

Conformational statistics of ribbonlike semiflexible polymer chains

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The conformational statistics of ribbonlike polymers possessing bending and twist rigidity are considered on the basis of a lattice model of directed self-correlated walks. It was assumed that local properties of the ribbonlike chain are strongly anisotropic: bending is possible only in the plane of the ribbon (the orientation of this plane can vary due to twist). The generating function for the distribution of a chain segment that is non-Gaussian is constructed. It is shown that in the isotropic environment the twist degree of freedom has no effect on the state of such macromolecules as a whole, and the consideration of rigidity alone in bending results in correct statistical features of a polymer chain. This model is suitable in accounting for the twist degree of freedom in the system with broken rotary symmetry.

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I. INTRODUCTION

For many polymer systems, the simplest review is too inaccurate and does not take into account the important local properties of macromolecules. Hence, the polyethylene chains have the ribbonlike structure which originates from the trans-gauche isomerism [1,2]. The concept of the trans-gauche isomerism requires considering the trimers and allows one to calculate some features of the macromolecule (low-order moments of distribution, for example). At the same time, the construction of the full distribution function in the framework of this model is a very difficult and, perhaps, an unsolvable problem.

However, consideration of the effective chain being anisotropic in cross section can somewhat simplify the problem. The geometric anisotropy of such macromolecules results, in particular, in an anisotropy of bending rigidity of the polymer chain and in an appearance of an additional degree of freedom. Indeed, each monomer of such molecules is to be thought of as a three-axial ellipsoid but not as a cylinder. That means that the conformational state of the molecules being anisotropic in cross sections is determined by relative orientations of two axes of the neighboring monomers. The relative orientation of the neighboring monomers along the molecule contour corresponds to the bending of a chain, and the relative orientation of the neighboring monomers in the perpendicular plane determines the twist corresponding to an additional degree of freedom. Moreover, the possibilities of the bends of a molecule in the directions of the second and the third axes are not equal: the probability of the bend in direction of the smallest axis is much higher than in perpendicular direction. Therefore, the flexural stiffness of such a chain is also anisotropic. If the anisotropy of macromolecules is strong enough, these polymers are referred to as

ribbonlike polymers. The polymers of such a type are the subject of our analyses.¹

It is clear that the introduced ellipsoids (chain units) are not elementary objects and contain several bonds, like trimers in the Flory approach. However, the anisotropy of these ellipsoids takes into account their internal structure, omitting the details as being of no importance. In this connection the polymer units are to be characterized by an additional parameter, called “polarization.” Such a representation allows one to classify the degrees of freedom of a chain into two types: bending and twisting ones; thus, the polarization of monomers is related to the rotational degree of freedom, although the possibility of bend depends on the polarization of the chain.

All the abovementioned circumstances can be taken into account in the context of the discrete semi phenomenological model of *directed self-correlated walks*² on the regular lattice (DSCW) [6–8]. This model has been successfully applied to the description of conformational statistics of polymer chains with arbitrary rigidity and length [9–14]. The discrete character of the model allows one to consider the large local bends of a macromolecule that correspond to trans-gauche transitions, while in continuous models only small bends corresponding to the fluctuations of a chain are possible.

II. LATTICE MODEL OF A POLYMER CHAIN WITH INTERNAL DEGREES OF FREEDOM

In order to get the correct effective description of the ribbonlike macromolecule as a linear one possessing some internal structure, let us consider the placing of a polymer chain on a regular cubic lattice. In doing so, a monomer unit is presented as a plane zigzag [see Fig. 1(a)]. Each monomer

¹Note that the concept of ribbon-like polymers can be useful for description of double-stranded semiflexible proteins, especially DNA [3–5].

²In cited papers the appellation “*directed self-avoiding walks*” is used, but, in our opinion, “*directed self-correlated walks*” is more suitable and corresponds to the physical sense of the problem more precisely.

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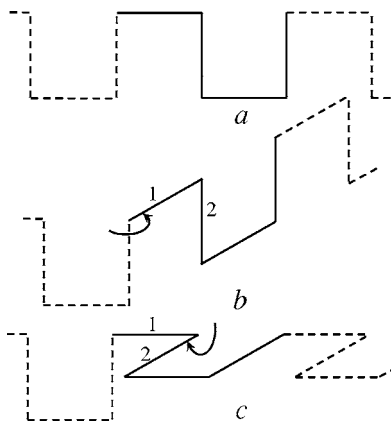


FIG. 1. Polymer chain on a regular cubic lattice. The planar configuration corresponds to the basic conformation (a). The elementary monomer unit of a chain is marked by solid lines (the other part of a chain is pictured by dashed lines). The chain bending takes place at the turn of edge 1 at 90° in the plane perpendicular to the previous edge (b), and the chain twist (polarization change) occurs at the turn of edge 2 (c). The placing direction is from left to right.

unit includes four bonds. The first and second units can be rotated at 90° in a plane being perpendicular to the placing plane, and the orientation of the third and the fourth edges are fixed. The rotation of the first edge corresponds to chain bending [see Fig. 1(b)] and the rotation of the second edge corresponds to a twist of a chain (polarization change) [see Fig. 1(c)].

Such a description of the structure of a monomer is not the sole possibility, chain bending can occur as a result of rotation not only of the first element of the monomer, but also of the third one, and the chain twist can occur as a result of rotation of the second bond as well as of the fourth one. However, such a choice of mobile monomer units results in a displacement that corresponds to an effective monomer of a chain and equals the two edges of the lattice, irrespective of the bending or twist of the chain (or of their absence). At the same time, depending on polarization, the bending of a chain can be realized as follows: bending from a direction x only in a direction y , from a direction y only in a direction z , and from a direction z only in a direction x ; i.e., according to a cycle of the right-hand triple of vectors: $x \rightarrow y \rightarrow z$. Another possible direction of bending is of the left-hand triple of vectors, $x \rightarrow z \rightarrow y$; i.e., from direction x only in direction z , from direction z only in direction y , and from direction y

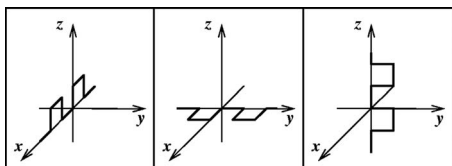


FIG. 2. The right-hand polarization of a polymer chain. The bending can be realized only from direction x in direction y , from direction y in direction z , and from direction z in direction x ; i.e., according to a cycle of the right-hand triple of vectors: $x \rightarrow y \rightarrow z$.

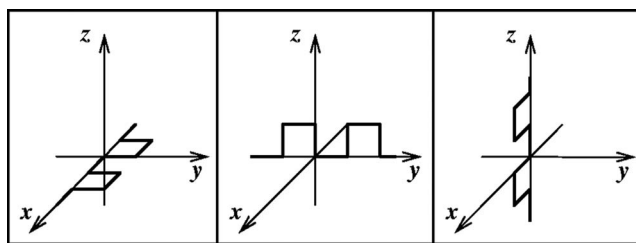


FIG. 3. The left-hand polarization of a polymer chain. The bending can be realized only from direction x in direction z , from direction z in direction y , and from direction y in direction x , i.e., according to a cycle of the left-hand triple of vectors: $x \rightarrow z \rightarrow y$.

only in direction x . These two types of polarization will be termed as right-hand [see Fig. 2] and left-hand polarizations (see Fig. 3). Note that at each bending of a chain, the chain polarization changes to the opposite one.

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 the polarization “of the walking particle” at the previous step. Such random walks correspond to the DSCW model. The pathway of the particle that performs a random motion corresponds to conformations of a ribbonlike chain of an arbitrary rigidity.

Let $e(n)$ be the vector that depends on the jump at the n th step of a random walk and corresponds to the position of the n th monomer of the chain. The stiffness and polarization of a macromolecule are specified by the distribution of conditional probabilities of the direction and polarizability at the step $(n+1)$, $e(n+1)$, at the given direction and polarization of the previous step, $e(n)$. The possibilities are as follows: a particle may maintain the direction [with probability $(1-\beta)$]; or move in a perpendicular direction that is permissible by polarization (with probability β). Analogously, let the probability maintain a given polarization be $(1-\omega)$ and the probability to change polarization be ω . In general, these probabilities depend both on polymer type and external conditions (for example, on the temperature) but these dependences are of no importance for our goals, and parameters β and ω are taken as constants.

After the enumeration of the directions on the lattice (see Fig. 4), the column vectors of a probability distribution of moving directions and polarizations of the n th step of the walk can be introduced as follows:

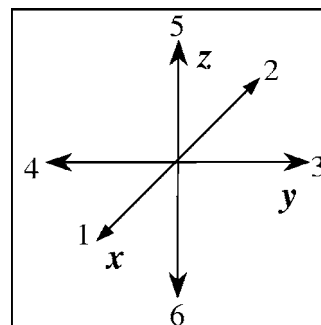


FIG. 4. The numbering of the directions on the lattice.

$$|P(n)\rangle = \begin{pmatrix} P_1(n) \\ P_2(n) \\ \vdots \\ P_6(n) \end{pmatrix}, \quad (1)$$

where the elements of a column vector $|P(n)\rangle$ are spinors

$$P_i(n) = \begin{pmatrix} P_i^+(n) \\ P_i^-(n) \end{pmatrix}.$$

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

$$|P(n+1)\rangle = \hat{\mathbf{T}}|P(n)\rangle, \quad (2)$$

where the transfer-matrix $\hat{\mathbf{T}}$ is a 12×12 block matrix

$$\hat{\mathbf{T}} = \begin{pmatrix} (1-\beta)\omega & 0 & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_+ & \frac{1}{2}\beta\omega_+ \\ 0 & (1-\beta)\omega & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_+ & \frac{1}{2}\beta\omega_+ \\ \frac{1}{2}\beta\omega_+ & \frac{1}{2}\beta\omega_+ & (1-\beta)\omega & 0 & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_- \\ \frac{1}{2}\beta\omega_+ & \frac{1}{2}\beta\omega_+ & 0 & (1-\beta)\omega & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_- \\ \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_+ & \frac{1}{2}\beta\omega_+ & (1-\beta)\omega & 0 \\ \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_- & \frac{1}{2}\beta\omega_+ & \frac{1}{2}\beta\omega_+ & 0 & (1-\beta)\omega \end{pmatrix} \quad (3)$$

and the matrices

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

act also on spinor elements of $P_i(n)$.

Generally, the arbitrary anisotropy of the bending degree of freedom can be considered. In this case two parameters of bending are to be introduced: the probabilities to bend in the directions being perpendicular (β_\perp) and parallel (β_\parallel) to the plane of a chain and the matrixes ω_\pm in Eq. (3) will have the form of

$$\omega_+ = \frac{1}{\beta_\perp + \beta_\parallel} \begin{pmatrix} 0 & \beta_\parallel \\ \beta_\perp & 0 \end{pmatrix}, \quad \omega_- = \frac{1}{\beta_\perp + \beta_\parallel} \begin{pmatrix} 0 & \beta_\perp \\ \beta_\parallel & 0 \end{pmatrix},$$

where $(\beta_\perp + \beta_\parallel = \beta)$. However, such a generalization results in no interesting effects and we will restrict our consideration to the case of the extreme anisotropy ($\beta_\parallel = 0$ and $\beta_\perp = \beta$).

The column vectors of a probability distribution $|P(n)\rangle$ can be represented as the direct product of three column vectors:

$$|P(n)\rangle = |p^{(c)}(n)\rangle \otimes |p^{(d)}(n)\rangle \otimes |p^{(\omega)}(n)\rangle, \quad (4)$$

where

$$|p^{(c)}(n)\rangle = \begin{pmatrix} p_x^{(c)}(n) \\ p_y^{(c)}(n) \\ p_z^{(c)}(n) \end{pmatrix}$$

corresponds to the coordinate axes x, y, z ;

$$|p^{(d)}(n)\rangle = \begin{pmatrix} p_+^{(d)}(n) \\ p_-^{(d)}(n) \end{pmatrix}$$

corresponds to the positive and negative directions along each coordinate axis, and

$$|p^{(\omega)}(n)\rangle = \begin{pmatrix} p_+^{(\omega)}(n) \\ p_-^{(\omega)}(n) \end{pmatrix}$$

corresponds to the polarization of the n th chain bond.

The transfer-matrix $\hat{\mathbf{T}}$ in this representation has a form

$$\hat{\mathbf{T}} = \begin{pmatrix} \mathbf{A} & \mathbf{B}_- & \mathbf{B}_+ \\ \mathbf{B}_+ & \mathbf{A} & \mathbf{B}_- \\ \mathbf{B}_- & \mathbf{B}_+ & \mathbf{A} \end{pmatrix}, \quad (5)$$

with matrix blocks 4×4 : $\mathbf{A} = \mathbf{I}^{(d)} \otimes (1-\beta)\omega$, $\mathbf{B}_\pm = \sigma \otimes \beta\omega_\pm$,

$$\sigma = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = \frac{1}{2} (1 \ 1) \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \mathbf{I}^{(d)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The distribution function of orientation and polarization of monomers is expressed in terms of the powers of the matrix $\hat{\mathbf{T}}$, and the spatial distribution function (in Fourier representation) can be also expressed in terms of the powers of a matrix $\hat{\mathbf{q}}\hat{\mathbf{T}}$ [13,14]:

$$\hat{\mathbf{G}}(\mathbf{q}, n) = (\hat{\mathbf{q}} \cdot \hat{\mathbf{T}})^{n-1} \hat{\mathbf{q}}, \quad (6)$$

where $\hat{\mathbf{q}}$ is the diagonal matrix 6×6 :

$$\hat{\mathbf{q}} = \begin{pmatrix} \tilde{\mathbf{q}}_x & 0 & 0 \\ 0 & \tilde{\mathbf{q}}_y & 0 \\ 0 & 0 & \tilde{\mathbf{q}}_z \end{pmatrix}, \quad \tilde{\mathbf{q}}_{x,y,z} = \begin{pmatrix} e^{iq_{x,y,z}} & 0 \\ 0 & e^{-iq_{x,y,z}} \end{pmatrix}.$$

Unfortunately, the matrix blocks \mathbf{A} , \mathbf{B}_\pm , and $\tilde{\mathbf{q}}_{x,y,z}$ do not commute and, therefore, the problem of calculation of the distribution function is reduced to the diagonalization of the 12×12 matrix; i.e., to the solution of an algebraic equation of the sixth order which, in general, has no analytical solution. Instead, one can use the method of the generating function corresponding in the case of a continuous limit to the Laplace transformation over the argument of the chain length. This method is commonly used for studies of systems with a varying number of particles.

III. THE GENERATING FUNCTION FOR THE SPATIAL DISTRIBUTION OF A CHAIN

Now, we will calculate the matrix generating function as

$$\tilde{\mathbf{G}}(\xi, \mathbf{q}) = \sum_{n=0}^{\infty} \xi^n \hat{\mathbf{G}}(\mathbf{q}, n) = \mathbf{1} + \sum_{n=0}^{\infty} (\xi \hat{\mathbf{q}} \cdot \hat{\mathbf{T}})^n \xi \hat{\mathbf{q}}, \quad (7)$$

which is to be averaged over the states of the extreme monomers of a chain:

$$K(\xi, \mathbf{q}) = \frac{1}{12} \langle \tilde{\mathbf{G}}(\xi, n) \rangle = \mathbf{1} + \frac{1}{12} \sum_{n=0}^{\infty} \langle (\xi \hat{\mathbf{q}} \cdot \hat{\mathbf{T}})^n \xi \hat{\mathbf{q}} \rangle, \quad (8)$$

where brackets $\langle \dots \rangle$ mean the sum of all matrix elements.

Let us present $\hat{\mathbf{T}}$ as a quasideagonal block matrix:

$$\begin{aligned} \hat{\mathbf{T}} &= \begin{pmatrix} \mathbf{A} & \mathbf{B}_- & \mathbf{0} \\ \mathbf{B}_+ & \mathbf{A} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{A} \end{pmatrix} + \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{B}_+ \\ \mathbf{0} & \mathbf{0} & \mathbf{B}_- \\ \mathbf{B}_- & \mathbf{B}_+ & \mathbf{0} \end{pmatrix} \\ &= \begin{pmatrix} \hat{\mathbf{T}}_2 & \mathbf{0} \\ \mathbf{0} & \mathbf{A} \end{pmatrix} + \begin{pmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^t & \mathbf{0} \end{pmatrix}, \end{aligned} \quad (9)$$

where

$$\hat{\mathbf{T}}_2 = \begin{pmatrix} \mathbf{A} & \mathbf{B}_- \\ \mathbf{B}_+ & \mathbf{A} \end{pmatrix}, \quad \mathbf{B} = \begin{pmatrix} \mathbf{B}_+ \\ \mathbf{B}_- \end{pmatrix}, \quad \mathbf{B}^t = (\mathbf{B}_- \ \mathbf{B}_+).$$

Such a representation of the transfer-matrix $\hat{\mathbf{T}}$ allows one to reduce the problem to calculation of the two- and one-dimensional generating functions. In fact, using Eq. (9), the generating function $\tilde{\mathbf{G}}(\xi, \mathbf{q})$ can be represented as

$$\begin{aligned} \tilde{\mathbf{G}}(\xi, \mathbf{q}) &= \sum_{k=0}^{\infty} \left\{ \sum_{n=0}^{\infty} \left[\xi \hat{\mathbf{q}} \begin{pmatrix} \hat{\mathbf{T}}_2 & \mathbf{0} \\ \mathbf{0} & \mathbf{A} \end{pmatrix} \right]^n \xi \hat{\mathbf{q}} \begin{pmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^t & \mathbf{0} \end{pmatrix} \right\}^k \\ &\quad \times \sum_{n=0}^{\infty} \left[\xi \hat{\mathbf{q}} \begin{pmatrix} \hat{\mathbf{T}}_2 & \mathbf{0} \\ \mathbf{0} & \mathbf{A} \end{pmatrix} \right]^n \xi \hat{\mathbf{q}} \\ &= \sum_{k=0}^{\infty} \left\{ \begin{pmatrix} \mathbf{0} & \tilde{\mathbf{G}}_2(\xi, q_x, q_y) \mathbf{B} \\ \tilde{\mathbf{G}}_1(\xi, q_z) \mathbf{B}^t & \mathbf{0} \end{pmatrix} \right\}^k \\ &\quad \times \begin{pmatrix} \tilde{\mathbf{G}}_2(\xi, q_x, q_y) & \mathbf{0} \\ \mathbf{0} & \tilde{\mathbf{G}}_1(\xi, q_z) \end{pmatrix}, \end{aligned} \quad (10)$$

where

$$\tilde{\mathbf{G}}_1(\xi, q_z) = \sum_{n=0}^{\infty} (\xi \tilde{\mathbf{q}}_z \mathbf{A})^n \xi \tilde{\mathbf{q}}_z,$$

$$\tilde{\mathbf{G}}_2(\xi, q_x, q_y) = \sum_{n=0}^{\infty} (\xi \hat{\mathbf{q}}_2 \hat{\mathbf{T}}_2)^n \xi \hat{\mathbf{q}}_2, \quad \hat{\mathbf{q}}_2 = \begin{pmatrix} \tilde{\mathbf{q}}_x & \mathbf{0} \\ \mathbf{0} & \tilde{\mathbf{q}}_y \end{pmatrix}.$$

Taking into account the structure of the matrices \mathbf{B}_\pm (more exactly, of the matrix σ) the averaging over indexes corresponding to the positive and negative directions along each coordinate axis of the generating function (10) is appropriate. This averaging reduces the dimension of all matrixes by half; i.e., the two-dimensional generating function will be the 4×4 matrix and the one-dimensional generating function will be the simplest 2×2 matrix.

$$\begin{aligned} \bar{\mathbf{G}}(\xi, \mathbf{q}) &= \frac{1}{2} (1 \ 1)^{(d)} \tilde{\mathbf{G}}(\xi, \mathbf{q}) \begin{pmatrix} 1 \\ 1 \end{pmatrix}^{(d)} \\ &= \sum_{k=0}^{\infty} \left\{ \begin{pmatrix} \mathbf{0} & \bar{\mathbf{G}}_2(\xi, q_x, q_y) \bar{\mathbf{B}} \\ \bar{\mathbf{G}}_1(\xi, q_z) \bar{\mathbf{B}}^t & \mathbf{0} \end{pmatrix} \right\}^k \\ &\quad \times \begin{pmatrix} \bar{\mathbf{G}}_2(\xi, q_x, q_y) & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{G}}_1(\xi, q_z) \end{pmatrix}, \end{aligned} \quad (11)$$

where

$$\bar{\mathbf{G}}_2(\xi, \mathbf{q}) = \frac{1}{2} (1 \ 1)^{(d)} \tilde{\mathbf{G}}_2(\xi, \mathbf{q}) \begin{pmatrix} 1 \\ 1 \end{pmatrix}^{(d)},$$

$$\bar{\mathbf{G}}_1(\xi, q_z) = \frac{1}{2} (1 \ 1)^{(d)} \tilde{\mathbf{G}}_1(\xi, q_z) \begin{pmatrix} 1 \\ 1 \end{pmatrix}^{(d)},$$

$$\bar{\mathbf{B}} = \beta \begin{pmatrix} \omega_+ \\ \omega_- \end{pmatrix}, \quad \bar{\mathbf{B}}^t = \beta (\omega_- \ \omega_+).$$

Summing singly the odd and even powers of the series in the Eq. (11), we get the generating function $\bar{\mathbf{G}}(\xi, \mathbf{q})$ in the form

$$\begin{aligned} \bar{\mathbf{G}}(\xi, \mathbf{q}) &= \sum_{k=0}^{\infty} \left\{ \begin{pmatrix} \mathbf{0} & \bar{\mathbf{G}}_2 \bar{\mathbf{B}} \\ \bar{\mathbf{G}}_1 \bar{\mathbf{B}}^t & \mathbf{0} \end{pmatrix} \right\}^{2k} \begin{pmatrix} \bar{\mathbf{G}}_2 & \bar{\mathbf{G}}_2 \bar{\mathbf{B}} \bar{\mathbf{G}}_1 \\ \bar{\mathbf{G}}_1 \bar{\mathbf{B}}^t \bar{\mathbf{G}}_2 & \bar{\mathbf{G}}_1 \end{pmatrix} \\ &= \begin{pmatrix} \bar{\mathbf{G}}_2 + \bar{\mathbf{G}}_2 \bar{\mathbf{B}} \bar{\mathbf{G}}_0 \bar{\mathbf{G}}_1 \bar{\mathbf{B}}^t \bar{\mathbf{G}}_2 & \bar{\mathbf{G}}_2 \bar{\mathbf{B}} \bar{\mathbf{G}}_0 \bar{\mathbf{G}}_1 \\ \bar{\mathbf{G}}_0 \bar{\mathbf{G}}_1 \bar{\mathbf{B}}^t \bar{\mathbf{G}}_2 & \bar{\mathbf{G}}_0 \bar{\mathbf{G}}_1 \end{pmatrix}, \end{aligned} \quad (12)$$

where the arguments in the generating functions $\bar{\mathbf{G}}_1$ and $\bar{\mathbf{G}}_2$ are omitted and $\bar{\mathbf{G}}_0 \equiv \bar{\mathbf{G}}_0(\xi, \mathbf{q})$ is the 2×2 matrix having a form

$$\begin{aligned} \bar{\mathbf{G}}_0(\xi, \mathbf{q}) &= \sum_{k=0}^{\infty} \{ \bar{\mathbf{G}}_1(\xi, q_z) \bar{\mathbf{B}}^t \bar{\mathbf{G}}_2(\xi, q_x, q_y) \bar{\mathbf{B}} \}^k \\ &= \{ \mathbf{I} - \bar{\mathbf{G}}_1(\xi, q_z) \bar{\mathbf{B}}^t \bar{\mathbf{G}}_2(\xi, q_x, q_y) \bar{\mathbf{B}} \}^{-1}. \end{aligned} \quad (13)$$

The calculation of the generating function $\bar{\mathbf{G}}_1$ reduces to the summation of a geometric series, and thereafter to calculation of the 2×2 inverse matrix. As a result, the generating function $\bar{\mathbf{G}}_1$ gets the form

$$\begin{aligned} \overline{\mathbf{G}}_1(\xi, q) = \begin{pmatrix} a(\xi, q) & b(\xi, q) \\ b(\xi, q) & a(\xi, q) \end{pmatrix} = \frac{1}{2} \left\{ \frac{\xi[\cos q - (1 - \beta)\xi]}{1 - 2(1 - \beta)\xi \cos q + (1 - \beta)^2 \xi^2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \right. \\ \left. + \frac{\xi[\cos q - (1 - \beta)(1 - 2\omega)\xi]}{1 - 2(1 - \beta)(1 - 2\omega)\xi \cos q + (1 - \beta)^2(1 - 2\omega)^2 \xi^2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right\}. \end{aligned} \quad (14)$$

The generating function $\overline{\mathbf{G}}_2$ is the 4×4 matrix, and the procedure like that used above for the three-dimensional generating function is to be applied to its calculation. Representing the matrix $\hat{\mathbf{T}}_2$ as

$$\hat{\mathbf{T}}_2 = \begin{pmatrix} \mathbf{A} & \mathbf{B}_- \\ \mathbf{B}_+ & \mathbf{A} \end{pmatrix} = \begin{pmatrix} \mathbf{A} & 0 \\ 0 & \mathbf{A} \end{pmatrix} + \begin{pmatrix} 0 & \mathbf{B}_- \\ \mathbf{B}_+ & 0 \end{pmatrix}, \quad (15)$$

and repeating the calculations as in Eqs. (10)–(12), one can get the generating function $\overline{\mathbf{G}}_2$ in the form containing only one-dimensional generating function $\overline{\mathbf{G}}_1$:

$$\overline{\mathbf{G}}_2(\xi, q_x, q_y) = \begin{pmatrix} \mathbf{G}_0^{(+)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_x) & \mathbf{G}_0^{(+)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_x) \beta \omega_- \overline{\mathbf{G}}_1(\xi, q_y) \\ \mathbf{G}_0^{(\pm)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_y) \beta \omega_+ \overline{\mathbf{G}}_1(\xi, q_x) & \mathbf{G}_0^{(\pm)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_y) \end{pmatrix}, \quad (16)$$

where

$$\begin{aligned} \mathbf{G}_0^{(+)}(\xi, q_x, q_y) &= \sum_{n=0}^{\infty} [\overline{\mathbf{G}}_1(\xi, q_x) \beta \omega_- \overline{\mathbf{G}}_1(\xi, q_y) \beta \omega_+]^n \\ &= [\mathbf{I} - \overline{\mathbf{G}}_1(\xi, q_x) \beta \omega_- \overline{\mathbf{G}}_1(\xi, q_y) \beta \omega_+]^{-1}, \end{aligned} \quad (17)$$

$$\begin{aligned} \mathbf{G}_0^{(\pm)}(\xi, q_x, q_y) &= \sum_{n=0}^{\infty} [\overline{\mathbf{G}}_1(\xi, q_y) \beta \omega_+ \overline{\mathbf{G}}_1(\xi, q_x) \beta \omega_-]^n \\ &= [\mathbf{I} - \overline{\mathbf{G}}_1(\xi, q_y) \beta \omega_+ \overline{\mathbf{G}}_1(\xi, q_x) \beta \omega_-]^{-1}. \end{aligned} \quad (18)$$

Equations (16)–(18) allow one to express the three-dimensional generating function $\overline{\mathbf{G}}(\xi, \mathbf{q})$ (12) by a one-dimensional one $\overline{\mathbf{G}}_1(\xi, q)$ (14). The obtained expressions are too cumbersome for calculations, but their form can be simplified by means of the procedure of averaging over directions and polarizations of the both extreme monomers of a chain.

IV. AVERAGING OVER DIRECTIONS AND POLARIZATIONS OF BOTH EXTREME MONOMERS OF A CHAIN

The symmetry of the problem in question results, in particular, in the fact that only three independent elements are contained in the 3×3 matrix of the generating function $\overline{\mathbf{G}}(\xi, \mathbf{q})$ having, in effect, the following form:

$$\overline{\mathbf{G}}(\xi, \mathbf{q}) = \begin{pmatrix} \overline{\mathbf{G}}_{11} & \overline{\mathbf{G}}_{12} & \overline{\mathbf{G}}_{13} \\ \overline{\mathbf{G}}_{13} & \overline{\mathbf{G}}_{11} & \overline{\mathbf{G}}_{12} \\ \overline{\mathbf{G}}_{12} & \overline{\mathbf{G}}_{13} & \overline{\mathbf{G}}_{11} \end{pmatrix}.$$

The element $\overline{\mathbf{G}}_{11}$ corresponds to the relative parallel orientation of the extreme monomers of a chain whereas the ele-

ments $\overline{\mathbf{G}}_{12}$ and $\overline{\mathbf{G}}_{13}$ correspond to their relative perpendicular orientations (two relative perpendicular orientations: the right-hand and the left-hand orientations are possibly due to the polarization of the monomers). After averaging over polarizations of the extreme monomers of a chain, full rotational symmetry will be restored and the matrix of the generating function contains only two independent elements corresponding to the relative parallel (diagonal elements) and perpendicular (nondiagonal elements) orientations of the extreme monomers of a chain.

At first glance, the averaging of the generating function (12) seemingly gives no simplifications, and results only in the symmetrization over the arguments $q_{x,y,z}$. However, if the continuous approximation is used (i.e., $\cos q \approx 1 - q^2/2$) this symmetrization allows one to simplify the equations, replacing each of the arguments $q_{x,y,z}$ (components of the vector \mathbf{q}) of the one-dimensional generating function $\overline{\mathbf{G}}_1(\xi, q_{x,y,z})$ by the scalar $q = \sqrt{\mathbf{q}^2/3} = \sqrt{(q_x^2 + q_y^2 + q_z^2)/3}$. Thereafter, the averaged generating function has the form

$$K(\xi, \mathbf{q}) \equiv K(\xi, q) = \frac{1}{2} \langle [\mathbf{I} + \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \overline{\mathbf{G}}_2(\xi, q) \overline{\mathbf{B}}] \overline{\mathbf{G}}_0(\xi, q) \overline{\mathbf{G}}_1(\xi, q) \rangle, \quad (19)$$

where the fact that $\overline{\mathbf{G}}_0(\xi, q) \overline{\mathbf{G}}_1(\xi, q) = \overline{\mathbf{G}}_1(\xi, q) \overline{\mathbf{G}}_0(\xi, q)$ is taken into account, $q = \sqrt{(q_x^2 + q_y^2 + q_z^2)/3}$, the brackets $\langle \dots \rangle$ mean the sum of all matrix elements corresponding to the polarizations of the extreme monomers of a chain, the one-dimensional generating function $\overline{\mathbf{G}}_1(\xi, q)$ is defined by Eq. (14), and the averaged generating functions $\overline{\mathbf{G}}_2(\xi, q)$, and $\overline{\mathbf{G}}_0^{(x,y),(y,x)}(\xi, q)$ are as follows:

$$\overline{\mathbf{G}}_0(\xi, q) = \{\mathbf{I} - \overline{\mathbf{G}}_1(\xi, q) \overline{\mathbf{B}} \tilde{\mathbf{G}}_2(\xi, q) \overline{\mathbf{B}}\}^{-1}, \quad (20)$$

$$\tilde{\mathbf{G}}_2(\xi, q) = \begin{pmatrix} \overline{\mathbf{G}}_0^{(+)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_x) & \overline{\mathbf{G}}_0^{(+)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_x) \beta \omega_- \overline{\mathbf{G}}_1(\xi, q_y) \\ \overline{\mathbf{G}}_0^{(\pm)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_y) \beta \omega_+ \overline{\mathbf{G}}_1(\xi, q_x) & \overline{\mathbf{G}}_0^{(\pm)}(\xi, q_x, q_y) \overline{\mathbf{G}}_1(\xi, q_y) \end{pmatrix}, \quad (21)$$

$$\overline{\mathbf{G}}_0^{(+)}(\xi, q) = [\mathbf{I} - \overline{\mathbf{G}}_1(\xi, q) \beta \omega_- \overline{\mathbf{G}}_1(\xi, q) \beta \omega_+]^{-1}, \quad (22)$$

$$\begin{aligned} \overline{\mathbf{G}}_0^{(\pm)}(\xi, q) &= [\mathbf{I} - \overline{\mathbf{G}}_1(\xi, q) \beta \omega_+ \overline{\mathbf{G}}_1(\xi, q) \beta \omega_-]^{-1} \\ &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \overline{\mathbf{G}}_0^{(+)}(\xi, q) \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \end{aligned} \quad (23)$$

Using the features of the structure of the matrices $\overline{\mathbf{G}}_0(\xi, q)$ and $\overline{\mathbf{G}}_1(\xi, q)$, which have a symmetric form

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix},$$

eq. (19) for the generating function $K(\xi, q)$ can be simplified and the final equation for the averaged generating function is as follows:

$$K(\xi, q) = \frac{\xi[\cos q - (1 - \beta)\xi]}{1 - (2 - \beta)\xi \cos q + (1 - \beta)\xi^2}. \quad (24)$$

The last equation coincides exactly with the generating function for the semiflexible linear polymer chain [9–14]. This means that the twist degree of freedom has no effect on the statistics of the macromolecules in question. At first glance, this outcome seems unexpected but this fact actually reflects the rotational symmetry of the problem. At the same time, the local properties of the chain in question (the distribution of orientations, for example) depend on the twist parameter. Indeed, the diagonal (d) and nondiagonal ($n-d$) matrix elements of the generating function (12) after replacing all arguments $q_{x,y,z}$ by the one $q = \sqrt{(q_x^2 + q_y^2 + q_z^2)}/3$ and after averaging over polarizations of the extreme monomers of a chain have the following form containing the twist parameter ω as

$$\begin{aligned} K_d(\xi, q) &= \frac{1}{2} \langle \overline{\mathbf{G}}_0(\xi, q) \overline{\mathbf{G}}_1(\xi, q) \rangle \\ &= \frac{(a+b)(1-\beta a)}{[1-\beta(a+b)][1+\beta b-\beta(a-b)\beta(a+b)]}, \end{aligned} \quad (25)$$

$$\begin{aligned} K_{n-d}(\xi, q) &= \frac{1}{2} \langle (1 \ 0) \tilde{\mathbf{G}}_2(\xi, q) \overline{\mathbf{B}} \cdot \overline{\mathbf{G}}_0(\xi, q) \overline{\mathbf{G}}_1(\xi, q) \rangle \\ &= \frac{1}{2} \langle (0 \ 1) \tilde{\mathbf{G}}_2(\xi, q) \overline{\mathbf{B}} \cdot \overline{\mathbf{G}}_0(\xi, q) \overline{\mathbf{G}}_1(\xi, q) \rangle \\ &= \frac{1}{2} \frac{(a+b)[\beta(a+b) - \beta(a-b)\beta(a+b)]}{[1-\beta(a+b)][1+\beta b-\beta(a-b)\beta(a+b)]}, \end{aligned} \quad (26)$$

where the functions $a \equiv a(\xi, q)$ and $b \equiv b(\xi, q)$ are the matrix elements of the one-dimensional generating function

$\overline{\mathbf{G}}_1(\xi, q)$ (14) and their combinations $a-b$ and $a+b$ have a simple structure:

$$\begin{aligned} a(\xi, q) - b(\xi, q) &= \frac{\xi[\cos q - (1 - \beta)(1 - 2\omega)\xi]}{1 - 2(1 - \beta)(1 - 2\omega)\xi \cos q + (1 - \beta)^2(1 - 2\omega)^2\xi^2}, \\ & \quad (27) \end{aligned}$$

$$a(\xi, q) + b(\xi, q) = \frac{\xi[\cos q - (1 - \beta)\xi]}{1 - 2(1 - \beta)\xi \cos q + (1 - \beta)\xi^2}. \quad (28)$$

The first of them $K_d(\xi, q)$ (25) corresponds to the polymer chain, the extreme monomers of which are parallel and the second one $K_{n-d}(\xi, q)$ (26), corresponds to the polymer chain the extreme monomers of which are perpendicular to each other.

V. CONCLUSION

The analysis carried out demonstrated that the rotational degree of freedom of the ribbonlike macromolecule is of no importance in the isotropic polymer system, in the polymer melt, or solution, for example. The reason for this outcome is related to the symmetry of the system. That means that the approximation of the linear semiflexible macromolecule containing no internal degrees of freedom is applicable to ribbonlike polymers in the isotropic environment and the conformational statistics of such a polymer can be described by the following distribution function (in a Fourier representation) which can be obtained by means of the generating function (24) [9–14]:

$$\begin{aligned} K(l, \mathbf{p}) &= \frac{1+E}{2E} \exp\left[-\frac{\beta(1-E)l}{2(1-\beta)l_0}\right] \\ &\quad - \frac{1+E}{2E} \exp\left[-\frac{\beta(1+E)l}{2(1-\beta)l_0}\right], \end{aligned} \quad (29)$$

where $E = \sqrt{1 - l_0^2 \mathbf{p}^2 2(2-\beta)(1-\beta)/3\beta^2}$ and l_0 is the scale of one monomer of a chain.

This fact does not mean that the rotational degree of freedom generally is of no importance. For example, the state of short molecules containing a limited number of monomers depends on the rotational mobility of links even in the isotropic environment. Indeed, if this rotational mobility is extremely low, such a chain is located in a plane and is described by two-dimensional distribution. The third dimension becomes important when increasing the length of a chain or when increasing its rotational mobility (in both cases the correlation length of polarization becomes less than the chain length). With the increasing of the chain length the influence

of the rotational degree of freedom decreases and, finally, disappears. From a mathematical point of view, such influence of the rotational degree of freedom on the state of polymer molecules is related to the fact that the continuous approximation is inapplicable for short chains. For this reason, the substitution $q_{x,y,z} \rightarrow q = \sqrt{(q_x^2 + q_y^2 + q_z^2)}/3$ is impossible and the generating function is to be defined by the equation (12) in combination with Eqs. (13), (14), and (16)–(18). As a result, the dependence of the generating function on the twist parameter will be retained even for the isotropic case. If required, the necessary calculations can be performed, in spite of the fact that the resulting expressions are very unwieldy ones.

Finally, let us regard a special situation that is very important from a physical point of view. It is clear that the rotational degree of freedom of the ribbonlike polymer chains can manifest itself in anisotropic systems. However, even in the isotropic system the local intermolecular interactions of the ribbonlike chains result in local anisotropy. Under certain conditions this local anisotropy can lead to phase

transition, and global anisotropy springs up in the system. Inasmuch as in the anisotropic environment the rotational degree of freedom will influence the conformational state of the macromolecules in question, the conditions of the phase transition in the anisotropic phase must depend on the twist parameter. In doing so, such an influence has to increase for short polymer chains, whereas this influence can be negligibly small for the infinitely long molecules as a result of averaging. Such a situation can take place in the rotator phase of some polymers, and in our opinion the proposed model is suitable for explaining some features of this phenomenon [15]. This problem requires additional study and will be discussed in a special article in the near future.

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