# STATISTICS OF POLYMER-CHAIN CONFORMATIONS IN THE INTRINSIC COORDINATE SYSTEM

**A. É. Arinshtein**                                                                                              UDC 541.1

*The statistics of polymer-chain conformations in the intrinsic coordinate system, the directions of whose axes are determined by the anisotropy of a polymer coil at certain instantaneous distribution of the conformations, is considered. It is shown that even for an absolutely flexible polymer chain the shape of the coil in the intrinsic coordinate system is anisotropic. Full distribution functions of the chain links in space are constructed for both the absolutely flexible linear polymer and the linear polymer chain which possesses finite flexural rigidity, and degrees of anisotropy of these macromolecules are calculated.*

**Introduction.** According to the commonly accepted notions, a flexible macromolecule is a spherically isotropic Gaussian coil whose characteristic dimension is in proportion to the square root of the chain length (degree of polymerization). If a macromolecule possesses a certain flexural rigidity, the notion of the Kuhn segment (persistent length) is introduced and on the scales larger than the Kuhn segment we can consider a polymer chain as being absolutely flexible and also as rolling up to a spherically isotropic Gaussian coil. This shape of the polymer macromolecule is obtained as a result of averaging over all possible conformations of it. We note that this averaging is made over either the ensemble of identical chains or the time in which the macromolecule succeeds in multiply exhausting all possible conformations. However, if we are interested in the structure of the polymer system on small scales, we must consider the instantaneous (rather than ensemble-averaged) conformation of *one* trial chain. It is obvious that its shape will greatly differ from a sphere. Consequently, at each instant of time a polymer system is a statistical ensemble of anisotropic elements. If this system is not affected by internal and/or external orienting factors, all the orientations of its anisotropic elements will be equiprobable and ensemble-averaging will lead to the fact that the entire system will be isotropic. It is precisely this situation that takes place in diluted and weakly diluted solutions and nonstructurized melts of polymers. However, if the external orienting force (e.g., in flow) is applied to polymer solutions or supramolecular structures are formed in a concentrated polymer matrix, the situation can change drastically: the orientation distribution of polymer chains becomes nonuniform and both local and global anisotropes appear in the system and the macroscopic properties of this system change appreciably (Fig. 1).

Despite the apparent simplicity, a mathematical formulation of the problem under consideration turns out to be nontrivial. The fact is that from all the possible conformations of the chain it is necessary to set off only a part which corresponds to the mean degree of its anisotropy. In this case, the Markovian character of the process of macromolecular packing is disturbed and the statistics of conformations of the polymer chain is described by a non-Markovian process. The problem of unambiguity in choosing the criterion of sampling of conformations arises in addition to the fact that this problem (account for a part of the conformations within the framework of the non-Markovian process) is rather complex in itself. One version of solution of this problem was suggested as early as the 1950s (see [1], pp. 134–154); however, attempts to describe local anisotropy in more detail are still in progress [2–12]. The main results, especially recently, are obtained from numerical experiments as a rule [2–5, 8–12], and analytical methods of investigation [6, 7] can be used only in exceptional cases.

The key point in description of the anisotropic shape of flexible polymer chains is choosing the local coordinate system related to the characteristic points of the macromolecule (e.g., its ends and center). Indeed, a whole set of conformations which can be obtained from the rotations of a chain about a certain point can be suggested for each fixed conformation of the chain. It is natural to restrict oneself to consideration of only those conformations of the
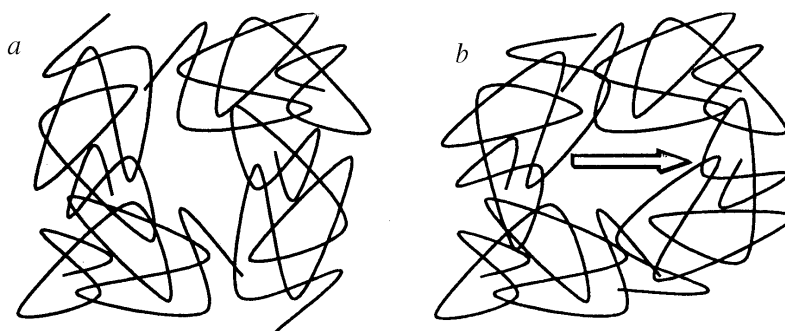
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Fig. 1. Isotropic macrostate of the polymeric system (a) and its anisotropic macrostate under the external orienting effect (b).
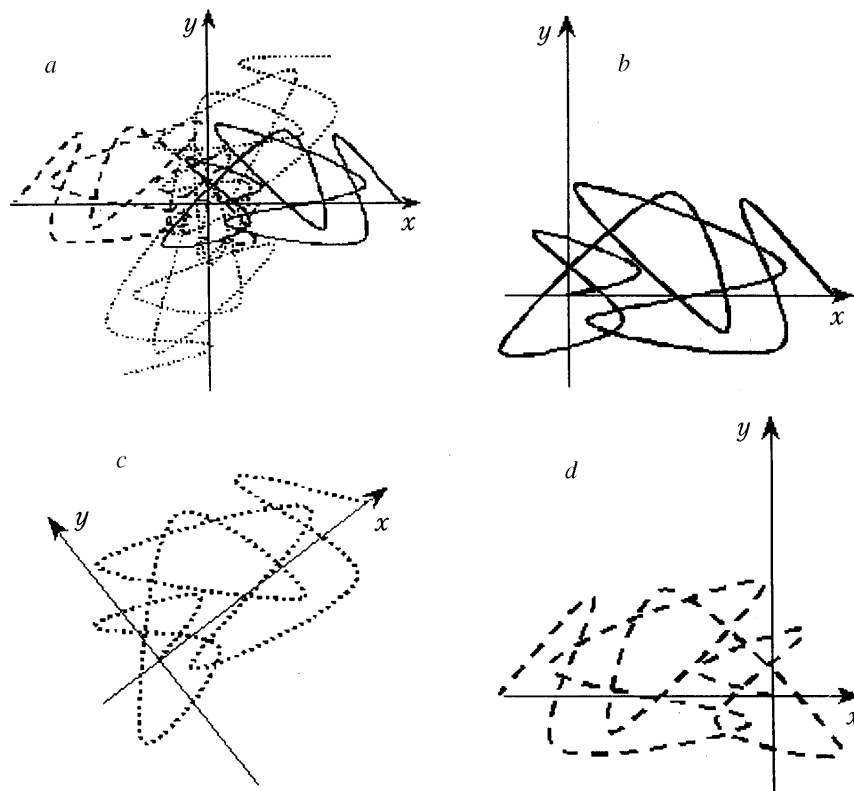


Fig. 2. Isotropic shape of the polymer coil (a); instantaneous anisotropic conformation of the macromolecule (b); transition from one anisotropic conformation to another due to rotation (c) and mirror reflection (d) of the coordinate system.

macromolecule which cannot be obtained from one another in rotation of the chain. This requirement means that we observe a polymer molecule from the moving coordinate system which rotates simultaneously with the macromolecule with change in its conformation, if this change is reduced to the rotation of the molecule as a whole. Moreover, to provide interchangeability of the chain ends, it is necessary to perform averaging over the set of its conformations, which is obtained in mirror reflections of the molecule (Fig. 2).

Below we suggest an analytical method of description of the anisotropic spatial distribution of monomeric links of macromolecules both on the plane (in a two-dimensional space) and in a three-dimensional space.

**Local Description of a Polymer Chain on the Plane** ($d = 2$)**.** We specify the coordinate system on the plane as follows: the origin of coordinates is located at one end of the chain (for definiteness, at the beginning), and the orientation of the coordinate system (positive direction of the $x$ axis) is determined by the vector which connects the

beginning and the end of the molecule. To make the beginning and the end of the chain interchangeable, it is necessary to average the initial conformations and those mirror-reflected relative to the $y$ axis. With this choice of the coordinate system we consider only such chain conformations where the chain ends are on the $x$ axis and the remaining conformations are obtained by rotating the coordinate system about the fixed coordinate origin. It is obvious that the center of gravity of this chain is at the origin of coordinates and the moments of inertia or the root-mean-square dimensions along the $x$ and $y$ axes are different. However, quantitative estimates of these characteristics require exact calculation.

Thus, we introduce the distribution function of the links of the chain of length $L$, which specifies the probability density of finding the link at a distance $l$ from the beginning of the chain (along its contour) in the vicinity of point $\mathbf{R}$:

$$G\,(\mathbf{R},\,l\,|\,L) = \int d\mathbf{R}_e W\,(\mathbf{R}_e)\,G_0\,(\mathbf{R}_e - \mathbf{R},\,L - l)\,G_0\,(\mathbf{R}_e,\,l)\,,\tag{1}$$

where $W(\mathbf{R}_e) = 2\pi\theta(x_e)\delta(y_e)R_e = 2\pi\theta(x_e)\delta(y_e)x_e$, $G_0(\mathbf{R},\,l) = (d/4\pi l_0 l))\exp(-\mathbf{R}^2/2l_0 l)$ is the Gaussian distribution function, $\delta(y)$ is the Dirac function, and $\theta(x) = 1$ if $x \ge 0$ and $\theta(x) = 0$ when $x < 0$.

One main property of the Markovian process $G_0(\mathbf{R},\,L) = \int d\mathbf{r} G_0(\mathbf{R} - \mathbf{r}, L - l)G_0(\mathbf{r},\,l)$, which holds at any $0 \le l \le L$, is used in expression (1). However, (1) is integrated with respect to the end of the "trajectory" rather than with respect to its intermediate point, with account for the introduced limitation.

Having applied the Fourier transformation in (1), we obtain

$$\hat{G}\,(\mathbf{p},\,l\,|\,L) = \frac{1}{2\pi}\int d\mathbf{q}\,\hat{W}\,(\mathbf{q})\,\hat{G}_0\,(\mathbf{q},\,L - l)\,\hat{G}_0\,(\mathbf{p} + \mathbf{q},\,l)\,,\tag{2}$$

where $\hat{G}(\mathbf{q},\,l) = (2\pi)^{-2}\int d\mathbf{R} G_0(\mathbf{R},\,l)\exp(i\mathbf{q}\mathbf{R}) = \exp(-l l_0\mathbf{q}^2)$ is the Fourier transform of the Gaussian distribution function and $\hat{W}(\mathbf{q}) = \frac{1}{2\pi}\int d\mathbf{R} W(\mathbf{R})\exp(-i\mathbf{q}\mathbf{R}) = -1/q_x^2$ is the Fourier transform of the function $W(\mathbf{R})$; in integration of $\hat{W}(\mathbf{q})$ with respect to the real axis $q_x$, its pole at $q_x = 0$ is bypassed from below.

Thus, the distribution function of the inner links of the $L$-long chain, which is of interest to us, in the $p$-representation has the form

$$\hat{G}\,(\mathbf{p},\,l\,|\,L) = \frac{-1}{2\pi}\int \hat{G}_0\,(\mathbf{q},\,L - l)\,\hat{G}_0\,(\mathbf{p} + \mathbf{q},\,l)\,d\mathbf{q}/q_x^2\,.\tag{3}$$

In the case where we are interested in the chain characteristics averaged over all the links, we can integrate Eq. (3) for $l$ from 0 to $L$ and divide this integral by $L$:

$$\hat{\bar{G}}\,(\mathbf{p},\,L) = \frac{-1}{2\pi L}\int (d\mathbf{q}/q_x^2)\int_0^L \hat{G}_0\,(\mathbf{q},\,L - l)\,\hat{G}_0\,(\mathbf{p} + \mathbf{q},\,l)\,dl\,.\tag{4}$$

Since expression (4) has the form of a convolution with respect to the variable $l$, the Laplace transform for the distribution function $\hat{G}_m(\mathbf{p},\,L)$ has a simple form convenient for further calculations:

$$\tilde{\bar{G}}\,(\mathbf{p},\,s) = \int_0^L \exp(-sL)\,\hat{\bar{G}}\,(\mathbf{q},\,L)\,dL = \frac{-1}{2\pi}\int_s^\infty ds \int \tilde{G}_0\,(\mathbf{q},\,s)\,\tilde{G}_0\,(\mathbf{p} + \mathbf{q},\,s)\,\frac{d\mathbf{q}}{q_x^2}\,,\tag{5}$$

where $\tilde{G}_0(\mathbf{q},\,s) = 1/(s + l_0\mathbf{q}^2/4)$ is the Laplace transform of the distribution function $\hat{G}_0(\mathbf{q},\,l)$.

Using (5), we can find the mean characteristics of a two-dimensional polymer coil. For example, second moments of distribution, in terms of which the chain size is expressed, are calculated as follows:

$$\overline{x^2}(s) = \frac{\partial^2 \overline{\tilde{G}}(\mathbf{p}, s)}{\partial p_x^2}\Bigg|_{\mathbf{p}=0} = \frac{1}{2\pi}\int\limits_s ds \int \frac{d\mathbf{q}}{q_x^2}\,\tilde{G}_0(\mathbf{q}, s)\frac{\partial^2 \tilde{G}_0(\mathbf{q}, s)}{\partial q_x^2} =$$

$$= \frac{5l_0^2}{24\pi}\int d\mathbf{q}\,\tilde{G}_0^3(\mathbf{q}, s) = \frac{5l_0^2}{24\pi}\int\limits_0^{2\pi} d\varphi \int\limits_0^{\infty} \frac{q\,dq}{\left(s + \frac{1}{4}l_0 q^2\right)^3} = \frac{5l_0}{12s^2}. \tag{6}$$

Having applied the inverse Laplace transformation, we obtain that the root-mean-square dimension of the chain along the $x$ axis is

$$\overline{x^2}(L) = 5l_0 L/12. \tag{7}$$

Similarly

$$\overline{y^2}(s) = \frac{\partial^2 \overline{\tilde{G}}(\mathbf{p}, s)}{\partial p_y^2}\Bigg|_{\mathbf{p}=0} = \frac{1}{2\pi}\int\limits_s ds \int \frac{d\mathbf{q}}{q_x^2}\,\tilde{G}_0(\mathbf{q}, s)\frac{\partial^2 \tilde{G}_0(\mathbf{q}, s)}{\partial q_y^2} =$$

$$= \frac{l_0^2}{24\pi}\int d\mathbf{q}\,\tilde{G}_0^3(\mathbf{q}, s) = \frac{l_0^2}{24\pi}\int\limits_0^{2\pi} d\varphi \int\limits_0^{\infty} \frac{q\,dq}{\left(s + \frac{1}{4}l_0 q^2\right)^3} = \frac{l_0}{12s^2}, \tag{8}$$

and after the inverse Laplace transformation we have

$$\overline{y^2}(L) = \frac{l_0 L}{12}. \tag{9}$$

Expressions (7) and (9) show that the characteristic root-mean-square dimensions of the coil toward the $x$ and $y$ axes differ from each other by 5 times and the linear dimensions differ about 2.5 times:

$$\frac{\overline{x^2}}{\overline{y^2}} = 5, \quad \frac{d_x}{d_y} = \sqrt{\frac{\overline{x^2}}{\overline{y^2}}} \approx 2.24. \tag{10}$$

**Local Description of the Polymer Chain in a Three-Dimensional Space.** In a three-dimensional space, in choosing the intrinsic coordinate system it is necessary to fix (relate to the characteristic points of the molecule) the directions of two axes. This can be done, for example, in the following way. Locate the beginning of the chain origin at the origin of coordinates and draw the positive semiaxis $z$ through the end of the chain. The remaining arbitrariness relative to rotation about the $z$ axis can be fixed provided that the plane $y0z$ ($y = 0$) passes through the center of the chain. It is precisely the way in which the intrinsic coordinate system has been chosen in [1]. However, in this case, the expressions for the distribution function (by which, in particular, the distribution moments are calculated) turn out to be extremely cumbersome and inconvenient for calculation.

As has already been noted, rather substantial arbitrariness exists in choosing the criterion of selection of conformations and the intrinsic coordinate system corresponding to this choice. Therefore, we have a good chance to gain it by other means — to make the expressions for the spatial distribution function of monomers in this coordinate system rather simple and allow all the required calculations to be performed analytically, without resorting to numerical calculations.

Thus, let the origin of the introduced coordinate system pass through the chain center. We draw the positive semiaxis $z$ through one end of the chain and fix the remaining arbitrariness of rotation about the $z$ axis, having located

the other end of the chain at the half-plane $y0x$ (positive $y$). Thus, the chain can be represented as two half-chains related to each other in the origin of coordinates. We can exhaust all conformations, rotating the $z$ axis about the entire solid angle and also swinging the coordinate system about the $z$ axis by the angle $2\pi$. And finally, similar to the two-dimensional case, to make the beginning and the end of the chain interchangeable it is necessary to average both the initial conformations and those obtained in mirror refection relative to the planes $x0y$ and $y0z$.

In the chosen coordinate system, the distribution function will be constructed separately for each half of the chain. For the links of one half-chain whose end lies on the positive semiaxis $z$, the distribution function is

$$G_+ (\mathbf{R}, l \,|\, L) = \int d\mathbf{R}_e W_+ (\mathbf{R}_e) \, G_0 (\mathbf{R}_e - \mathbf{R}, L - l) \, G_0 (\mathbf{R}, l - L/2) \,, \tag{11}$$

where $W_+(\mathbf{R}_e) = 4\pi\delta(x_e)\delta(y_e)\theta(z_e)R_e^2 = 4\pi\delta(x_e)\delta(y_e)\theta(z_e)z_e^2$, $L/2 \le l \le L$, and $\delta(x)$ is the Dirac function; and for the links of the other half-chain whose end lies on the plane $x0z$ we have

$$G_- (\mathbf{R}, l \,|\, L) = \int d\mathbf{R}_b W_- (\mathbf{R}_b) \, G_0 (\mathbf{R}_b - \mathbf{R}, L/2 - l) \, G_0 (\mathbf{R}, l) \,, \tag{12}$$

Here $W_-(\mathbf{R}_b) = 2\pi\delta(x_b)\theta(y_b)R_b = 2\pi\delta(x_b)\theta(y_b)y_b$ and $0 \le l \le L/2$. The full distribution function is written as

$$G (\mathbf{R}, l \,|\, L) = \theta (l - L/2) \, G_+ (\mathbf{R}, l \,|\, L) + \theta (L/2 - l) \, G_- (\mathbf{R}, l \,|\, L) \,. \tag{13}$$

Having applied the Fourier transformation in (11)–(13), we write the distribution functions in the $p$-representation

$$\hat{G} (\mathbf{p}, l \,|\, L) = \theta (l - L/2) \, G_+ (\mathbf{p}, l \,|\, L) + \theta (L/2 - l) \, G_- (\mathbf{p}, l \,|\, L) \,, \tag{14}$$

$$\hat{G}_+ (\mathbf{p}, l \,|\, L) = \frac{i}{\pi^2} \int \hat{G}_0 (\mathbf{q}, L - l) \, \hat{G}_0 (\mathbf{p} + \mathbf{q}, l - L/2) \frac{d\mathbf{q}}{q_z^3} \,, \quad L/2 \le l \le L \,, \tag{15}$$

$$\hat{G}_- (\mathbf{p}, l \,|\, L) = \frac{-1}{2\pi} \int \hat{G}_0 (\mathbf{q}^{(2)}, L/2 - l) \, \hat{G}_0 (\mathbf{p} + \mathbf{q}^{(2)}, l) \frac{d\mathbf{q}^{(2)}}{q_y^2} \,, \quad 0 \le l \le L/2 \,, \tag{16}$$

where the differential $d\mathbf{q}^2$ means that integration in (16) is made only with respect to the two-dimensional vector $\mathbf{q}^2 = (q_x, q_y)$, whereas the vectors $\mathbf{p}$ and $\mathbf{q}$ are three-dimensional.

Then, to calculate the mean characteristics of the chain we can, similarly to the two-dimensional case, perform averaging over the inner links of the chain:

$$\bar{\hat{G}} (\mathbf{p}, L) = \frac{1}{L} \int_0^{L/2} \hat{G}_- (\mathbf{p}, l \,|\, L) \, dl + \frac{1}{L} \int_{L/2}^{L} \hat{G}_+ (\mathbf{p}, l \,|\, L) \, dl \,. \tag{17}$$

Having applied the Laplace transformation in the expressions, we obtain the corresponding relations for both parts of the chain:

$$\tilde{G} (\mathbf{p}, s) = \frac{1}{2} \left[ \tilde{G}_+ (\mathbf{p}, s) + \tilde{G}_- (\mathbf{p}, s) \right], \tag{18}$$

$$\tilde{G}_+ (\mathbf{p}, s) = \frac{i}{\pi^2} \int_s^\infty ds \int \tilde{G}_0 (\mathbf{q}, s) \, \tilde{G}_0 (\mathbf{p} + \mathbf{q}, s) \, d\mathbf{q} / q_z^3 \,, \tag{19}$$
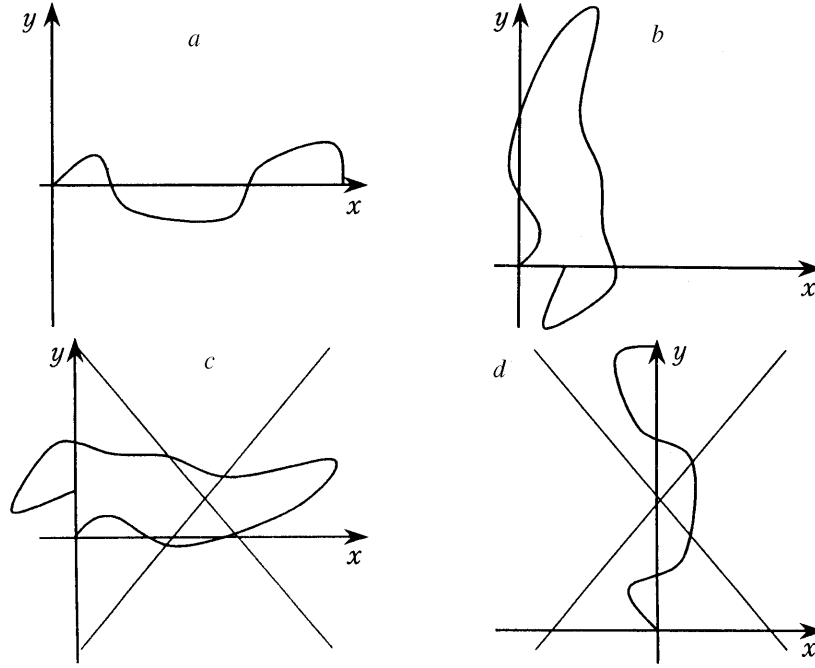
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Fig. 3. Regarded (a, b) and disregarded (c, d) conformations with the chosen criterion of selection. Conformations a and c strengthen local anisotropy, whereas b and d weaken it.

$$\widetilde{G}_{-}(\mathbf{p}, s) = \frac{-1}{2\pi} \int\limits_{s}^{\infty} ds \int \overline{G}_{0} (\mathbf{q}^{(2)}, s) \, \overline{G}_{0} (\mathbf{p} + \mathbf{q}^{(2)}, s) \, d\mathbf{q}^{(2)} / q_y^2 \; ; \tag{20}$$

here, $\widetilde{G}_0(\mathbf{q}, s) = (s + l_0\mathbf{q}^2/6)^{-1}$.

Determination of the mean characteristics of the polymer coil in the three-dimensional space is similar to that in the two-dimensional case and does not involve difficulties, although one special feature is worthy of note: in calculation of the inverse Laplace transform (by the parameter corresponding to the chain length) for the $L$-long chain, the value of the argument must be set equal to $L/2$.

For second moments of distribution, in terms of which the inertia moments of the coil and, correspondingly, its dimensions are expressed, we obtain

$$\overline{x^2}, \overline{y^2}, \overline{z^2} \, (s) = -\frac{1}{2} \left[ \frac{\partial^2 \widetilde{G}_{+}(\mathbf{p}, s)}{\partial p_{x,y,z}^2} + \frac{\partial^2 \widetilde{G}_{-}(\mathbf{p}, s)}{\partial p_{x,y,z}^2} \right]\Bigg|_{\mathbf{p}=0} \; ; \tag{21}$$

$$\overline{x_{\pm}^2} \, (s) = l_0 / 18s^2 \, , \quad \overline{x_{\pm}^2} \, (L/2) = Ll_0 / 36 \, , \quad \overline{x^2} \, (L) = Ll_0 / 36 \; ; \tag{22}$$

$$\overline{y_+^2} \, (s) = l_0 / 18s^2 \, , \quad \overline{y_-^2} \, (s) = 5l_0 / 18s^2 \, , \quad \overline{y_+^2} \, (L/2) = Ll_0 / 36 \, , \quad \overline{y_-^2} \, (L/2) = 5Ll_0 / 36 \, , \quad \overline{y^2} \, (L) = 3Ll_0 / 36 \; ; \tag{23}$$

$$\overline{z_+^2} \, (s) = 7l_0 / 18s^2 \, , \quad \overline{z_-^2} \, (s) = l_0 / 6s^2 \, , \quad \overline{z_+^2} \, (L/2) = 7Ll_0 / 36 \, , \quad \overline{z_-^2} \, (L/2) = Ll_0 / 12 \, , \quad \overline{z^2} \, (L) = 5Ll_0 / 36 \, . \tag{24}$$

Thus, in the three-dimensional space a polymer chain (even absolutely flexible) has a shape similar to a three-axial ellipsoid the ratio of the squares of whose axes is

$$d_z : d_y : d_x = \sqrt{\overline{z^2}} : \sqrt{\overline{y^2}} : \sqrt{\overline{x^2}} = \sqrt{5} : \sqrt{3} : \sqrt{1} \approx 2.24 : 1.733 : 1 . \tag{25}$$

**Degree of Anisotropy of a Flexible Polymer Chain in the Local Coordinate System.** The results obtained are in good agreement with the data given in the literature. The estimates from [1] predict asymmetry of a macromolecule in the intrinsic coordinate system, which virtually coincides with that obtained (the ratio of the root-mean-square dimensions $d_z^2 : d_y^2 : d_x^2 \approx 4.9 : 2.45 : 1$). Numerical calculations show that the degree of anisotropy of the polymer coil in the intrinsic coordinate system is somewhat higher. True enough, the spread in the data of different authors is rather large. Thus, for example, it has been obtained in [11] that the ratio of the squares of the largest and smallest axes does not exceed 3. In [5], a ratio of root-mean-square dimensions of the coil which differs slightly from that predicted by M. V. Vol'kenshtein, $d_z^2 : d_y^2 : d_x^2 \approx 5.9 : 2.1 : 1$ [5], has been given, although the authors of [4, 10, 12] have obtained much higher degrees of anisotropy of the instantaneous conformation of the polymeric molecule with the ratio of the root-mean-square dimensions $d_z^2 : d_y^2 : d_x^2 \approx 11.7 : 2.7 : 1$, $d_z^2 : d_y^2 : d_x^2 \approx 12 : 2.72 : 1$, and $d_z^2 : d_y^2 : d_x^2 \approx 9.2 : 2.5 : 1$, respectively.

This spread in the estimates is related, first of all, to the ambiguity of choosing the intrinsic coordinate system mentioned above. In particular, with the chosen criterion of selection of conformations we allow for the conformations presented in both Fig. 3a and 3b. The first conformations strengthen local anisotropy; the second, on the contrary, weaken it. At the same time, the conformations presented in Fig. 3c and d are not taken into account, although the first of them strengthens the local anisotropy of the coil. It is obvious that if we considered only the conformations given in Fig. 3a and c, the chain anisotropy would be much higher. However, it is hardly possible to make such a separation in analytical form.

**Local Description of a Macromolecule with Finite Rigidity.** As in the case with a flexible chain, we use the coordinate system related to local orientation of the molecule itself (we restrict ourselves to consideration of a plane problem only, since the three-dimensional case does not involve fundamental difficulties but it requires cumbersome computations). The origin of reckoning of this system is located at one end of the chain (for certainty, at the beginning) and its orientation (positive direction of the $x$ axis) is determined by the vector connecting the origin and the end of the molecule. The distribution function of the links of the chain of length $L$, which specifies the probability density of determining the link at a distance $l$ from the beginning of the chain (along its contour) in the vicinity of point $\mathbf{R}$ is found similarly to the distribution function (1); however, in this case, it is necessary to allow for the fact that "seeding" distribution functions depend on the choice of the direction of the first and last steps of wandering, respectively. Therefore, the sought distribution function is written in the form

$$G(\mathbf{R}, l \,|\, L) = \frac{1}{4} \sum_{klij} \int d\mathbf{R}_e W(\mathbf{R}_e) \, (G_0(\mathbf{R}_e - \mathbf{R}, L - l))_{ik} (\mathbf{T}_2)_{kl} (G_0(\mathbf{R}_e, l))_{lj} , \tag{26}$$

where $\mathbf{T}_2 = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$ is the block matrix, $\mathbf{A} = \begin{pmatrix} \alpha_+ & \alpha_- \\ \alpha_- & \alpha_+ \end{pmatrix}$, $\mathbf{B} = \begin{pmatrix} \alpha_\perp & \alpha_\perp \\ \alpha_\perp & \alpha_\perp \end{pmatrix}$, $\alpha_{\pm, \perp}$ are the probabilities of rectilinear, flexural, and folded local conformations of the chain [13, 14], $(\mathbf{T}_2)_{kl}$ are its matrix elements, and $(G_0(\mathbf{R}, l))_{ij}$ are the distribution functions specifying the probability of displacement by the vector $\mathbf{R}$ in $l$ steps provided that the first step is taken in the $j$ direction and the last step is taken in the $i$ direction, with these functions being symmetric in their indices $(G_0(\mathbf{R}, l))_{ij} = (G_0(\mathbf{R}, l))_{ji}$; the function $W(\mathbf{R})$ is determined in (1).

Having applied the Fourier transformation in (26), we obtain

$$\hat{G}(\mathbf{p}, l \,|\, L) = \frac{-1}{8\pi} \sum_{kl} \int \sum_i (\hat{G}_0(\mathbf{q} + \mathbf{p}, L - l))_{ik} (\mathbf{T}_2)_{kl} \sum_j (\hat{G}_0(\mathbf{q}, l))_{lj} \frac{d\mathbf{q}}{q_x^2} . \tag{27}$$

The next step is the averaging over the position of an intermediate link and the Laplace transformation

$$\tilde{G}(\mathbf{p}, s) = \frac{-1}{8\pi} \int \sum_{kl} \tilde{\Gamma}_k^{(2)}(\mathbf{q} + \mathbf{p}, s) (\mathbf{T}_2)_{kl} \tilde{\Gamma}_l^{(2)}(\mathbf{q}, s) \frac{d\mathbf{q}}{q_x^2} , \tag{28}$$

where $\tilde{\Gamma}_k^{(2)}(\mathbf{p}, s)$ are obtained from the function nonaveraged toward the first step

$$\tilde{\Gamma}^{(2)}(\mathbf{q}, \xi) = 1 + \frac{[1 + \overline{P}(q_y, \xi)] P(q_x, \xi)}{1 - \overline{P}(q_x, \xi) \overline{P}(q_y, \xi)}, \quad \overline{P}(q, \xi) = \frac{2\alpha_\perp \xi [\cos q - (\alpha_+ - \alpha_-) \xi]}{1 - 2\alpha_+ \xi \cos q + (\alpha_+^2 - \alpha_-^2) \xi^2}$$

after the transition to the continuous limit [13, 14].

On transition to the continuous limit it is necessary to keep the terms no higher than second order in $p$. Then, allowing for the structure of the matrix $\mathbf{T}_2$, we can write

$$\sum_{kl} \tilde{\Gamma}_k^{(2)}(\mathbf{q} + \mathbf{p}, s)\, (\mathbf{T}_2)_{kl}\, \tilde{\Gamma}_l^{(2)}(\mathbf{q}, s) == \frac{4\left(s + \dfrac{1-\theta}{l_0\theta}\right)^2 + \left(s + \dfrac{1-\theta}{l_0\theta}\right)\left[l_0(\mathbf{p}+\mathbf{q})^2 + l_0\mathbf{q}^2\right] - \dfrac{2(\mathbf{p}+\mathbf{q})\mathbf{q}}{\theta}}{\left[s^2 + s\dfrac{1-\theta}{l_0\theta} + (\mathbf{q}+\mathbf{p})^2\dfrac{1+\theta}{4\theta}\right]\left[s^2 + s\dfrac{1-\theta}{l_0\theta} + \mathbf{q}^2\dfrac{1+\theta}{4\theta}\right]} . \tag{29}$$

Having substituted (29) into (28), we obtain that the distribution function of the macromolecule links in the Fourier–Laplace transforms has the form

$$\tilde{G}(\mathbf{p}, s) = \frac{-1}{2\pi} \int \frac{\left(s + \dfrac{1-\theta}{l_0\theta}\right)^2 + \dfrac{1}{4}\left(s + \dfrac{1-\theta}{l_0\theta}\right)\left[l_0(\mathbf{p}+\mathbf{q})^2 + l_0\mathbf{q}^2\right] - \dfrac{(\mathbf{p}+\mathbf{q})\mathbf{q}}{2\theta}}{\left[s^2 + s\dfrac{1-\theta}{l_0\theta} + (\mathbf{q}+\mathbf{p})^2\dfrac{1+\theta}{4\theta}\right]\left[s^2 + s\dfrac{1-\theta}{l_0\theta} + \mathbf{q}^2\dfrac{1+\theta}{4\theta}\right]q_x^2} \, d\mathbf{q} . \tag{30}$$

Using (30), we can calculate the distribution moments, e.g., second moments which specify the root-mean-square dimensions of the coil. Simple but cumbersome calculations yield

$$-\frac{l_0^2\theta}{2(1-\theta+\theta l_0 s)\, s^2} - \frac{l_0^2\theta^2}{12(1-\theta+\theta l_0 s)^2\, s^2} + \frac{l_0^3\theta^2}{12(1-\theta+\theta l_0 s)^2\, s}, \tag{31}$$

$$\overline{y^2}(s) = -\frac{\partial^2}{\partial p_y^2}\tilde{G}(\mathbf{p}, s)\Big|_{\mathbf{p}=0} = \frac{l_0(1+\theta)}{6(1-\theta+\theta l_0 s)\, s^3} -$$

$$-\frac{l_0^2\theta}{2(1-\theta+\theta l_0 s)\, s^2} + \frac{l_0^2\theta^2}{12(1-\theta+\theta l_0 s)^2\, s^2} - \frac{l_0^3\theta^2}{12(1-\theta+\theta l_0 s)^2\, s} . \tag{32}$$

It is seen that if the length of a macromolecule $L$ is large, in inverse Laplace transformation the principal terms in (31) and (32) are represented by the first terms which are proportional to $s^{-3}$. It is precisely these terms that make the linearly increasing contribution to the root-mean-square dimensions of the molecule

$$\overline{x^2}(L) = -\frac{1}{2\pi i}\int_\gamma \exp(Ls)\frac{\partial^2}{\partial p_x^2}\tilde{G}(\mathbf{p}, s)\Big|_{\mathbf{p}=0} ds =$$

$$= \frac{1}{2\pi i}\int_\gamma \exp(Ls)\left(\frac{5 l_0(1+\theta)}{6(1-\theta+\theta l_0 s)\, s^3} + \dots\right) ds = \frac{5(1+\theta) l_0 L}{12(1-\theta)}\left[1 + O\left(\frac{1}{L}\right)\right], \tag{33}$$

$$\overline{y^2(L)} = -\frac{1}{2\pi i} \int_\gamma \exp(Ls) \frac{\partial^2}{\partial p_y^2} \tilde{G}(\mathbf{p}, s)\big|_{\mathbf{p}=0} \, ds =$$

$$= \frac{1}{2\pi i} \int_\gamma \exp(Ls) \left( \frac{l_0(1+\theta)}{6(1-\theta+\theta l_0 s) s^3} + ... \right) ds = \frac{(1+\theta) l_0 L}{12(1-\theta)} \left[ 1 + O\left(\frac{1}{L}\right) \right]. \tag{34}$$

It is seen from (33) and (34) that the asymmetry in the local coordinate system for the long rigid molecule is the same as for the flexible one:

$$\frac{\overline{x^2(L)}}{\overline{y^2(L)}} = 5 + O\left(\frac{1}{L}\right). \tag{35}$$

## CONCLUSIONS

The analysis made shows that in the polymeric system individual molecules are in an anisotropic state. Although the chosen criterion of selection of conformations, does not allow one to take into account this effect as a whole, it still makes it possible to completely solve the formulated problem analytically. We note that the anisotropy of the flexible and rigid molecules will in fact differ on scales of the order $l_0(\alpha_+ - \alpha_-)/(1 - \alpha_+ + \alpha_-)$, which correspond to the Kuhn segment, i.e., if the length of the rigid molecule slightly exceeds its persistent length. These macromolecules are oligomers whose properties strongly differ from ordinary macromolecular systems.

## NOTATION

$L$, chain length, m; $l$, contour distance, m; $l_0$, size of a monomeric link; $\mathbf{r}$ and $\mathbf{R}$, displacement vectors, m; $x$, $y$, $z$, space coordinates, m; $\mathbf{q}(q_x, q_y, q_z)$ and $\mathbf{p}(p_x, p_y, p_z)$, wave vectors (their Fourier coordinates), 1/m; $s$, parameter of the Laplace transformation, 1/m; $d$, dimension of the space ($d = 2$, plane; $d = 3$, three-dimensional space); $d_x$, $d_y$, and $d_z$, transverse dimensions of the polymer coil; $\varphi$, polar angle; $R$, module of the vector $\mathbf{R}$, m; $Q(1/L)$, small quantity of the order of $1/L$. Subscripts: e, end; b, beginning; m, mean; overbar, averaging over the inner chain links; +, positive; −, negative semiaxis.

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