$\eta = \frac{n_z - n_\perp}{n_z + n_\perp}, \tag{9}$$

where n_z is the fraction of monomers directed along the z-axis, and $n_\perp$ is the fraction of monomers in the perpendicular directions ($n_x = n_y \equiv n_\perp$), so that $n_z + 2n_\perp = 1$.

In the case of the isotropic space orientation of monomers, $n_x = n_y = n_z$, and hence $\eta = 0$. In the opposite case of a full nematic ordering, all polymer units are oriented in the z-direction, which leads to $\eta = 1$. The negative values of the order parameter correspond to the prevailing planar orientation of the chain, but this case is of no interest to us.

Until now symmetrical systems have been considered. If symmetry is absent, and the transition from x- and y-directions to the z-direction is preferable as compared to the transition in the opposite direction, then the probability of these transitions $\beta_+(\eta)$ is larger than the original one β, $\beta_+(\eta) \geqslant \beta$, while the probability of the opposite transition $\beta_-(\eta)$ is smaller than β, $\beta_-(\eta) \leqslant \beta$. At the same time, if the system remains symmetric in the x-y plane, the probabilities of $x \to y$ and $y \to x$ transitions have equal β.

The functions $\beta_\pm(\eta)$ should be monotonic, having the following "boundary" conditions:

$$\beta_+(\eta) = \begin{cases} 1 - \varepsilon_+(T), & \eta = 1, \\ \beta, & \eta = 0, \end{cases} \qquad \beta_-(\eta) = \begin{cases} \varepsilon_-(T), & \eta = 1, \\ \beta, & \eta = 0, \end{cases} \tag{10}$$

where $\beta \leqslant 1 - \varepsilon_+(T)$, $\varepsilon_-(T) \leqslant \beta$, and $\varepsilon_\pm(T \to 0) \to 0$.

The functions $\beta_\pm(\eta)$ can be approximated by an Arrhenius-type form,

$$\beta_\pm(\eta, T) = \frac{\exp\{-[E_\beta \mp E(\eta)]/T\}}{1 + \exp\{-[E_\beta \mp E(\eta)]/T\}}, \tag{11}$$

where $E(\eta)$ is the energy gain of the monomer with the orientation along an effective field. Due to the symmetry, $\beta_+(-\eta) = \beta_-(\eta)$, $E(\eta)$ should be the odd function of η.

In line with definition (10), the functions $\varepsilon_\pm(T)$ are expressed in terms of the functions $\beta_\pm(\eta, T)$, defined in (11), which give

$$\varepsilon_+(T) = \frac{1}{1 + \exp\{[E(1) - E_\beta]/T\}}, \quad \varepsilon_-(T) = \frac{\exp\{[E(1) - E_\beta]/T\}}{1 + \exp\{[E(1) - E_\beta]/T\}}. \tag{12}$$

The matrices $\mathbf{B}^\pm$ and $D(\xi)$, describing chain bends and straight line portions of molecule, respectively, have to be modified due to the symmetry breaking. As shown in Appendix B, the properties of the generating functions $\mathbf{G}^{i,j}(\xi)$ are determined by the generating function $\mathbf{G}_0(\xi)$ of the symmetric case, which has the form

$$\mathbf{G}_0(\xi) = |\xi\rangle_0 \frac{1}{1-\xi} \langle\tilde{\xi}|_0 + \sum_{j=1,2} |\xi\rangle_j \frac{1}{1 - \xi + \lambda_j(\xi)} \langle\tilde{\xi}|_j, \tag{13}$$

where $\lambda_{1,2}(\xi)$ are the nonzero eigenvalues of the matrix $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)$ ($\lambda_0 = 0$) and $|\xi\rangle_i$ are the eigenvectors of this matrix; $\langle\tilde{\xi}|_i \cdot |\xi\rangle_k = \delta_{ik}$. The matrices $\mathbf{W}(\xi)$ and $\mathbf{D}_0(\xi)$ have the following form:

$$\mathbf{W}(\xi) = \begin{pmatrix} \gamma_+\delta + \gamma_-\delta_+ & -\gamma\delta & -\gamma_-\delta_- \\ -\gamma_+\delta & \gamma\delta + \gamma\delta_+ & -\gamma_+\delta_- \\ -\gamma_-\delta_+ & -\gamma\delta_+ & \gamma_-\delta_- + \gamma_+\delta_- \end{pmatrix}, \quad \mathbf{D}_0(\xi) = \begin{pmatrix} d_1 & 0 & 0 \\ 0 & d_2 & 0 \\ 0 & 0 & d_3 \end{pmatrix}, \tag{14}$$

where $d_1 = 1/z_+ + \gamma_+/z + \delta_+/z_-$, $d_2 = 1/z + \gamma/z_+ + \delta/z$, $d_3 = 1/z_- + \gamma_-/z_- + \delta_-/z_+$, $\gamma_{\pm,0} = \xi(1-\beta_{\pm,0})\omega/z_{\pm,0}$, $\delta_{\pm,0} = \xi\beta_{\pm,0}/z_{\pm,0}$, $z_{\pm,0} = 1 - (1-\omega)(1-\beta_{\pm,0})\xi$ (0 corresponds to index absence). Note that the functions $\lambda_{1,2}(\xi)$ depend on parameters $\beta_{\pm,0}$ and ω, and this fact is of major significance from a physical point of view.

One must now perform the averaging over all the possible polarizations and orientations of monomers in a chain. The averaging over orientations of the N monomers can be written in the form of the contour integral

$$n_i = \frac{1}{N}\sum_{n=1}^{N} \frac{1}{2\pi i} \oint \frac{1}{2} \sum_{\substack{\alpha,\beta=1,2 \\ j=x,y,z}} \mathbf{G}_{i,j}^{\alpha\beta}(\xi) \langle n_j^0 \rangle \frac{d\xi}{\xi^{n+1}}, \quad i = x, y, z, \tag{15}$$

where n_j^0 define the orientation of the first monomer in a chain containing N monomers, and brackets $\langle \cdots \rangle$. denote averaging over all chains of the system. Note that the structure of the generating functions $\mathbf{G}^{\alpha\beta}(\xi)$ results in the fact that orientation distribution of chain monomers is isotropic in a plane perpendicular to the nematic axis ($n_x = n_y$), which is specific for nematic ordering.

The extent of the ordering of the environment of a trial chain in a mean-field approximation should be regarded as equal to the one of the trial chain. This means that after averaging, the orientation of the first monomer of a chain should be equal to the averaged orientation of all the monomers (i.e., $\langle n_i^0 \rangle = n_i$), and values of the parameters $\beta_{\pm}(\eta, T)$ have to correspond to the same extent of the ordering [the order parameter η is defined by n_i in Eq. (9)]. Such approximation results in the fact that Eq. (15) is, indeed, the self-consistent equation determining the state of the system.

The integral in Eq. (15) is determined by the poles of the matrix $\hat{\mathbf{G}}_0(\xi)$ (13), which are located outside the unit circle in the complex plane ξ. However, for long chains ($N \to \infty$), only one pole, $\xi = 1 + 0$, has to be taken into account since the contribution of poles with $|\xi| > 1$ tends to zero due to the limit $N \to \infty$. The required pole of the matrix $\mathbf{G}_0(\xi)$ corresponds, according to (13), to a zero eigenvalue of the matrix $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)$. Taking into account all of these facts, the fraction of monomers oriented along each axis can be easily calculated:

$$\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \frac{1}{(1-\beta)\beta_+ + 2[1-(\beta+\beta_+)/2]\beta_-} \times \begin{pmatrix} [1-(\beta+\beta_+)/2]\beta_- \\ [1-(\beta+\beta_+)/2]\beta_- \\ (1-\beta)\beta_+ \end{pmatrix}. \tag{16}$$

Substituting (16) into (9), we obtain the following self-consistent equation:

$$\eta = \frac{(1-\beta)\beta_+(\eta) - \{1-[\beta+\beta_+(\eta)]/2\}\beta_-(\eta)}{(1-\beta)\beta_+(\eta) + \{1-[\beta+\beta_+(\eta)]/2\}\beta_-(\eta)}. \tag{17}$$

It transpires that Eq. (17) does not contain the argument ω that defines the chain polarization distribution. This has an obvious explanation: the interaction of the chain with an environment in fact depends on neither the environment polarization nor the local polarization of the trial chain.

By introducing the denotations

$$w(\eta, T) = 1 - \frac{\beta_+(\eta) - \beta}{2(1-\beta)} = 1 - \frac{1 - \exp[-E(\eta)/T]}{2(1 + \exp\{[E_\beta - E(\eta)]/T\})},$$

$$r(\eta, T) = \frac{\beta_+(\eta)}{\beta_-(\eta)} = \frac{1 + \exp\{[E_\beta - E(\eta)]/T\}}{1 + \exp\{[E_\beta + E(\eta)]/T\}},$$

one can represent the Eq. (17) in a more convenient form:

$$w(\eta, T) = \frac{1-\eta}{1+\eta} r(\eta, T). \tag{18}$$

The function $w(\eta)$ decreases monotonically on the interval $\eta = (0,1)$ from the maximum value $w(\eta = 0, T) = 1$ to $w(\eta = 1, T) = w_1(T)$. As a function of T, $w_1(T)$ increases in $T = (0, \infty)$ from $w_1(T=0) = 0.5$ to $w_1(T = \infty) = 1$.

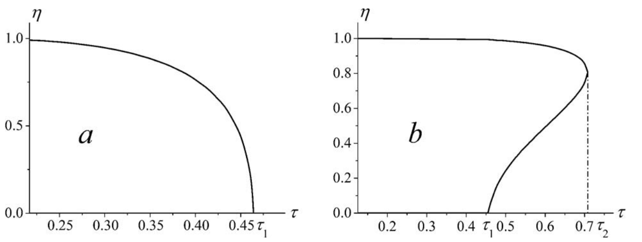

FIG. 1. The order parameter η as a function of reduced temperature τ. (a) $\kappa_3 = 0.2$, $\tau_1 = 0.462$ and (b) $\kappa_3 = 2$, $\tau_1 = 0.462$, $\tau_2 = 0.707$.

Since the left-hand side of Eq. (18) is monotonic in η, the number of solutions of (18) is determined by the right-hand side of (18); namely, by the function

$$h(\eta, T) = \frac{1-\eta}{1+\eta} r(\eta, T) = \frac{1-\eta}{1+\eta} \frac{1 + \exp\{[E_\beta - E(\eta)]/T\}}{1 + \exp\{[E_\beta + E(\eta)]/T\}}, \tag{19}$$

which can be both monotonic and nonmonotonic depending on its parameter values.

It can be easily seen that $\eta = 0$ is a trivial solution of Eq. (18). The existence of other solutions is determined by the energy of the interchain interaction $E(\eta)$. For physical reasons, it is clear that this energy $E(\eta)$ has to increase monotonically with the increase of the ordering in the system. Let us use the polynomial form of the function $E(\eta)$ for the quantitative analysis. Since $E(\eta)$ is an odd function of η, the first terms in the series are

$$E(\eta) = E_1 \eta + E_3 \eta^3. \tag{20}$$

In order to find the numerical solution of Eq. (18), it is convenient to use the dimensionless parameters $\kappa = E_1/E_\beta$ and $\kappa_3 = E_3/E_\beta$, and the reduced temperature $\tau = T/E_\beta$. The parameter κ_3 defines the extent of nonlinearity of the interchain interaction. The parameter κ defines a ratio of interaction energy of monomer with environment and elastic chain bend energy. We set $\kappa = 0.5$ for the numerical calculations[2].

The numerical analysis shows that, depending on the value of the coefficient κ_3, two different types of solutions are possible. There are zero solutions of Eq. (18) for comparatively high temperature independent of the value of κ_3. The nontrivial solutions of Eq. (18) appear only for comparatively low temperatures, and their structure depends on the value of the coefficient κ_3. For $\kappa_3 < \kappa_{3cr}$, only one nonzero solution exists for all temperatures [Fig. 1(a)]. However if $\kappa_3 > \kappa_{3cr}$, Eq. (18) has three nontrivial solutions within some temperature interval and only one nonzero solution for a low temperature [Fig. 1(b)]. The transition between these two types of behavior occurs at $\kappa_{3cr} = 0.3$ for $\kappa = 0.5$.

The appropriate bifurcation diagrams are shown in Fig. 1. For $\kappa_3 = 0.2$ ($\kappa_3 < \kappa_{3cr}$) the ordered phase appears continuously, which corresponds to the phase transition of the second order. For $\kappa_3 = 2$ ($\kappa_3 > \kappa_{3cr}$), however the ordered phase appears abruptly, corresponding to the first-order phase transition.

Hence, for the weak nonlinearity of effective interchain interaction, as for the excluded volume system wherein steric

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[2] Such a choice of κ results in good agreement with experimental data.

interactions are dominant, transition into a nematic state is of the second order, as in the classic Onsager model [8]. However, if the nonlinearity of effective interchain interaction is large enough, transition into the nematic state is of the first order.

IV. EFFECTIVE FREE ENERGY OF POLYMER MACROMOLECULE

As one can see from Fig. 1(b), transition from the isotropic to the nematic state occurs at any temperature τ_1, while the reverse transition from the nematic to the isotropic state takes place at a different temperature τ_2, which represents the hysteresis. However, if the temperature is being changed slowly, the phase transition point is determined not by kinetic but by thermodynamic properties of a system. Therefore, in order to determine the temperature of the first-order phase transition, one has to calculate the free energy of a system in both disordered and ordered states and find the temperature τ_{cr} at which these two values of the free energy are equal. Clearly, $\tau_1 < \tau_{cr} < \tau_2$.

In general, finding the exact form of the free energy of a macromolecule is a hard task. However, one can construct an approximating form of free energy per monomer $F(\eta,T)$ by using some simple arguments. Equation (18) has to be equivalent to the minimum of the free energy; i.e., it must be equivalent to the following equation:

$$\frac{\partial F(\eta,T)}{\partial \eta} = 0. \tag{21}$$

As shown in Appendix C, one can rewrite Eq. (21) in the following form:

$$\frac{\partial F(\eta,T)}{\partial \eta} = \frac{4T}{(3-\eta)^2}\left[\ln\frac{1+\eta}{1-\eta} - \ln\frac{r(\eta,T)}{w(\eta,T)}\right] = 0. \tag{22}$$

Integration of Eq. (22) gives the effective free energy of macromolecule $F(\eta,T)$ per one monomer unit as

$$F(\eta,T) = \frac{T}{3-\eta}\Bigg[(1+\eta)\ln(1+\eta) + 2(1-\eta)\ln(1-\eta) - 3\left(1-\frac{\eta}{3}\right)\ln\left(1-\frac{\eta}{3}\right)\Bigg] - 4T\int_0^{\eta}\frac{\ln[r(x)/w(x)]}{(3-x)^2}dx, \tag{23}$$

where the η-independent part of the free energy, F_0, is omitted, at $\eta=0$.

This form of free energy (23) differs from the usually used fourth-power polynomial in η, with temperature-dependent coefficients. Although one can bring (23) to the latter form using the Taylor series, this series expansion results in no new features of the system, having changed the values of critical points to only a small extent.

Graph of free energy (23) is shown in Fig. 2. At high temperature there is only one minimum at $\eta=0$ (curve 1). An additional local minimum appears at the reduced temperature $\tau=\tau_2$, and the value of function $F(\eta,T)$ at this local minimum is higher than that at $\eta=0$ (curve 2). At phase transition temperature τ_{cr}, the function $F(\eta,T)$ in both minima become equal (curve 3). Finally, at temperature $\tau=\tau_1$, the local minimum at $\eta=0$ disappears, converting into a local maximum corresponding to an unstable state of the system (curve 4). The reduced temperature τ_{cr} ($\tau_1 < \tau_{cr} < \tau_2$) of the first-order phase transition for the parameters used in the bifurcation diagram [Fig. 1(b)] was obtained numerically $\tau_{cr}=0.655$.

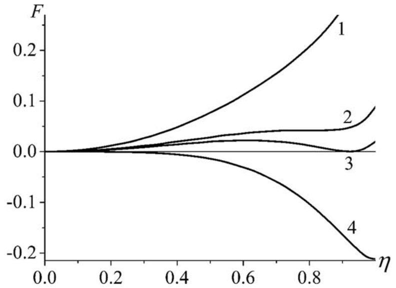

FIG. 2. The free energy F as a function of the order parameter η for different values of the reduced temperature ($\kappa_3=2$). (1) $\tau=1>\tau_2$; (2) $\tau=\tau_2$; (3) $\tau=\tau_{cr}$; (4) $\tau=\tau_1$; where $\tau_1=0.462$, $\tau_{cr}=0.655$, $\tau_2=0.707$.

It should be noted in conclusion of this section that one must include: the kinetic, rather than thermodynamic nature of the first-order phase transition. Including the latter will mean that the isotropic-nematic phase transition will be accompanied by a hysteresis which was, indeed, observed experimentally [6].

V. PHASE TRANSITION TEMPERATURE DEPENDENCE ON CHAIN LENGTH

All of the above analysis refers to asymptotically long polymer chains. In fact, we assumed that the persistent length in disordered and ordered phases is much smaller than the contour length of a chain; i.e., the number of Kuhn segments of the chain is large. We now wish to generalize our analyses to relatively short chains, for which the contour length of a macromolecule is of the order of its persistence length. Such a situation takes place, for example, for oligomers.

In order to take into account the finite length of a polymer, one has to keep finite the parameter N in Eq. (15). That means that the others poles of the generation $\mathbf{G}_0(\xi)$ (13) are to be taken into account. However, in the framework of our approximations, the inclusion of only two poles $\xi_{1,2}$ with the smallest absolute values results in the necessary corrections of Eq. (18). Thereafter, according to the calculations performed in Appendix D, the self-consistent equation has the following form:

$$w(\eta,T) + \frac{3-\eta}{1+\eta}\Delta_-(\eta)[r(\eta,T) + 2w(\eta,T)]\phi_0(N,\xi_1,\xi_2) = \frac{1-\eta}{1+\eta}r(\eta,T), \tag{24}$$

where

$$\phi_0(N,\xi_1,\xi_2) = \frac{\phi_2(N,\xi_2) - \phi_1(N,\xi_1)}{\phi_2(N,\xi_2) + \phi_1(N,\xi_1)}, \quad \phi_{1,2}(N,\xi_{1,2}) = \frac{1-\exp(-N/N_{1,2})}{N/N_{1,2}},$$
$$N_{1,2} = 1/\ln(\xi_{1,2}). \qquad (25)$$

Comparison with the results of the previous section shows that a finite length of the chain results in the following generalization of function $w(\eta,T)$:

$$\widetilde{w}(\eta,N) = w(\eta) + \frac{3-\eta}{1+\eta}\Delta_{-}(\eta)[r(\eta)+2w(\eta)]\phi_0(N,\xi_1,\xi_2). \qquad (26)$$

Function $\Delta_{-}(\eta)$ remains unknown in Eq. (26). Although it is difficult to find the exact form of this function $\Delta_{-}(\eta)$, it is sufficient for our purposes to take into account that this function is proportional to $\xi_2(\eta)-\xi_1(\eta)$,

$$\Delta_{-}(\eta) = k_{\Delta}[\xi_2(\eta) - \xi_1(\eta)]. \qquad (27)$$

It turns out that this approximation describes correctly the behavior of function $\Delta_{-}(\eta)$ in a qualitative sense: function $\Delta_{-}(\eta)$ vanishes at $\eta=0$, afterwards increases initially with η, then attains the maximum (which depends on temperature), and finally decreases when η approaches unity.

The generalization of the free energy for a macromolecule of arbitrary length N can be easily calculated from Eq. (26):

$$F(\eta,T) = \frac{T}{3-\eta}\left[(1+\eta)\ln(1+\eta) + 2(1-\eta)\ln(1-\eta) - 3\left(1-\frac{\eta}{3}\right)\ln\left(1-\frac{\eta}{3}\right)\right] - 4T\int_0^{\eta}\frac{\ln[r(x)/\widetilde{w}(x,N)]}{(3-x)^2}dx. \qquad (28)$$

Note that the free energy (28) depends implicitly on both the twist and bending rigidities, $\omega(T)$ and $\beta(T)$, through the poles $\xi_{1,2}$ in Eq. (13).

Numerical analysis shows that the best agreement with the experimental data occurs for the following values of the parameters: the ratio of energy parameters E_{ω} and E_{β} in Eq. (1) is equal to 2 ($E_{\beta}/E_{\omega}=2$), the dimensionless coefficient k_{Δ} is equal to 4, and the effective length of monomer of a model chain is 5% less than a monomer of the real chain. Such a choice of parameters gives a quantitatively correct estimation of the temperature of phase transition as well as of other experimental data. The latter requires taking into account the rotational degrees of freedom of polymer chains. This is considered in the next section.

In Fig. 3 we show the dependence of the phase transition temperature on the chain length. As one can see from Fig. 3, there is no visible difference between the theoretical curve and the experimental data [6] for chains containing more than 30 elementary units. The theory gives slightly higher temperatures of phase transition only for shorter chains. This distinction may be connected with contribution of the translational entropy of the chain ends neglected in our model, which is certainly correct for long chains. However, for the ordered phase of short chains there are correlations in the position of the chain ends that result in decreasing translational entropy and, hence, in decreasing the transition temperature. This effect should be observed for the chains the length of which is comparable with the molecule persistence length or, more precisely, with the correlation length of a chain along the axis of orientational ordering. The estimations show that for $\tau/\tau_{cr}\approx 0.79$, this correlation length is approximately equal to 40 units. The latter estimation refers to the ordered phase, while for the disordered state the persistence length is equal to eight units.

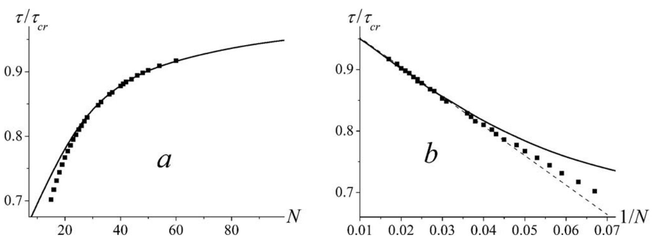

FIG. 3. The reduced temperature of phase transition into rotator phase τ/τ_{cr} as a function of chain length N (a) and of reciprocal length $1/N$ (b) ($\kappa_3=2$, $k_{\Delta}=4$, $E_{\omega}=0.5E_{\beta}$). The points are the experimental data [6].

In Fig. 3(b) we demonstrate phase transition temperature dependence on the reciprocal chain length. This dependence is linear for chains longer than the persistence length, but one can see some departure from linearity for shorter chains. Such a deviation from the linear dependence has been observed experimentally [6].

The nonlinear dependence for short chains is related to a possible coupling between rotational and bending degrees of freedom due to anisotropy of bending. The latter effect is of no importance for long chains and results in only a decrease of the effective rigidity with the chain length increase.

VI. INFLUENCE OF THE ROTATIONAL DEGREES OF FREEDOM ON THE PHASE TRANSITION INTO ROTATOR PHASE

As we have seen in Fig. 3, the properties of short and long chains are different. The short-long crossover occurs at molecular lengths of about 30-40 monomer units. Another way of looking at these data is to consider the properties of the correction function $\phi_0(N)$ in the self-consistent equation (26) [Fig. 4(a)].

This function can be approximated by an exponential for short chains (a dashed line), and by a power function for long chains (dotted line).The region of a crossover in Fig. 4(a) coincides with the the region of a crossover for the phase transition temperature shown in Fig. 3(a). This common crossover chain length corresponds to the correlation length of a chain along a nematic axis in the ordered state. The latter is obvious from Fig. 4(b), where the amplitude $\phi_{fl}(N)$ of the orientation distribution difference of extreme monomers of a chain increases at the beginning up to some

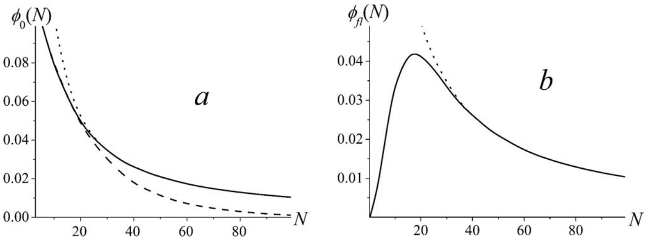

FIG. 4. The correction function $\phi_0(N)$ in the self-consistent Eq. (26) (a) and the amplitude $\phi_{fl}(N)$ of the difference of orientation distribution of the end of a chain from the orientation distribution of its beginning as a function of the length of a chain at phase transition temperature (b). The dashed and dotted lines represent the exponential [coincides with $\phi_0(N)$ for $N \leqslant 20$] and power dependence [coincides with $\phi_0(N)$ and $\phi_{fl}(N)$ for $N \geqslant 30$], respectively.

characteristic length and decreases afterwards. Such a behavior means that for a short chain, both its ends are located within the persistence length of the chain, while in the case of a long chain, the correlation between chain ends is of no importance, and their state is governed by the averaged orientational distribution.

The characteristic parameters of a chain in the ordered state depend on parameter E_ω and this fact shows the importance of the rotational degrees of freedom. The latter statement is supported by the experimentally observed nontrivial dependence of the specific jump of entropy at phase transition $\Delta S(N)$. It turns out that for quite long chains ($N > 30$) the entropy jump does not depend on length, while for short chains ($N < 30$) the entropy jump starts to depend on the length of a chain [6] [see Fig. 5(a), points].

The theoretical calculation gives results very similar to the experiment: the entropy jump $\Delta S(N)$ weakly decreases for the chain length from 200 up to 40 units. However, for the smaller lengths (with further chain length decrease), $\Delta S(N)$ sharply increases, passing through the minima at $N \approx 40$ monomer units. Thus, for $N > 40$ the theoretical calculation coincides with the experimental result. A slight disagreement appears only for short chains [see Fig. 5(a)]. The reason for such disagreement is the same as in the case of dependence of the phase transition temperature on chain length. In both cases, the model does not take into account translational entropy of the chain ends.

The difference in behavior of the entropy jump ΔS for short and long chains, shown in Fig. 5(a), can be explained by taking into account that ΔS is defined by a ratio of energy and temperature rather than by each of them separately. For short chains, the effective persistent length along with the effective rigidity decreases when the chain length is decreased. The latter results in a decrease of both transition temperature and energy gain at ordering, so that their ratio remains almost constant. This compensation is not complete since the energy consists of two parts (bend and twist) and the effective values of each one can depend differently on the chain length.

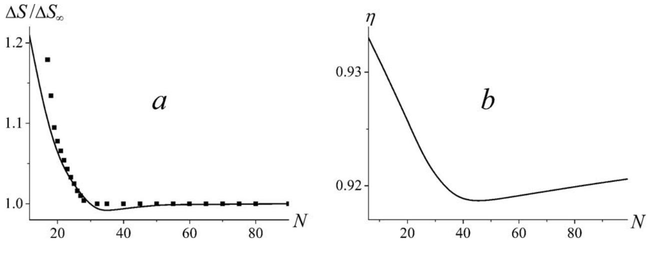

FIG. 5. Dependence of the specific entropy jump $\Delta S(N)/\Delta S_\infty$ (a) and of the order parameter η (b) on chain length N at the phase transition temperature. The continuous lines are the theoretical estimates for parameters $\kappa_3=2$, $k_\Delta=4$, $E_\omega=0.5E_\beta$, where the points represent the experimental data [6].

As indicated above, the decrease of the effective chain rigidity with the decrease of the length can be characterized by the amplitude of deviation of orientation distribution of the ends of a chain $\phi_{fl}(N)$. It turns out that for the chosen value of system parameters and for the chain length longer than 40 monomers, the function $\phi_{fl}(N)$ practically coincides with amplitude of the correction function $\phi_0(N)$ in Eq. (24). The latter means that in this case one gets almost full compensation of change of energy and temperature, as can be seen from Fig. 4(b).

Another quantity that depends nonmonotonically on the chain length is the order parameter η. As shown in Fig. 5(b), the jump of the order parameter at the phase transition temperature changes gradually for long chains, but one gets the abrupt changes for short chains. Such behavior is quite different from that in the theory of nematic ordering of the polymers, wherein a monotonic dependence is predicted [7]. Unfortunately, due to lack of experimental data, it is impossible to decide between these two possibilities.

The bend and twist degrees of freedom of polymer chains are usually considered to be independent. This is true for the disordered phase and for the rotator phase of infinitely long macromolecules. However, for chains of finite length in the orientation-ordered state, the bend and twist become correlated since the different directions of chain orientation become nonequivalent due to the local anisotropy of the bending rigidity of the chain. This correlation is of no importance in the isotropic phase since the system is isotropic as a whole. However, after transition into the ordered phase the isotropy is broken. The anisotropy occurs only for directions that are perpendicular to the axis of the nematic ordering, while a system remains isotropic for the direction parallel to the ordering axis. The correlation between bend and twist becomes evident from the following considerations. The most probable next step of monomer located at the plane perpendicular to the nematic axis will be that in the direction of the nematic axes. However, the necessary bend can occur only if there is favorable polarization. This means that the chain bend depends on polarization; i.e., on the activation energy of the internal rotation. The latter fact is present in our theory. Indeed, poles $\xi_{1,2}$ in Eqs. (25) which determine the characteristic scale of the chains, located in the plane perpendicular to the ordering axis, depend on parameter ω.

Interaction between bend and twist is different for long and short chains. For long chains, the twist activation energy E_ω divided by temperature T is quite small ($E_\omega/T \ll 1$), and a monomer located in a plane perpendicular to the ordering axis will bend only in this plane and will remain there until the polarization becomes favorable for returning the chain in the direction of the nematic axis. This is the very reason the order parameter of long chains will not increase with a decrease in chain length.

The opposite situation occurs for short chains when $E_\omega/T \gg 1$, and the chain returns to the direction of the ordering axis without a change in the polarization. In other words, the rotational degree of freedom is "frozen." The ordering of a rotational degree of freedom results, in particular, in a breakdown of the compensation mechanism discussed above. Then the jump of the specific entropy at phase transition starts to increase with the decrease of the chain length. For the same reason, the order parameter will sufficiently increase.

VII. CONCLUSION

Our analysis shows that there are two important factors in the process of the rotator phase formation: the local anisotropy of bending rigidity of a macromolecule and the restrictions in chain conformations in the rotational phase caused by this anisotropy. The local anisotropy of bending rigidity of a macromolecule does not show up in the isotropic phase, but the local anisotropy becomes important for the ordered state in regions perpendicular to the nematic axis.

If the twist energy is large in comparison with the bend energy ($E_\omega \gg E_\beta$), i.e., the probability of the change of a chain polarization is low, the rotational degree of freedom is frozen in a plane perpendicular to the nematic axis. In the opposite limit, when the probability of polarization change is high ($E_\omega \ll E_\beta$), the fast polarization change restores completely the broken isotropy, and rotational degrees of freedom are of no importance in the process of formation of the rotator phase.

For the intermediate values of the twist activation energy ($E_\omega \approx 0.5E_\beta$), the behavior will be different for long and short macromolecules. Only weak restrictions on rotational degrees of freedom arise in regions perpendicular to the nematic axis for long chains. These restrictions will be more severe with a decrease in the length of a chain. However, for short chains, these restrictions will be weaker due to effective "softening" of the short chains. This compensation of the two factors explains the fact that the jump of the entropy at the phase transition does not depend on the chain length. "Freezing" of the rotational degree of freedom in the disordered part of a macromolecule results in the break of the compensation mechanism for short chains. Both the bend and twist degrees of freedom are related to a tranes-gauche isomerism of normal alkanes, whereas the distinction between them is caused by the steric (geometrical) restrictions. The used ratio of the activation energies of a bend and twist ($E_\omega \approx 0.5E_\beta$) seems to be reasonable, and, indeed, the results of our theory are in good agreement with experimental data.

It seems plausible that our analysis opens the way to understanding the existence of five different types of the rotational phase. Indeed, the properties of the different rotational phases are connected with the extent of ordering of the rotational degree of freedom, since the interchain interaction in the ordered polymer system depends on the relative polarizations of interacting monomers. Therefore, one must take into account the energy dependence of the interchain interaction on the extent of the ordering of the rotational degree of freedom of a polymer. It is this problem that has been analyzed in the present model.

ACKNOWLEDGMENTS

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APPENDIX A: THE GENERATING FUNCTION FOR THE ISOTROPIC SYSTEM

We consider arbitrary distribution of polarizations along a chain with a positive polarization of the extreme left monomer. Let us divide the whole chain into K segments, each containing two parts with different polarizations. The number of monomers with positive polarization in a kth segment ($k=0,1,\ldots,K$) is n_k, and those with negative polarization are m_k, where n_k, $m_k=0,1,2,\ldots$. The probabilities to form the first and the second parts of the kth segment of a chain are equal to $[(1-\beta)(1-\omega)]^{n_k}$ and $[(1-\beta)(1-\omega)]^{m_k}$, respectively. The change of polarization takes place at the twist or bend. The direction of the bend depends on the polarization of the unit in which this bending occurs. The probability of a chain twist without a bend is equal to $(1-\beta)\omega$, and the probability of a chain bend is equal to $(1-\beta)(1-\omega)$.

The first part (positive polarization) of the kth chain segments is associated with the propagator $[(1-\beta)(1-\omega)]^{n_k}$, while the second one (negative polarization) is associated with the propagator $[(1-\beta)(1-\omega)]^{m_k}$. The positive-negative polarization switching is defined by factor $\mathbf{B}^{+}$, and the opposite one is defined by factor $\mathbf{B}^{-}$, where

$$\mathbf{B}^{+} = \begin{pmatrix} (1-\beta)\omega & \beta & 0 \\ 0 & (1-\beta)\omega & \beta \\ \beta & 0 & (1-\beta)\omega \end{pmatrix}, \quad \mathbf{B}^{-} = \begin{pmatrix} (1-\beta)\omega & 0 & \beta \\ \beta & (1-\beta)\omega & 0 \\ 0 & \beta & (1-\beta)\omega \end{pmatrix} \tag{A1}$$

Thus, each of the kth segments of the chain (except of the last one) is defined by the following factor:

$$\mathbf{B}^{-}[(1-\beta)(1-\omega)]^{m_k}\mathbf{B}^{+}[(1-\beta)(1-\omega)]^{n_k}. \tag{A2}$$

The product of these factors describes the whole chain composed of K rectilinear segments

$$\prod_{k=1}^{K} \{\hat{\mathbf{B}}^{-}[(1-\beta)(1-\omega)]^{m_k}\hat{\mathbf{B}}^{+}[(1-\beta)(1-\omega)]^{n_k}\}. \tag{A3}$$

Depending on the polarization of the chain end, additional factors have to be added to Eq. (A3) from the left. Namely, if the chain end has negative polarization, this factor will be $[(1-\beta)(1-\omega)]^{m_{K+1}}\mathbf{B}^{+}[(1-\beta)(1-\omega)]^{n_{K+1}}$, and if the chain end has positive polarization, this factor will be $[(1-\beta)(1-\omega)]^{n_{K+1}}$.

The following expression corresponds to the chain with positive polarization at the two ends:

$$[(1-\beta)(1-\omega)]^{n_{K+1}}\prod_{k=1}^{K}\{\mathbf{B}^{-}[(1-\beta)(1-\omega)]^{m_k}\mathbf{B}^{+}[(1-\beta)\times(1-\omega)]^{n_k}\}. \tag{A4}$$

Analogously, for the chain which has the positive polarization at one end and the negative polarization at the other end, one gets

$$[(1-\beta)(1-\omega)]^{m_{K+1}}\mathbf{B}^{+}[(1-\beta)(1-\omega)]^{n_{K+1}}\prod_{k=1}^{K}\{\mathbf{B}^{-}[(1-\beta)(1-\omega)]^{m_k}\mathbf{B}^{+}[(1-\beta)(1-\omega)]^{n_k}\}. \tag{A5}$$

The obtained expression has to be averaged over all the possible lengths of each chain segment with a given polarization on condition that the total length N of a chain is fixed, which gives

$$\bar{\mathbf{G}}^{+,+}(N)=\sum_{K}\sum_{\{n_k,m_k\}}[(1-\beta)(1-\omega)]^{n_{K+1}}\prod_{k=1}^{K}\{\mathbf{B}^{-}[(1-\beta)(1-\omega)]^{m_k}\mathbf{B}^{+}[(1-\beta)(1-\omega)]^{n_k}\}\Bigg|_{\Sigma_{k=1}^{K}m_k+n_k+2K=N}, \tag{A6}$$

$$\bar{\mathbf{G}}^{-,+}(N)=\sum_{K}\sum_{\{n_k,m_k\}}[(1-\beta)(1-\omega)]^{m_{K+1}}\mathbf{B}^{+}[(1-\beta)\times(1-\omega)]^{n_{K+1}}\prod_{k=1}^{K}\{\mathbf{B}^{-}[(1-\beta)(1-\omega)]^{m_k}\mathbf{B}^{+}[(1-\beta)(1-\omega)]^{n_k}\}\Bigg|_{\Sigma_{k=1}^{K}m_k+n_k+2K=N}. \tag{A7}$$

One can overcome the difficulties associated with the restrictions in the summation by using the technique of the generating function which reduces the problem to the summation of two infinite geometric series,

$$\begin{aligned}\mathbf{G}^{+,+}(\xi)&=D(\xi)\sum_{K}^{\infty}[\xi^2D^2(\xi)\mathbf{B}^{-}\mathbf{B}^{+}]^{K}\\&=D(\xi)[\hat{\mathbf{I}}-\xi^2D^2(\xi)\mathbf{B}^{-}\mathbf{B}^{+}]^{-1},\end{aligned} \tag{A8}$$

$$\mathbf{G}^{-,+}(\xi)=\xi D^2(\xi)^{-}\mathbf{B}^{+}\sum_{K}^{\infty}[\xi^2D^2(\xi)\mathbf{B}^{-}\mathbf{B}^{+}]^{K}=\xi D(\xi)^{-}\mathbf{B}^{+}\mathbf{G}^{+,+}(\xi), \tag{A9}$$

where $\mathbf{G}^{\pm,+}(\xi)=\sum_{N=1}^{\infty}\xi^{N}\bar{\mathbf{G}}^{\pm,+}(N)$.

Finally the generating functions for the chain with the same negative polarizations at the two ends ($\mathbf{G}^{-,-}$) and with opposite polarizations ($\mathbf{G}^{+,-}$) have the following form:

$$\begin{aligned}\mathbf{G}^{-,-}(\xi)&=D(\xi)\sum_{K}^{\infty}[\xi^2D^2(\xi)\mathbf{B}^{+}\mathbf{B}^{-}]^{K}\\&=D(\xi)[\hat{\mathbf{I}}-\xi^2D^2(\xi)\mathbf{B}^{+}\mathbf{B}^{-}]^{-1},\end{aligned} \tag{A10}$$

$$\mathbf{G}^{+,-}(\xi)=\xi D^2(\xi)\mathbf{B}^{-}\sum_{K}^{\infty}[\xi^2D^2(\xi)\mathbf{B}^{+}\mathbf{B}^{-}]^{K}=\xi D(\xi)\mathbf{B}^{-}\mathbf{G}^{-,-}(\xi), \tag{A11}$$

with $D(\xi)=\sum_{n}[\xi(1-\beta)(1-\omega)]^{n}=[1-\xi(1-\beta)(1-\omega)]^{-1}$.

APPENDIX B: THE GENERATING FUNCTION FOR THE ORDERED SYSTEM

The construction of a generating function in the case of broken symmetry requires some extension compared with the isotropic system considered in Appendix A. Namely, the propagator $(1-\beta)(1-\omega)$ and the matrixes $\mathbf{B}^{\pm}$ describing the bends of the chain, are to be modified

$$(1-\beta)(1-\omega)\to\begin{cases}\mathbf{D}_0^{-}=(1-\omega)\begin{pmatrix}1-\beta&0&0\\0&1-\beta_{+}&0\\0&0&1-\beta_{-}\end{pmatrix},\\[2ex]\mathbf{D}_0^{+}=(1-\omega)\begin{pmatrix}1-\beta_{+}&0&0\\0&1-\beta&0\\0&0&1-\beta_{-}\end{pmatrix},\end{cases} \tag{B1}$$

$$\mathbf{B}^{+}\to\hat{\mathbf{B}}^{+}=\begin{pmatrix}(1-\beta_{+})\omega&\beta&0\\0&(1-\beta)\omega&\beta_{-}\\\beta_{+}&0&(1-\beta_{-})\omega\end{pmatrix}, \tag{B2}$$

$$\mathbf{B}^{-}\to\hat{\mathbf{B}}^{-}=\begin{pmatrix}(1-\beta)\omega&0&\beta_{-}\\\beta&(1-\beta_{+})\omega&0\\0&\beta_{+}&(1-\beta_{-})\omega\end{pmatrix}. \tag{B3}$$

Revising the argumentation of Appendix A, one obtains the following expressions for the generating function for a chain with the positive polarization of both ends:

$$\begin{aligned}\hat{\mathbf{G}}^{+,+}(\xi)&=\sum_{K}\sum_{\{n_k,m_k\}}(\xi\mathbf{D}_0^{+})^{n_{K+1}}\prod_{k=1}^{K}\{\xi\hat{\mathbf{B}}^{-}(\xi\hat{\mathbf{D}}_0^{-})^{m_k}\xi\hat{\mathbf{B}}^{+}(\xi\mathbf{D}_0^{+})^{n_k}\}\\&=\mathbf{D}^{+}(\xi)[\hat{\mathbf{I}}-\xi^2\hat{\mathbf{B}}^{-}\mathbf{D}^{-}(\xi)\hat{\mathbf{B}}^{+}\mathbf{D}^{+}(\xi)]^{-1},\end{aligned} \tag{B4}$$

with

$$\mathbf{D}^{+}(\xi)=\begin{pmatrix}1-\delta_{+}-\gamma_{+}&0&0\\0&1-\delta-\gamma&0\\0&0&1-\delta_{-}-\gamma_{-}\end{pmatrix},$$

$$\mathbf{D}^{-}(\xi)=\begin{pmatrix}1-\delta-\gamma & 0 & 0\\ 0 & 1-\delta_{+}-\gamma_{+} & 0\\ 0 & 0 & 1-\delta_{-}-\gamma_{-}\end{pmatrix}, \qquad \text{(B5)}$$

where $\delta_{\pm,0}=\xi\beta_{\pm,0}/z_{\pm,0}$, $\gamma_{\pm,0}=\xi(1-\beta_{\pm,0})\omega/z_{\pm,0}$, $z_{\pm,0}=1-(1-\omega)(1-\beta_{\pm,0})\xi$, $\delta_{\pm,0}+\gamma_{\pm,0}=1-(1-\xi)/z_{\pm,0}$ ("0" corresponds to index absence).

The matrix $\mathbf{I}-\xi^2\hat{\mathbf{B}}^{-}\mathbf{D}^{-}(\xi)\hat{\mathbf{B}}^{+}\mathbf{D}^{+}(\xi)$ can be rewritten as

$$\begin{aligned}\hat{\mathbf{I}}-\xi\hat{\mathbf{B}}^{-}\mathbf{D}^{-}(\xi)\hat{\mathbf{B}}^{+}\mathbf{D}^{+}(\xi)&=(1-\xi)\mathbf{D}_0(\xi)+\mathbf{W}(\xi)\\ &=(1-\xi)\left[\mathbf{I}+\frac{1}{1-\xi}\mathbf{W}(\xi)\right.\\ &\qquad\left.\times\mathbf{D}_0^{-1}(\xi)\right]\mathbf{D}_0(\xi),\end{aligned} \qquad \text{(B6)}$$

with

$$\mathbf{W}(\xi)=\begin{pmatrix}\gamma_{+}\delta+\gamma_{-}\delta_{+} & -\gamma\delta & -\gamma_{-}\delta_{-}\\ -\gamma_{+}\delta & \gamma\delta+\gamma\delta_{+} & -\gamma_{+}\delta_{-}\\ -\gamma_{-}\delta_{+} & -\gamma\delta_{+} & \gamma_{-}\delta_{-}+\gamma_{+}\delta_{-}\end{pmatrix}, \quad \mathbf{D}_0(\xi)=\begin{pmatrix}d_1 & 0 & 0\\ 0 & d_2 & 0\\ 0 & 0 & d_3\end{pmatrix} \qquad \text{(B7)}$$

and $d_1=1/z_{+}+\gamma_{+}/z+\delta_{+}/z_{-}$, $d_2=1/z+\gamma/z_{+}+\delta/z$, $d_3=1/z_{-}+\gamma_{-}/z_{-}+\delta_{-}/z_{+}$.

The convenience of expression (B6) lies in the fact that the determinant of the matrix $\mathbf{W}(\xi)$ is equal to zero. The latter allows one to transform matrix $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)$ into diagonal form, $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)=\mathbf{O}\cdot\mathbf{\Lambda}\cdot\mathbf{O}^{-1}$, where $\mathbf{\Lambda}$ is the diagonal matrix. Thus, we have

$$\begin{aligned}&\frac{1}{1-\xi}\left[\hat{\mathbf{I}}+\frac{1}{1-\xi}\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)\right]^{-1}\\ &\quad=\mathbf{G}_0(\xi)=|\xi\rangle_0\frac{1}{1-\xi}\langle\tilde{\xi}|_0+\sum_{j=1,2}|\xi\rangle_j\frac{1}{1-\xi+\lambda_j(\xi)}\langle\tilde{\xi}|_j,\end{aligned} \qquad \text{(B8)}$$

where $\lambda_{1,2}(\xi)$ are the nonzero eigenvalues of the matrix $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)$ ($\lambda_0=0$), and $|\xi\rangle_i$ and $\langle\tilde{\xi}|_j$ are the columns and rows of matrixes $\mathbf{O}$ and $\mathbf{O}^{-1}$, respectively.

The generating function for the chains with arbitrary polarizations at its ends can be achieved analogously in an isotropic case by the use of matrix $\mathbf{G}_0(\xi)$:

$$\hat{\mathbf{G}}^{+,+}(\xi)=\mathbf{D}^{+}(\xi)\mathbf{D}_0^{-1}(\xi)\mathbf{G}_0(\xi), \qquad \text{(B9)}$$

$$\hat{\mathbf{G}}^{-,+}(\xi)=\xi\mathbf{D}^{-}(\xi)\hat{\mathbf{B}}^{+}\hat{\mathbf{G}}^{+,+}(\xi), \qquad \text{(B10)}$$

$$\hat{\mathbf{G}}^{-,-}(\xi)=\mathbf{V}\hat{\mathbf{G}}^{+,+}(\xi)\mathbf{V}, \qquad \text{(B11)}$$

$$\hat{\mathbf{G}}^{+,-}(\xi)=\mathbf{V}\hat{\mathbf{G}}^{-,+}(\xi)\mathbf{V}, \qquad \text{(B12)}$$

where $\mathbf{V}=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$.

APPENDIX C: THE FREE ENERGY OF A POLYMER CHAIN

The free energy of a chain having a given fraction n_z of monomers oriented along the z-axis, where $n_z=(1+\eta)/(3-\eta)$, is defined by the following expression:

$$\begin{aligned}\exp\left[-\frac{NF(\eta,T)}{T}\right]&=\sum_{N_x+N_y+N_z=N}\frac{N!}{N_x!N_y!N_z!}n_x^{N_x}n_y^{N_y}n_z^{N_z}\\ &\qquad\times\exp\left[-\frac{N\Delta\tilde{F}(\eta,T)}{T}\right]\\ &=\frac{N!}{N_z!(N-N_z)!}\left(\frac{n_z}{n_\perp}\right)^{N_z}\exp\left[\right.\\ &\qquad\left.-\frac{N\Delta F(\eta,T)}{T}\right],\end{aligned} \qquad \text{(C1)}$$

where N is the number of units in a macromolecule; N_i ($i=x,y,z$) are the numbers of units that are oriented along the ith axis; n_i are the probabilities of orientations of polymer chain units parallel to the ith axis given by Eq. (16); $n_x=n_y=n_\perp$, $n_z=N_z/N$. The factor $\Delta\tilde{F}(\eta,T)=\Delta F(\eta,T)+T\ln(2n_\perp)$ takes into account the correlations in the monomer sequence.

Taking the logarithm of Eq. (C1) and using the Stirling formula, one gets the free energy per monomer,

$$\begin{aligned}F(\eta,T)&=\frac{T}{3-\eta}\left[(1+\eta)\ln(1+\eta)+2(1-\eta)\ln(1-\eta)\right.\\ &\qquad\left.-(3-\eta)\ln\left(1-\frac{\eta}{3}\right)-(1+\eta)\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)\right]\\ &\qquad+\Delta F(\eta,T),\end{aligned} \qquad \text{(C2)}$$

where functions $r(\eta,T)$ and $w(\eta,T)$ have been defined in Eq. (18).

Using (C2), one gets for the steady states

$$\begin{aligned}\frac{\partial F(\eta,T)}{\partial\eta}=0&=\frac{4T}{(3-\eta)^2}\left[\ln\left(\frac{1+\eta}{1-\eta}\right)-\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)\right]\\ &\qquad-T\frac{1+\eta}{3-\eta}\frac{\partial}{\partial\eta}\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)+\frac{\partial\Delta F(\eta,T)}{\partial\eta}.\end{aligned} \qquad \text{(C3)}$$

The expression in the square brackets corresponds to the right-hand side of Eq. (18) which can be transformed into the following form:

$$T\left[\ln\left(\frac{1+\eta}{1-\eta}\right)-\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)\right]=0. \qquad \text{(C4)}$$

Therefore, the derivation of the free energy is defined by the following condition:

$$\frac{\partial F(\eta,T)}{\partial\eta}=\frac{4T}{(3-\eta)^2}\left[\ln\left(\frac{1+\eta}{1-\eta}\right)-\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)\right]=0, \qquad \text{(C5)}$$

and, using Eq. (C3), one gets the function $\Delta F(\eta,T)$:

$$\Delta F(\eta,T) = T\int_0^{\eta} \frac{1+x}{3-x}\frac{\partial \ln(r(x,T)/w(x,T))}{\partial x}dx = T\frac{1+\eta}{3-\eta}\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right) - 4T\int_0^{\eta}\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)\frac{dx}{(3-x)^2}. \tag{C6}$$

The final expression for the free energy per one monomer of the macromolecule is obtained by integration of Eq. (C5), which gives

$$F(\eta,T) = \frac{T}{3-\eta}\left[(1+\eta)\ln(1+\eta) + 2(1-\eta)\ln(1-\eta) - (3-\eta)\ln\left(1-\frac{\eta}{3}\right)\right] - 4T\int_0^{\eta}\ln\left(\frac{r(\eta,T)}{w(\eta,T)}\right)\frac{dx}{(3-x)^2}. \tag{C7}$$

We omit in Eq. (C7) all the terms which do not depend on the η, and the bottom limit of integration meets the condition $F(\eta=0,T)=0$.

APPENDIX D: THE ACCOUNTING OF THE CHAIN LENGTH FINITENESS

The nonzero eigenvalues $\lambda_{1,2}$ of the matrix $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)$ [compare (13)] are the roots of the quadratic equation $\lambda^2 - \mathrm{Tr}[\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)]\lambda + \mathrm{Tr}[\mathbf{M}(\xi)]=0$, where $\mathbf{M}$ is the matrix of minor determinants of the matrix $\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)$. These roots take the following form:

$$\lambda_{1,2} = \frac{1}{2}\mathrm{Tr}[\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)] \pm \sqrt{\frac{1}{4}\mathrm{Tr}[\mathbf{W}(\xi)\mathbf{D}_0^{-1}(\xi)]^2 - \mathrm{Tr}[\mathbf{M}(\xi)]}, \tag{D1}$$

where

$$\mathrm{Tr}\,\hat{\mathbf{M}} = \mathbf{M}_{11} + \mathbf{M}_{22} + \mathbf{M}_{33} = \frac{\mathbf{W}_{22}\mathbf{W}_{33} - \mathbf{W}_{23}\mathbf{W}_{32}}{d_2 d_3} + \frac{\mathbf{W}_{11}\mathbf{W}_{33} - \mathbf{W}_{13}\mathbf{W}_{31}}{d_1 d_3} + \frac{\mathbf{W}_{11}\mathbf{W}_{22} - \mathbf{W}_{12}\mathbf{W}_{21}}{d_1 d_2},$$

$$\mathrm{Tr}[\hat{\mathbf{W}}(\xi)\hat{\mathbf{D}}_0^{-1}(\xi)] = \frac{\mathbf{W}_{11}}{d_1} + \frac{\mathbf{W}_{22}}{d_2} + \frac{\mathbf{W}_{33}}{d_3} = \frac{\gamma_+\delta + \gamma_-\delta_+}{d_1} + \frac{\gamma\delta + \gamma\delta_+}{d_2} + \frac{\gamma_-\delta_- + \gamma_+\delta}{d_3}.$$

Only two poles $\xi_{1,2}$ with the smallest absolute magnitudes are to be taken into account in Eq. (13). All the other poles give a negligible contribution for chains longer than ten monomers. Note that these two poles correspond to pole ξ_3 in Eq. (8), which splits into 2 as a result of the broken symmetry.

The orientational distribution of a chain of arbitrary length can be written as

$$\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \frac{1}{r(\eta)+2w(\eta)}\begin{pmatrix} w(\eta) \\ w(\eta) \\ r(\eta) \end{pmatrix} + [\Delta_+(\eta)\phi_+(N,\xi_1,\xi_2) + \Delta_-(\eta)\phi_-(N,\xi_1,\xi_2)]\begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix}, \tag{D2}$$

where

$$\phi_{\pm}(N,\xi_1,\xi_2) = \frac{1}{2}[\phi_2(N,\xi_2) \pm \phi_1(N,\xi_1)], \quad \phi_{1,2}(N,\xi_{1,2}) = \frac{1-\exp(-N/N_{1,2})}{N/N_{1,2}},$$

$$N_{1,2} = 1/\ln(\xi_{1,2}), \quad \Delta_{\pm}(\eta) = \Delta_2(\eta) \pm \Delta_1(\eta), \quad \Delta_{1,2} = \langle\tilde{\xi} = \xi_{1,2}|_{1,2}\begin{pmatrix} 1-\eta \\ 1-\eta \\ 1+\eta \end{pmatrix}. \tag{D3}$$

The explicit form of function $\Delta_+(\eta)$ can be found by use of the limiting form of functions $\phi_{\pm}(N,\xi_1,\xi_2)$ for $N\rightarrow 0$; namely, $\phi_+(N\rightarrow 0,\xi_1,\xi_2)\rightarrow 1$ and $\phi_-(N\rightarrow 0,\xi_1,\xi_2)\rightarrow 0$. Then, $n_x=n_y=(1-\eta)/(3-\eta)$ and $n_z=(1+\eta)/(3-\eta)$, which result in

$$\Delta_+(\eta) = \frac{1-\eta}{3-\eta} - \frac{w(\eta)}{r(\eta)+2w(\eta)} = -\frac{1}{2}\left[\frac{1+\eta}{3-\eta} - \frac{r(\eta)}{r(\eta)+2w(\eta)}\right]. \tag{D4}$$

Hence, the orientational distribution of the chain units can be written as

$$\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \frac{1-\phi_+(N,\xi_1,\xi_2)}{r(\eta)+2w(\eta)}\begin{pmatrix} w(\eta) \\ w(\eta) \\ r(\eta) \end{pmatrix} + \frac{\phi_+(N,\xi_1,\xi_2)}{3-\eta}\begin{pmatrix} 1-\eta \\ 1-\eta \\ 1+\eta \end{pmatrix} + \Delta_-(\eta)\phi_-(N,\xi_1,\xi_2)\begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix}, \tag{D5}$$

and the self-consistent equation for a chain of arbitrary length will have the following form:

$$w(\eta) + \frac{3-\eta}{1+\eta}\Delta_-(\eta)[r(\eta)+2w(\eta)]\phi_0(N,\xi_1,\xi_2) = \frac{1-\eta}{1+\eta}r(\eta), \tag{D6}$$

with $\phi_0(N,\xi_1,\xi_2)=\phi_-(N,\xi_1,\xi_2)/\phi_+(N,\xi_1,\xi_2)$.

[1] A. Müller, Proc. R. Soc. London, Ser. A **138**, 514 (1932).
[2] J. Doucet, I. Denicolo, and A. Craievich, J. Chem. Phys. **75**, 1523 (1981); **75**, 5125 (1981).
[3] A. F. Craievich, I. Denicolo, and J. Doucet, Phys. Rev. B **30**, 4782 (1984), **32**, 4164 (1985).
[4] E. B. Sirota, H. E. King Jr., D. M. Singer, and Henry H. Shao, J. Chem. Phys. **98**(7), 5809 (1993).
[5] E. B. Sirota and D. M. Singer, J. Chem. Phys. **101**(12), 10873 (1994).
[6] H. Kraack, E. B. Sirota, and M. Deutsch, J. Chem. Phys. **112**(15), 6873 (2000).
[7] A. Tkachenko and Y. Rabin, Macromolecules **28**, 8646 (1995).
[8] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).
[9] A. R. Khokhlov and A. N. Semenov, Sov. Phys. Usp. **31**, 988 (1988).
[10] G. Ronca and D. Y. Yoon, J. Chem. Phys. **76**(6), 3295 (1982); **80**(2), 925 (1984).
[11] A. M. Gupta and S. F. Edwards, J. Chem. Phys. **98**(2), 1588 (1993).
[12] O. Kratky and G. Porod, Recl. Trav. Chim. Pays-Bas **68**, 1106 (1949).
[13] V. Privman and N. Svrakic, *Directed Models of Polymers, Interfaces and Clusters: Scaling and Finite-Size Properties* (Springer-Verlag, Berlin, 1989).
[14] P. Devillard and H. E. Stanley, Phys. Rev. A **41**, 2942 (1990).
[15] B. Derrida, Physica A **163**, 71 (1990).
[16] A. L. Kholodenko, Ann. Phys. (N.Y.) **202**, 186 (1990).
[17] A. L. Kholodenko, J. Stat. Phys. **65**, 291 (1991).
[18] A. L. Kholodenko, Macromolecules **26**(16), 1479 (1993).
[19] A. L. Kholodenko, Physica A **260**, 267 (1998).
[20] A. E. Arinstein, J. Exp. Theor. Phys. **91**(1), 206 (2000).
[21] A. E. Arinstein, in *Mathematical Modeling Problems, Methods, Applications* (Kluwer Academic/Plenum, New York, 2001), p. 155.
[22] A. E. Arinstein, Phys. Rev. E (to be published).