

Rheological properties of a nematic solution of semiflexible macromolecules

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An investigation is made of the orientational dynamics of an athermal nematic solution of semiflexible persistent macromolecules. Reptational concepts are used to derive a closed diffusion equation describing relaxation of the orientational distribution function. Expressions for the Leslie coefficient α_2 and α_3 , asymptotically exact in the limit $L \gg l, l \gg d$ (L is the total length of the molecule, l is a Kuhn segment, and d is diameter), are obtained. It is shown that:

1) the effective diffusion coefficient D^* for the motion of a macromolecule along its axis decreases on appearance of orientational order in the system; 2) the ratio α_3/α_2 is always positive, so that the Couette flow of a solution should be very stable.

I. INTRODUCTION

The dynamic properties of nematic polymer solutions are currently attracting much attention from specialists.¹⁻³ The majority of real polymers, which become liquid crystals in solution, is described well by the persistent model representing a flexible rod of diameter d , which is much less than the length of a Kuhn segment l , i.e., the length of a segment of a polymer chain in which the memory of the initial orientation is lost.⁴ An athermal solution of semiflexible persistent macromolecules (of total length $L \gg l$) goes over completely to the nematic state if⁵

$$\varphi \gg \varphi^* = 11.5d/l, \quad \varphi \ll 1, \quad (1.1)$$

where $\varphi = \frac{1}{4}\pi L d^2 c$ is the volume concentration of the polymer (c is the concentration of polymer chains).

Our aim will be to investigate theoretically some dynamic properties of a nematic solution of semiflexible persistent macromolecules. If $\varphi \gg \varphi^*$, then after a sufficiently long time the dynamics of polymer chains is of reptational nature: each chain is surrounded by so many neighboring chains that they effectively prevent shifting in the transverse direction and the only allowed motion is sliding (reptation) of a macromolecule along its axis (Fig. 1).⁶⁻⁸ In the next section we shall derive the fundamental diffusion transport equation describing reptational dynamics of polymer chains. We shall use this equation in Sec. 3 to calculate the Leslie viscosity coefficients α_2 and α_3 (Ref. 9), the relationship between which has a strong influence on the stability of flow of the solution.¹⁰ In the rest of the present section we shall describe some of the equilibrium properties of a liquid crystal solution of persistent macromolecules which will be required later.

The free energy F of an athermal solution of semiflexible macromolecules⁵ is

$$F = F_0 + F_{int}, \quad (1.2)$$

where

$$F_0 = \frac{1}{4} \int \frac{(\nabla_n f)^2}{f} d^2 n \quad (1.3)$$

is the "ideal-gas" part of the free energy (calculated per one Kuhn segment), which is related to the orientational ordering;

$$F_{int} = \frac{cL}{2l} \int B(\mathbf{n}, \mathbf{n}') f(\mathbf{n}) f(\mathbf{n}') d^2 n d^2 n' \quad (1.4)$$

is the free energy of the steric interaction between macromolecules.¹⁾ In Eqs. (1.3) and (1.4) the quantity $f(\mathbf{n})$ is the distribution in the orientation of a unit vector \mathbf{n} tangent to the polymer chain, normalized by the condition

$$\int f(\mathbf{n}) d^2 n = 1; \quad (1.5)$$

$B(\mathbf{n}, \mathbf{n}')$ is the excluded volume of two parts of macromolecules of length l and with the orientations \mathbf{n} and \mathbf{n}' :

$$B(\mathbf{n}, \mathbf{n}') = 2l^2 d \sin \gamma, \quad (1.6)$$

where γ is the angle between \mathbf{n} and \mathbf{n}' . The equilibrium distribution $f(\mathbf{n})$ minimizing the free energy satisfies the equation

$$\delta F_0 / \delta f(\mathbf{n}) + U_{int}(\mathbf{n}) = 0, \quad (1.7)$$

where

$$U_{int}(\mathbf{n}) = \frac{\delta F_{int}}{\delta f(\mathbf{n})} = \frac{cL}{l} \int B(\mathbf{n}, \mathbf{n}') f(\mathbf{n}') d^2 n' \quad (1.8)$$

is the potential energy of a Kuhn segment aligned in the direction \mathbf{n} in the average molecular field. If the external orienting field $U_{ext}(\mathbf{n})$ also acts on the macromolecules, then the molecular field $U_{int}(\mathbf{n})$ in Eq. (1.7) should be replaced with the total field:

$$U(\mathbf{n}) = U_{int}(\mathbf{n}) + U_{ext}(\mathbf{n}). \quad (1.9)$$

The orientational ordering of this system is described by the order parameter

$$s = \int P_2(\cos \theta) f(\mathbf{n}) d^2 n, \quad (1.10)$$

where θ is the angle between \mathbf{n} and the director \mathbf{u} of the nematic. In the nematic phase with $\varphi = \varphi^*$ the order parameter is $s = 0.49$ (Ref. 5).

2. KINETIC EQUATION

In a nonequilibrium state the various parts of a macromolecule may be oriented on the average in various degrees so that the distribution function of the orientations $f(\mathbf{n}|\mathbf{x};t)$ for a set of regions located at a distance x from the end of the chain should be introduced²⁾ separately for each x . The normalization condition, and the relationship between this

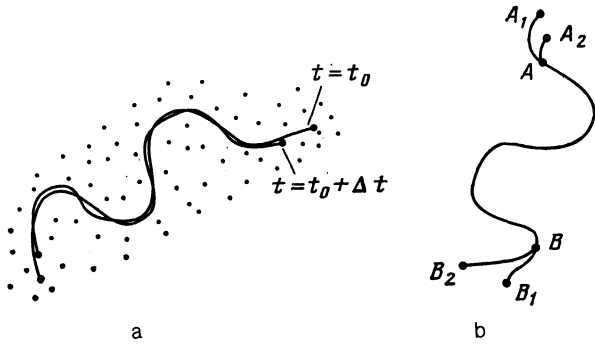


FIG. 1. a) Diagram showing the only allowed large-scale motion of a macromolecule, which is reptational along its axis (the points identify surrounding polymers). b) Change in the conformation of a macromolecule in a short time t ($A_1 A B B_1$ is the initial conformation, and $A_2 A B B_2$ is the conformation at a moment t ; the length of the segment AA_1 is y_1 and that of AA_2 is y_2)

function and the function $f(\mathbf{n}|t)$ introduced earlier are as follows:

$$\int f(\mathbf{n}|x, t) d^2n = 1; \quad (2.1)$$

$$f(\mathbf{n}|t) = L^{-1} \int_0^L dx f(\mathbf{n}|x; t). \quad (2.2)$$

We shall first consider the case when a macromolecule is not affected by any orienting field at all, i.e., when $U(\mathbf{n}) = 0$. Then, the reptational dynamics of macromolecules is described by the following simple diffusion equation⁸:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2} \quad (2.3)$$

subject to the boundary conditions

$$l \frac{\partial f}{\partial x} \Big|_{x=0} = -\nabla_{\mathbf{n}}^2 f, \quad (2.4)$$

$$l \frac{\partial f}{\partial x} \Big|_{x=L} = \nabla_{\mathbf{n}}^2 f, \quad (2.5)$$

where

$$D = \ln(l/d) / 2\pi\eta_s L \quad (2.6)$$

is the diffusion coefficient for the reptational motion (η_s is the viscosity of the solvent). The conditions (2.4) and (2.5) follow from the fact that the conformations of very short end regions are intentionally made to satisfy an equilibrium distribution.

The time in which a chain transverses (along its axis) a distance of the order of the Kuhn segment l is $\tau_0 = l^2/D$. On the other hand, the maximum orientational relaxation time of the system is⁸

$$\tau_{max} = L^2 / \pi^2 D \gg \tau_0. \quad (2.7)$$

We can easily show that, irrespective of the initial state of the system, in a time $t \gg \tau_0$ the orientational functions $f(\mathbf{n}|0; t)$ and $f(\mathbf{n}|L; t)$ of the end parts of the macromolecules relax to an almost isotropic distribution.⁸ In other words, after a time $t \gg \tau_0$ not only the conformational, but also the orientational distributions of the end parts reach equilibrium, i.e., they

become isotropic in the absence of an orienting field. Therefore, if we are interested in quantities for which the characteristic time $t \sim \tau_{max}$ is much longer than τ_0 (these quantities include, for example, the viscosity), then the boundary conditions (2.4) and (2.5) may be replaced with

$$f(\mathbf{n}|0; t) = f(\mathbf{n}|L; t) = 1. \quad (2.8)$$

We shall now consider the general situation when macromolecules are subject to an orienting field described by Eq. (1.9). Clearly, the order of magnitude of characteristic time τ_0 of the orientational relaxation of the end parts does not alter if $U(\mathbf{n}) \sim 1$. Consequently, after a times $t \sim \tau_{max} \gg \tau_0$ the boundary conditions can, by analogy with Eq. (2.8), be written in the form

$$f(\mathbf{n}|0; t) = f(\mathbf{n}|L; t) = f_{eq}(\mathbf{n}), \quad (2.9)$$

where the function $f_{eq}(\mathbf{n})$ is the solution of the equation [compare with Eq. (1.9)]

$$\delta F_0 / \delta f(\mathbf{n}) + U(\mathbf{n}) = 0. \quad (2.10)$$

A macromolecule moves along its axis under the action of two forces: a random force $h_1(t)$ which obeys

$$\langle h_1(t) \rangle = 0, \quad \langle h_1(t) h_1(t') \rangle = 2D^{-1} \delta(t-t'), \quad (2.11)$$

as well as a regular force

$$h_2(t) = U(\mathbf{n}_0)/l - U(\mathbf{n}_L)/l, \quad (2.12)$$

where \mathbf{n}_0 and \mathbf{n}_L are the orientations of the beginning and end of a chain. The displacement of a macromolecule along its axis Δx in a short time Δt is given by

$$\Delta x = D(h_1 + h_2)\Delta t. \quad (2.13)$$

It follows from the definition of the regular force of Eq. (2.12) that its autocorrelation is nonzero and, therefore, the process of reptation in the presence of a field $U(\mathbf{n})$ becomes non-Markovian. Consequently, in general, Eq. (2.3) ceases to be valid. However, it is clear that the correlation between the chain displacements is retained only for a time of order τ_0 , so that in the intervals $\Delta t \gg \tau_0$ the reptational process remains purely diffusive:

$$\langle \Delta x \rangle = 0, \quad \langle \Delta x^2 \rangle = 2D^* \Delta t,$$

where D^* is the renormalized diffusion coefficient. Therefore, at times $t \gg \tau_0$ Eq. (2.3) remains valid if we replace the coefficient D with D^* such that

$$\frac{\partial f}{\partial t} = D^* \frac{\partial^2 f}{\partial x^2}. \quad (2.14)$$

The effective coefficient D^* is calculated in the Appendix in the limit of a weak field U up to second order. If we assume that the orienting field has the form

$$U(n) = \text{const } P_2(\mathbf{n}u), \quad \text{const} \ll 1,$$

then using Eqs. (A15), (2.10), and (1.10) we can simplify Eq. (A14) and find the dependence of D^* on the order parameter:

$$D^* = D \{ 1 - 5/2 s^2 + O(s^4) \}. \quad s \rightarrow 0. \quad (2.15)$$

Using similarity concepts,¹¹ we can easily show that in the opposite limiting case of a very strong field and, consequent-

ly, a high degree of orientational order ($s \rightarrow 1$) the coefficient D^* tends to the constant value

$$D^* = \lambda D, \quad (2.16)$$

where $\lambda < 1$ is a numerical constant. Therefore, the dependence of D^* on s has the form shown schematically in Fig. 2.

3. LESLIE COEFFICIENTS α_2 AND α_3

We shall consider a slowly flowing nematic solution subjected to a weak external orienting field $U_{\text{ext}}(\mathbf{n})$. We shall assume that the velocity of hydrodynamic flow \mathbf{v} at a point \mathbf{r} is

$$v_\alpha = g_{\alpha\beta} r_\beta, \quad g_{\alpha\alpha} = 0. \quad (3.1)$$

The motion of macromolecules under these conditions is described as follows: an external field U_{ext} does not affect the form of the kinetic equation (2.14) and its influence on the boundary conditions of Eq. (2.9) is included formally by the relationships (1.9) and (2.10). On the other hand, the presence of hydrodynamic flow requires modification of the transport equation (2.14). The action of the flow over a short time Δt reduces to a small affine deformation of the contour of a macromolecule in accordance with the law

$$r_\alpha \rightarrow r'_\alpha = r_\alpha + g_{\alpha\beta} r_\beta \Delta t. \quad (3.2)$$

As a result, some parts of the macromolecule become extended and others are compressed, so that on the average its length may change. Clearly, the length of the macromolecule should relax very rapidly to its initial value (see Ref. 7). Bearing in mind this relaxation process, the change in the distribution function due to hydrodynamic flow over a time Δt is

$$\Delta f = G \Delta t,$$

$$G = -\nabla_n (f_{\text{eq}} \dot{\mathbf{n}}) + f_{\text{eq}} g_{\alpha\beta} n_\alpha n_\beta - f_{\text{eq}} g_{\alpha\beta} \langle n_\alpha n_\beta \rangle, \quad (3.3)$$

where

$$\dot{n}_\alpha = g_{\alpha\beta} n_\beta - n_\alpha (g_{\beta\gamma} n_\beta n_\gamma), \quad \langle n_\alpha n_\beta \rangle = \int f_{\text{eq}}(\mathbf{n}) n_\alpha n_\beta d^2 n. \quad (3.4)$$

Equation (3.3) is derived on the assumption that the initial distribution of the orientations of all the parts of macromolecules differs little from f_{eq} . The first term in Eq. (3.3) describes the change in the function f due to rotation of the segments of the chain, the second describes the effect of the changes in the length terms of the segments, and the third is due to the process of relaxation of the length of a macromolecule as a whole.

We can therefore see that the action of hydrodynamic flow gives rise to an additional term G on the right-hand side of Eq. (2.14):

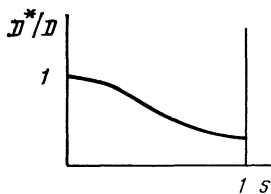


FIG. 2. Dependence of the effective diffusion coefficient D^* on the order parameter s .

$$\frac{\partial f}{\partial t} = D^* \frac{\partial^2 f}{\partial x^2} + G. \quad (3.5)$$

Equations (3.5) and (3.3), subject to the boundary conditions (2.9) and (2.10), describe completely the orientational dynamics of semiflexible macromolecules.

It follows from the linear macroscopic theory of Ref. 6 that the moment of an external field acting per unit volume of the system should be (square brackets denote vector products)

$$\Gamma = [\mathbf{u}\mathbf{h}], \quad (3.6)$$

where \mathbf{u} is the director of the nematic and the "force" \mathbf{h} is related to the gradient of the flow velocity:

$$h_\alpha = \alpha_2 g_{\alpha\beta} u_\beta - \alpha_3 g_{\beta\alpha} u_\beta, \quad (3.7)$$

where α_2 and α_3 are the Leslie viscosity coefficients. On the same time, the following "microscopic" expression obviously holds:

$$\Gamma = -\frac{cL}{l} \int f(\mathbf{n}) [\mathbf{n} \nabla_n U_{\text{ext}}(\mathbf{n})] d^2 n. \quad (3.8)$$

In this equation the field U_{ext} can be replaced with the total field U , since the moment of the internal forces due to the molecular field U_{int} should be identically equal to zero. We therefore have

$$\Gamma = -\frac{cL}{l} \int f(\mathbf{n}) [\mathbf{n} \nabla_n U(\mathbf{n})] d^2 n. \quad (3.9)$$

The steady-solution of Eqs. (2.9) and (3.5) can be written

$$f(\mathbf{n}|x) = f_{\text{eq}}(\mathbf{n}) + \frac{x(L-x)}{2D^*} G(\mathbf{n}),$$

where $f_{\text{eq}}(\mathbf{n})$ is described by Eq. (2.10). The average distribution function is therefore

$$f(\mathbf{n}) = f_{\text{eq}}(\mathbf{n}) + \frac{L^2}{12D^*} G(\mathbf{n}). \quad (3.10)$$

Substituting Eq. (3.10) into Eq. (3.9) and bearing in mind that in the equilibrium state the moment of the force acting on macromolecules vanishes identically on the average, i.e.,

$$\int f_{\text{eq}}(\mathbf{n}) [\mathbf{n} \nabla_n U(\mathbf{n})] d^2 n = 0,$$

we obtain

$$\Gamma = -\frac{cL}{l} \frac{L^2}{12D^*} \int G(\mathbf{n}) [\mathbf{n} \nabla_n U(\mathbf{n})] d^2 n. \quad (3.11)$$

The functions $f_{\text{eq}}(\mathbf{n})$ and $U(\mathbf{n})$ in Eqs. (3.3) and (3.11) can be replaced, in the linear approximation, with the functions $f_0(\mathbf{n} \cdot \mathbf{u})$ and $U_0(\mathbf{n} \cdot \mathbf{u})$ respectively, which characterize the state of complete equilibrium in the absence of any external forces. Comparing now Eq. (3.11) with Eqs. (3.6) and (3.7), we obtain after simple transformations the following results:

$$\alpha_2 = \kappa \int_{-1}^1 dz f_0(z) \{2zU_0'(z) - z^2(1-z^2)U_0''(z)\}, \quad (3.12)$$

$$\alpha_3 = \kappa \int_{-1}^1 f_0(z) (1-z^2)^2 U_0''(z) dz, \quad (3.13)$$

where $z = \mathbf{n} \cdot \mathbf{u}$ and $\kappa = (cL/4l)L^2/12D^*$. The relationship between the functions U_0 and f_0 follows from Eq. (2.10):

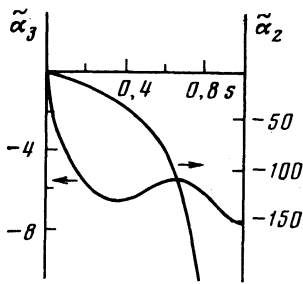


FIG. 3. Dependence of the reduced viscosities α_2 and α_3 on the order parameter.

$$U_0 = f_0^{-1/2} \nabla_n^2 f_0^{1/2} \quad (3.14)$$

We can find how the coefficients α_2 and α_3 depend on the order parameter s using a family of test functions of the form

$$f_0(z) = \text{const} \operatorname{ch}^2(\beta z), \quad (3.15)$$

where "const" represents a normalization constant and β is a parameter. The dependence of the reduced viscosities $\tilde{\alpha}_2 = \alpha_2/\kappa$ and $\tilde{\alpha}_3 = \alpha_3/\kappa$ on s , calculated with the aid of Eqs. (3.12)–(3.15) and (1.10), is shown in Fig. 3.

Note that both coefficients α_2 and α_3 are negative for any value of s , so that their ratio is always positive. This means that in Couette flow the director of the nematic could have a steady-state orientation at an angle of θ_L to the flow direction (without allowance for boundary effects)¹⁰:

$$\operatorname{tg}^2 \theta_L = \alpha_3/\alpha_2.$$

The dependence of θ_L on s is shown in Fig. 4. In a liquid crystal phase associated with an isotropic phase (i.e., if $s = 0.49$), the angle is $\theta_L = 20^\circ$. An increase in the order parameter (accompanied by an increase in the concentration of the solution) reduces considerably the value of θ_L ; in the limit $s \rightarrow 1$, we find that $\theta_L \rightarrow 0$.

CONCLUSIONS

We have studied the reptational dynamics of long persistent molecules in a nematic solution. The results obtained are exact in the asymptotic limit $L \gg l, l \gg d$, i.e., in the case of semiflexible polymer chains. The final expressions (3.12) and (3.13), which relate the viscosity coefficients to the equilibrium properties of a solution, are generally valid not only in the case of persistent chains, but also for any semi-

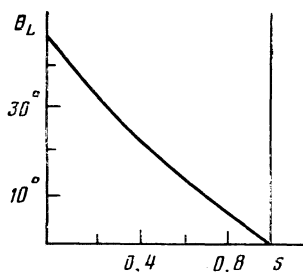


FIG. 4. Dependence of the Leslie angle θ_L on the order parameter.

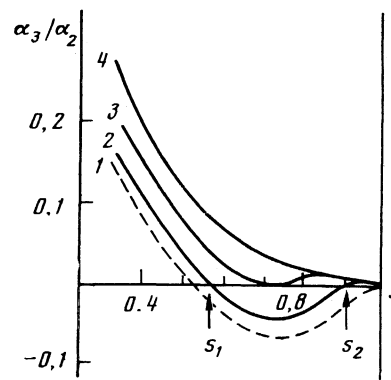


FIG. 5. Dependences of the ratio α_3/α_2 on the order parameter s for different values of L/l : 1) $L/l = 0$; 2) $L/l \ll 1$; 3) $L/l = (L/l)_c$; 4) $L/l \gg 1$.

flexible macromolecules with an arbitrary flexibility mechanism. The only "nonequilibrium" characteristic which depends strongly on the polymer structure (in particular, on the flexibility mechanism) is the effective diffusion coefficient D^* .

We found that the ratio of the Leslie coefficients α_3/α_2 for persistent macromolecules is always positive. This result is very different from that obtained for a nematic solution of extremely rigid chain molecules ($l \gg L \gg d$).^{12,13} In the latter case it was found that the ratio α_3/α_2 becomes negative even for $s \geq 0.53$ (Ref. 12), as shown in Fig. 5 (curve 1). It is known from Ref. 14 that if $\alpha_3/\alpha_2 < 0$, then the Couette flow becomes unstable even at very low Reynolds numbers (see also Ref. 12). It is therefore interesting to determine the sign of the ratio α_3/α_2 in the case when $L \sim l$, which represents the case intermediate between the two limits $L \ll l$ and $L \gg l$ already considered (this intermediate case is the one usually encountered in experiments).

Application of similarity concepts (see Ref. 10) makes it possible to show that if the degree of orientational order is very high ($s \rightarrow 1$), then the intermediate case $L \sim l$ is equivalent to the case of semiflexible macromolecules ($L \gg l$). Consequently, in the limit $s \rightarrow 1$ the ratio α_3/α_2 should be positive irrespective of the value of L/l . Figure 5 shows qualitatively the resulting dependence of α_3/α_2 on s for different values of L/l . If L/l is small (rod-shaped macromolecules), then α_3/α_2 is positive for $s < s_1 \sim 0.55$ or $s > s_2$ and negative for $s_1 < s < s_2$, where s_2 is close to unity. On the other hand, in the case of sufficiently large values of L/l the ratio α_3/α_2 is always positive. Consequently, there should be a critical value $(L/l)_c$ at which there is a transition between these two regimes (curve 3 in Fig. 5).

APPENDIX

Equation (2.13) can be rewritten in the form

$$\dot{x} = D(h_1 + h_2). \quad (A1)$$

The effective diffusion coefficient is clearly

$$D^* = \int_0^\infty \langle \dot{x}(0) \dot{x}(t) \rangle dt \\ = D^2 \int_0^\infty \langle [h_1(0) + h_2(0)] [h_1(t) + h_2(t)] \rangle dt. \quad (A2)$$

We shall consider the correlation function

$$\langle \dot{x}(0)h_2(t) \rangle. \quad (\text{A3})$$

If we change the sign of t , the first factor in Eq. (A3) changes its sign, whereas the second remains unaltered because of the definition given by Eq. (2.12). Hence, we have the following symmetry relationship:

$$\langle \dot{x}(0)h_2(t) \rangle = -\langle h_2(0)\dot{x}(t) \rangle. \quad (\text{A4})$$

Substituting Eq. (A1) into Eq. (A4) and using the trivial relationship

$$\langle h_2(0)h_1(t) \rangle = 0, \quad t > 0, \quad (\text{A5})$$

we obtain

$$\langle h_1(0)h_2(t) \rangle = -2\langle h_2(0)h_2(t) \rangle, \quad t > 0. \quad (\text{A6})$$

Substituting Eqs. (A5), (A6), and (2.11) into Eq. (A2), we obtain the expression

$$D^* = D - D^2 \int_0^\infty \langle h_2(0)h_2(t) \rangle dt, \quad (\text{A7})$$

from which it follows directly that the coefficient D^* is much smaller than the unrenormalized coefficient D .

We shall calculate the correlation function in Eq. (A7) to second order in U . Without limiting the generality of the treatment, we can assume that

$$\int U(\mathbf{n}) d^2n = 0. \quad (\text{A8})$$

Using the definition (2.12), we find that

$$\langle h_2(0)h_2(t) \rangle = 2 \int Q(\mathbf{n}, \mathbf{n}' | t) U(\mathbf{n}) U(\mathbf{n}') d^2n d^2n', \quad (\text{A9})$$

where $Q(\mathbf{n}, \mathbf{n}' | t)$ is the density of the probability that the end of a chain has the orientation \mathbf{n} initially and the orientation \mathbf{n}' at a time t ; the coefficient 2 in front of the integral is due to the fact that a chain has two independent ends. The function Q has to be calculated in the zeroth order, i.e., on the assumption that $U = 0$. We note in this connection that the change in the conformation of a long semiflexible macromolecule near one of its ends in a time $t \sim \tau_0 \ll \tau_{\max}$ amounts to replacement of the end part of length y_1 with a new part of length y_2 (Fig. 1b, where the displacement of the macromolecule along its axis is $y_2 - y_1$). The probability distribution for the quantities y_1 and y_2 is⁸

$$P(y_1, y_2 | t) = (4\pi)^{-1/2} (Dt)^{-1/2} y \exp(-y^2/4Dt), \quad (\text{A10})$$

where $y = y_1 + y_2$. We therefore have

$$Q(\mathbf{n}, \mathbf{n}' | t) = \int_0^\infty K(\mathbf{n}, \mathbf{n}' | y) P(y_1, y_2 | t) dy_1 dy_2, \quad (\text{A11})$$

where $K(\mathbf{n}, \mathbf{n}' | y)$ is the conditional probability that the end of a free persistent chain of length y has the orientation \mathbf{n}' if the beginning of the chain is oriented along \mathbf{n} . The function K satisfies the equations

$$l\partial K/\partial y = \nabla_{\mathbf{n}}^2 K, \quad y > 0, \quad (\text{A12})$$

$$K(\mathbf{n}, \mathbf{n}' | 0) = \delta(\mathbf{n} - \mathbf{n}'). \quad (\text{A13})$$

Substituting Eq. (A11) into Eq. (A9), and also Eq. (A9) into Eq. (A7), we obtain the following expression after some transformations:

$$D^* = D \left\{ 1 - 2 \int \varphi_0^2(\mathbf{n}) d^2n \right\}, \quad (\text{A14})$$

where the function φ_0 is the solution of the system of equations

$$\nabla_{\mathbf{n}}^2 \varphi_0 = U, \quad \int \varphi_0 d^2n = 0, \quad (\text{A15})$$

which has a unique solution on the basis of Eq. (A8).

¹Here and in what follows the temperature is assumed to be $T = 1$ and d^2n represents an element of a solid angle divided by 4π .

²Here and in what follows we shall consider only a system which is spatially homogeneous.

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