Fluctuation effects in the dynamics of concentrated polymer systems

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The motion of macromolecules in concentrated polymer solutions and melts is analyzed in the entanglement region ($M \gg M_e$, where M is the molecular weight of the polymer and M_e is the molecular weight per entanglement). Fluctuations in the molecular field can lead to a substantial renormalization of dynamic characteristics of the system such as the maximum conformational relaxation time t_r and the viscosity η. The effect of fluctuations is determined by the parameter $\alpha \propto M^{1/4}/M_e^{3/4}$. For $\alpha \ll 1$ we have $\eta \propto M^3(1+\alpha)$. For $\alpha \gg 1$ the viscosity increases exponentially with the molecular weight $\eta \propto \exp(\text{const}\cdot\alpha^{4/3})$.

1. INTRODUCTION

The rheological and relaxational properties of concentrated polymer solutions are attracting much interest.[1] The dynamics of such systems (for polymers of high molecular weight) is known to be determined primarily by topological limitations (entanglements), because different sections of the polymer chains cannot intersect each other. One of the most systematic (from the microscopic standpoint) theories describing polymer dynamics with topological limitations is based on a reptation model.[2] This model assumes that the polymer chains surrounding any selected chain create an effective "tube" for it: Sections of the selected chain can move a significant distance only along the axis of this tube. The basic motion of the macromolecule as a whole is also a "creep" (reptation) along the tube axis. It is not difficult to show that the maximum conformational relaxation time is[2]

$$t_r \propto N^3, \tag{1.1}$$

where N is the number of links in the polymer chain (in reptation theory, t_r is the time over which the macromolecule "creeps out" of its original tube).

The time t_r also determines the behavior of η, the viscosity of the system (a concentrated polymer solution or melt), as a function of N. The following general scaling holds[3]:

$$\eta \propto G_0 t_r, \tag{1.2}$$

where G_0 is the shear modulus of the system in the visoelastic plateau region (the elastic modulus of the network of quasientanglements), which is given by[4]

$$G_0 = c_0 T/N_e, \tag{1.3}$$

where c_0 is the average concentration of polymer units, and N_e is the average "length" of a section of a macromolecule between successive entanglements. We thus have $G_0 \propto N^0$; i.e., the reptation theory predicts

$$\eta \propto N^3, \quad N \gg N_e. \tag{1.4}$$

Experiments reveal a stronger dependence of η on N at large molecular weights:

$$\eta \propto N^z,$$

where[1)] $z = 3.4$. The discrepancy between prediction (1.4) and experiment is generally regarded as one of the basic deficiencies of reptation theory.

Several attempts have recently been made to modify the theory to eliminate this deficiency.[6–8] Such factors as fluctuations in the contour length of a tube and the presence of regions of "stored length" (Fig. 1) have been examined, among others. The agreement between theory and experiment has been improved as a result. We should stress, however, that all of the modifications have affected the N dependence of η only in a certain intermediate region of values of N, so that the asymptotic relation $\eta \propto N^3$ as $N \to \infty$ has always remained in force.

In the present paper we show (this is one of the basic results of this paper) that the N dependence of t_r (and thus of η) as $N \to \infty$ should be far stronger than N^3. The factor primarily responsible for the strengthening of this dependence is the occurrence of volume interactions, i.e., interactions between links which are greatly separated along a chain or which belong to different chains.

The question of the role played by volume interactions (more precisely, the role of fluctuations in the molecular field which is associated with these interactions) requires an explanatory introduction. It is well known that these interactions influence the equilibrium properties of a system[9]: In the case of a dilute or semidilute polymer solution, volume interactions can cause substantial changes in the conformations of macromolecules, of the osmotic pressure, and of other properties. On the other hand, in a concentrated polymer solution or melt the fluctuations in the molecular field are very small (in other words, the volume interactions are substantially screened, in a sense, in these systems), so that (for example) conformations of polymer chains are nearly unperturbed (Gaussian).[3] Since the fluctuations are small, a

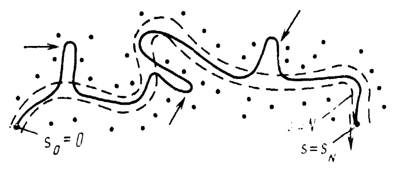

FIG. 1. Macromolecule (solid line) in a concentrated system. The dots are surrounding polmer chains, which create an effective tube (shown by the dashed lines) for the macromolecule shown by the solid line. Here s is the coordinate which is tied to the tube and directed along its axis. The arrows show regions of stored length.

mean-field theory can be applied to concentrated solutions and melts. This assertion, which is obviously correct for the equilibrium properties, is automatically extended to the dynamics: All the dynamic theories which have been proposed for these systems are essentially mean-field theories (see Ref. 10 and the bibliography there).

We will show below that the concept of a mean field is applicable in the dynamics only if the volume interaction is sufficiently weak: In general, fluctuations of the molecular field can have a very substantial effect on the motion of macromolecules in concentrated systems. The reason for this is roughly speaking, that although the fluctuation amplitude is always small the fluctuations act on a long polymer chain and may persist a very long time.

We note yet another important assertion, which immediately demonstrates the special role played by volume interactions: In the absence of such interactions, the maximum relaxation time t_r cannot grow more rapidly than N^3. More accurately consider a system of long, infinitely thin, linear macromolecules which are such that different sections of these molecules cannot intersect each other, while the excluded volume of any two sections is zero. It can be shown[11] that for such a system the classical prediction of reptation theory (for t_r) is an accurate upper-bound estimate:

$$t_r=O(N^3),\quad N\to\infty.$$

Consequently, if t_r increases more rapidly than N^3 (as it is observed to do experimentally), only volume interactions can be responsible. The suggestion that volume interactions have an important effect on the dynamics of concentrated systems was made by Deutsch[12] on the basis of numerical simulations.

In the following three sections of this paper, the effect of fluctuations in the molecular field on the properties of the system is analyzed by perturbation theory: the leading fluctuation correction is calculated. In Sec. 2 we describe the calculation method. In Sec. 3 we find the correction to the mean square distance between the ends of a macromolecule. In Sec. 4 we then calculate the correction to t_r and analyze the applicability of a mean-field theory in the dynamics. In Sec. 5 we study the behavior of η as a function of N in the fluctuation region. We end the paper with a comparison of these predictions with certain experimental data.

2. PERTURBATION THEORY

We consider a solution (everything written below also applies, without any changes, to melts) of long linear macromolecules each consisting of N links, where $N\gg N_e$. We denote by a the size of one unit, by c_0 the average concentration of links, and by

$$v=T^{-1}(\partial\mu/\partial c)_{c=c_0}\tag{2.1}$$

the parameter of the volume interactions (μ is the chemical potential of a unit). The molecular field acting on the links of the polymer chains is $h(\mathbf{r})=\mu(c(\mathbf{r}))-\mu(c_0)$, i.e.,

$$h(\mathbf{r})=Tv\tilde{c}(\mathbf{r}),\tag{2.2}$$

where $\tilde{c}(\mathbf{r})\equiv c(\mathbf{r})-c_0$ is the inhomogeneous part of the concentration (we are assuming $\tilde{c}\ll c_0$).

The reptation motion of a macromolecule may be thought of as a one-dimensional diffusion along the axis of a tube. We introduce the coordinate s along this axis, which is proportional to the instantaneous length of the tube (Fig. 1). The proportionality factor is conveniently chosen in such a way that the mean length of the macromolecule is equal to N:

$$\langle s_N-s_0\rangle=N.$$

Here s_n is the coordinate of the nth link, and $n=0,1,\ldots,N$ (note that Fig. 1 shows a state with $s_N-s_0>N$). The quation describing a one-dimensional diffusion of a macromolecule along a tube can be written in the form (Ref. 13, for example)

$$\frac{\partial s_n}{\partial t}=\frac{D_1}{T}\left[-\frac{\partial U_{el}}{\partial s_n}-\frac{\partial h(\mathbf{r}(s_n))}{\partial s_n}+\xi_n\right],\tag{2.3}$$

where $D_1=N_e\tau_0^{-1}$ is the effective coefficient of diffusion of one link along coordinate s (τ_0 is the time required for the diffusion of a link over a distance on the order of its own size), $U_{el}=U_{el}(s_0,s_1,\ldots,s_N)$ is the elastic energy of the molecule (which is associated with extensions and compressions of sections of the molecule with respect to the tube), $\mathbf{r}(s_n)\equiv\mathbf{r}_n$ is the radius vector of link n, and ξ_n is the random force acting on link n. Over a sufficiently long time $t\gg\tau_r$ ($\tau_R\sim\tau_0N^2$ is the Rouse relaxation time), the motion of the macromolecule is basically a displacement of the molecule as a whole along the tube axis.[1] Superimposed on this basic motion are fluctuations in the length of the tube (i.e., in the quantity s_N-s_0) and larger-scale fluctuations associated with extensions and compressions of sections of the chain. Using Eq. (2.3), we can show that these fluctuations have no substantial effect on the characteristics studied in the present paper: incorporating these fluctuations leads to only slight renormalizations of some of the numerical factors.[2] For simplicity we ignore these fluctuations, i.e., we treat the macromolecule as a flexible filament which can be neither stretched nor compressed. We can thus write

$$s_n-s_m=n-m,\quad \partial s_n/\partial t=\partial s_m/\partial t.\tag{2.4}$$

Substituting (2.4) into (2.3), and using

$$\int_0^N\frac{\partial U_{el}}{\partial s_n}dn=0,\quad \int_0^N\frac{\partial h(\mathbf{r}(s_n))}{\partial s_n}dn=h(\mathbf{r}_N)-h(\mathbf{r}_0),$$

we find

$$\langle\Delta s\rangle=-(D_\parallel/T)\Delta t[h(\mathbf{r}_N)-h(\mathbf{r}_0)],\quad \langle(\Delta s)^2\rangle=2D_\parallel\Delta t,\tag{2.5}$$

where Δs is the displacement of a macromolecule along the tube axis over the short time Δt, and

$$D_\parallel=D_1/N=N_e/(N\tau_0)\tag{2.6}$$

is the diffusion coefficient for the diffusion of a chain along the tube. We denote by $V^{-1}f_t(\mathbf{r}/n)d^3r$ the probability that unit n of a particular macromolecule of interest is in volume element d^3r at time t. The diffusion equation which follows for the function f_t from (2.5) is[3]

$$D_{\|}^{-1}\frac{\partial}{\partial t}f_t\binom{\mathbf{r}}{n}=\frac{\partial^2}{\partial n^2}f_t\binom{\mathbf{r}}{n}+\frac{\partial}{\partial n}\int d^3r'\,h(\mathbf{r}',t)\times\left\{f_t\begin{pmatrix}\mathbf{r} & \mathbf{r}'\\ n & 0\end{pmatrix}-f_t\begin{pmatrix}\mathbf{r} & \mathbf{r}'\\ n & N\end{pmatrix}\right\}, \qquad (2.7)$$

where $V^{-1}f_t(\mathbf{r}/n\,\mathbf{r}'/n')$ is the probability distribution for links n and n' simultaneously. The boundary conditions on Eq. (2.7) are

$$\frac{\partial f_t}{\partial n}=\begin{cases}-a^2\dfrac{\partial^2}{\partial \mathbf{r}^2}f_t, & n=0,\\ a^2\dfrac{\partial^2}{\partial \mathbf{r}^2}f_t, & n=N.\end{cases} \qquad (2.8)$$

Corresponding equations can be written for "many-particle" distribution functions $f^{(2)}\equiv f_t(\mathbf{r}/n\,\mathbf{r}'/n')$, $f^{(3)}$ etc. Each of these equations will have on its right-hand side a term which is proportional to h and which depends on a higher-order distribution function. We thus find a chain of coupled equations, which can be solved by a perturbation theory in h. It turns out that for $h=0$ each of the equations is closed and can be solved in its general form. To then find, say, $f^{(1)}$ in first order in h, it is sufficient to substitute the zeroth approximation for $f^{(2)}$ into (2.7) and to solve this equation. If it is necessary to find $f^{(1)}$ in a higher order, the number of equations considered must be increased.

We assumed above that the molecular field h is known. Actually, of course, this is a random field. In order to implement the general scheme described above, one must know the correlation functions of this field, $\langle h(\mathbf{r},t)\rangle$, $\langle h(\mathbf{r}',t')\rangle$, etc., and also the relationship between the field $h(\mathbf{r},t)$ and the conformations of the macromolecule at earlier times $t'<t$.

The molecular field h is conveniently broken up into three components:

$$h=h_{rand}+h_0+h_{ind}. \qquad (2.9)$$

Here $h_{\text{rand}}(\mathbf{r},t)$ is the molecular field which would exist in the system if the macromolecule of interest were not there at all (it is assumed here that the system is in an equilibrium state). By definition, the field h_{rand} does not depend on the conformation of the selected macromolecule. Obviously, we have

$$\langle h_{rand}\rangle=0,\quad \langle h_{rand}(\mathbf{r},t)\,h_{rand}(\mathbf{r}',t')\rangle=v^2T^2G_{t-t'}(\mathbf{r}-\mathbf{r}'), \qquad (2.10)$$

where

$$G_t(\mathbf{r})=\langle\tilde{c}(\mathbf{r},t)\tilde{c}(0,0)\rangle \qquad (2.11)$$

is the correlation function of the concentration fluctuations in the solution.

The second term in (2.9), h_0, is the intrinsic field produced directly by the links of the chain of interest:

$$h_0(\mathbf{r},t)=vT\int ds\,\delta(\mathbf{r}-\mathbf{r}_s(t)), \qquad (2.12)$$

where $\mathbf{r}_s(t)$ is the position of link s of the selected chain at time t. The third term, h_{ind}, is the induced field, which is related to the concentration change $\tilde{c}_{\text{ind}}$ caused by the intrinsic field:

$$\langle h_{ind}(\mathbf{r},t)\rangle=vT\langle\tilde{c}_{ind}(\mathbf{r},t)\rangle, \qquad (2.13)$$

$$\langle\tilde{c}_{ind}(\mathbf{r},t)\rangle=-\int_{-\infty}^{t}dt'\,d^3r'\,\varkappa_{t-t'}(\mathbf{r}-\mathbf{r}')\,h_0(\mathbf{r}',t')/T, \qquad (2.14)$$

where $\varkappa_t(\mathbf{r})$ is the generalized susceptibility of the system. The Laplace-Fourier transforms of the functions $\varkappa_t(\mathbf{r})$ and $G_t(\mathbf{r})$ are related by[10]

$$G(p,\mathbf{q})=[\varkappa(0,\mathbf{q})-\varkappa(p,\mathbf{q})]/p, \qquad (2.15)$$

where p is the Laplace parameter, and $\mathbf{q}$ is the wave vector.

To calculate the leading fluctuation corrections, it is sufficient to know the function $\varkappa$ (and the related function G) in the zeroth approximation, i.e., in the mean-field approximation. With $p=0$, the susceptibility is determined by the equilibrium properties of the system and is a well-known function (Ref. 3, for example):

$$\varkappa(0,q)=\frac{1}{v}\left\{1+\left[\frac{Nc_0v}{u^2}\left(u-\frac{1}{1+\operatorname{cth}u}\right)\right]^{-1}\right\}^{-1}, \qquad (2.16)$$

where

$$u=q^2a^2N/2. \qquad (2.17)$$

We would like to briefly discuss (see Ref. 13 for more details) the method for calculating the dynamic susceptibility $\varkappa(p,\mathbf{q})$ under the conditions $0<p\lesssim\tau_0^{-1}N^{-1}$, $N_e^{1/2}a\ll q^{-1}\lesssim N^{1/2}a$ (it is this region of p and q which is important for the discussion below). The case in which only purely reptation motions of a macromolecule are possible (i.e., the case in which the network of quasientanglements is assumed to be absolutely rigid and undeformable) was studied in Ref. 10. The result in that case was

$$\varkappa_{repl}(p,q\,|\,v)=\frac{1}{v}\left\{1+\left[\frac{Nc_0v}{u^2-\sigma^2}\left(\frac{u^2}{\sigma^2+u\sigma\operatorname{cth}\sigma}-\frac{1}{1+\operatorname{cth}u}\right)\right]^{-1}\right\}^{-1}, \qquad (2.18)$$

where

$$\sigma\equiv(pt^*)^{1/2},\quad t^*\equiv N^2/4D_{\|}={}^1/_4\tau_0N^3/N_e. \qquad (2.19)$$

We now consider the possibility of a deformation of the network of quasientanglements. Clearly, the external field $h_{\text{ext}}(\mathbf{q})$ should cause a spatially periodic deformation of this network (for definiteness we will assume that the wave vector $\mathbf{q}$ is directed along the z axis). It is easy to show that under the condition $q\gtrsim N^{-1/2}a^{-1}$ the deformation process (after the abrupt application of an external field) proceeds very rapidly, over a time scale[4] $\tau_c\lesssim\tau_0N$. During this process, the network of quasientanglements can thus be assumed to be the true, "infinitely long-lived" network. We denote by $\rho(z)$ the resultant displacement of the points of the network in the z direction over the time of the deformation. The corresponding change in concentration is

$$\delta c_{\rm I}=-\varepsilon c_0, \tag{2.20}$$

where $\varepsilon\equiv\partial\rho/\partial z$. The volume free-energy density of the network is

$$w=w_{el}+w_{int}+w_h, \tag{2.21}$$

where $w_{el}=M_0\varepsilon^2/2$ is the elastic energy, M_0 is the "longitudinal" elastic modulus of the network, $w_{\rm int}=Tv(\delta c)^2/2$ is the volume-interaction energy, and $w_h=h_{\rm ext}\delta c$ is the energy due to the external field. Here $\delta c_{\rm I'}$ is the total response to external field $h_{\rm ext}$ and is the sum of $\delta c_{\rm I'}$ due to deformation of the network, and $\delta c_{\rm II}$, due to purely reptation motions:

$$\delta c=\delta c_{\rm I}+\delta c_{\rm II}. \tag{2.22}$$

By minimizing free energy (2.21) with respect to ε and using (2.20) and (2.22) (this operation is valid because the time scales p^{-1} in which we are interested here are much longer than the network deformation time τ_c), we find

$$\delta c=-\frac{1}{v}\overset{+}{\left(}1-\frac{v^*}{v}\right)\frac{h_{ext}}{T}+\frac{v^*}{v}\delta c_{\rm II}, \tag{2.23}$$

where

$$v^*=vM_0/(M_0+Tvc_0^2)=v/(1+c_0vN_e/\nu), \tag{2.24}$$

and $\nu=M_0/G_0$ is the ratio of the longitudinal elastic modulus of the network to the shear modulus.

We now note that $\delta c_{\rm II}$ is the reptation response to the total field

$$h_{tot}=h_{ext}+Tv\delta c, \tag{2.25}$$

acting on the polymer units. Substituting (2.23) into (2.25), we find

$$h_{tot}=\frac{v^*}{v}(h_{ext}+Tv\delta c_{\rm II})=\frac{v^*}{v}h_{ext}+Tv^*\delta c_{\rm II}. \tag{2.26}$$

The quantity $h_{\rm tot}$ is thus the same as in the case of an absolutely rigid network (for whichy we would have $\delta c_{\rm I}\equiv 0$), but with a renormalized volume-interaction parameter v^* (instead of v). This renormalized parameter is also manifested in the replacement of the external field $h_{\rm ext}$ by an effective field $(v^*/v)h_{\rm ext}$. We thus have

$$\delta c_{\rm II}=-\varkappa_{rept}(p,q\,|\,v^*)\frac{v^*}{v}\frac{h_{ext}}{T}. \tag{2.27}$$

Substituting (2.27) into (2.23), we finally find $\delta c\equiv\varkappa h_{\rm ext}/T$, where

$$\varkappa(p,q)=\frac{1}{v}\left(1-\frac{v^*}{v}\right)+\left(\frac{v^*}{v}\right)^2\varkappa_{rept}(p,q\,|\,v^*),$$
$$p\lessapprox\frac{1}{\tau_0N},\quad\frac{1}{N^{1/2}a}\lessapprox q\ll\frac{1}{N_e^{1/2}a}, \tag{2.28}$$

and $\varkappa_{\rm rept}$ is given by (2.18). Note that (2.28) agrees with (2.16).

In the following section of the paper we calculate the fluctuation correction for the quantity R^2, which is the mean square distance between the ends of a selected macromolecule in the equilibrium state. This problem is of course easiest to solve by purely "equilibrium" methods. The solution of this problem given in Sec. 3 should be thought of as primarily an illustration of the method of dynamic calculations by perturbation theory.

3. CALCULATION OF R^2 BY PERTURBATION THEORY

We turn now to some specific calculations of R^2, which is the mean square distance between the ends of the polymer chain, by perturbation theory. By definition we have

$$R^2=\int d^dr\,r^2P_N(\mathbf{r}), \tag{3.1}$$

where d is the dimensionality of the space, and $P_N(\mathbf{r})$ is the distribution function of the vector $\mathbf{r}$, which connects the ends of the chain. Treating the molecular field h as a perturbation, and making use of the results of the preceding section of the paper, we easily find the following expression for $P_N(\mathbf{r})$ (only the leading corrections in h are taken into account):

$$\begin{aligned}P_N(\mathbf{r})={}&g_N(\mathbf{r})+vD_\parallel\int\limits_{-\infty}^{t}dt'\int\limits_{-\infty}^{t'}dt''\int d^d r_1d^dr_2d^dr'd^dr''\int\limits_0^N ds\int ds_1\,ds_2\\&\times K_{t-t'}\left(\begin{array}{cc|cc}0&\mathbf{r}&\mathbf{r}_1&\mathbf{r}_2\\0&N&s_1&s_2\end{array}\right)\Lambda_{t'-t''}(\mathbf{r}'-\mathbf{r}'')\left(\frac{\partial}{\partial s_1}+\frac{\partial}{\partial s_2}\right)\\&\times\left\{F_{t'-t''}\left(\begin{array}{ccc|c}\mathbf{r}'&\mathbf{r}_1&\mathbf{r}_2&\mathbf{r}''\\0&s_1&s_2&s\end{array}\right)-F_{t'-t''}\left(\begin{array}{ccc|c}\mathbf{r}'&\mathbf{r}_1&\mathbf{r}_2&\mathbf{r}''\\N&s_1&s_2&s\end{array}\right)\right\}\\&-v^2D_\parallel^2\left(\frac{\partial}{\partial s}\Big|_{s=0}-\frac{\partial}{\partial s}\Big|_{s=N}\right)\int\limits_{-\infty}^{t}dt'\int\limits_{-\infty}^{t'}dt''\int d^dr_1\,d^dr_2\\&\times d^dr'\,d^dr''\int ds_1\,ds_2K_{t-t'}\left(\begin{array}{cc|cc}0&\mathbf{r}&\mathbf{r}_1&\mathbf{r}_2\\0&N&s_1&s_2\end{array}\right)\\&\times G_{t'-t''}(\mathbf{r}'-\mathbf{r}'')\left(\frac{\partial}{\partial s_1}+\frac{\partial}{\partial s_2}\right)\\&\times\left\{F_{t'-t''}\left(\begin{array}{ccc|c}\mathbf{r}'&\mathbf{r}_1&\mathbf{r}_2&\mathbf{r}''\\0&s_1&s_2&s\end{array}\right)-F_{t'-t''}\left(\begin{array}{ccc|c}\mathbf{r}'&\mathbf{r}_1&\mathbf{r}_2&\mathbf{r}''\\N&s_1&s_2&s\end{array}\right)\right\}.\end{aligned} \tag{3.2}$$

The first term here,

$$g_N(\mathbf{r})=(4\pi Na^2)^{-d/2}\exp(-r^2/4Na^2), \tag{3.3}$$

is the unperturbed distribution function. The second is the correction for the intrinsic and induced fields ($h_0+h_{\rm ind}$), and the third is the correction for the "random" field $h_{\rm rand}$ [see (2.9)]. In (3.2) we are using

$$\Lambda_t(\mathbf{r})=\delta(t)\delta(\mathbf{r})-v\varkappa_t(\mathbf{r}), \tag{3.4}$$

where the first term corresponds to h_0, and the second to $h_{\rm ind}$. The function

$$K_t\left(\begin{array}{cc|cc}\mathbf{r}_1&\mathbf{r}_2&\mathbf{r}_1'&\mathbf{r}_2'\\s_1&s_2&s_1'&s_2'\end{array}\right)$$

is the Green's function of the unperturbed equation for $f^{(2)}$:

$$D_\parallel^{-1}\frac{\partial}{\partial t}f_t\begin{pmatrix}\mathbf{r}_1&\mathbf{r}_2\\s_1&s_2\end{pmatrix}=\left(\frac{\partial}{\partial s_1}+\frac{\partial}{\partial s_2}\right)^2f_t\begin{pmatrix}\mathbf{r}_1&\mathbf{r}_2\\s_1&s_2\end{pmatrix} \tag{3.5}$$

with the boundary conditions

$$\frac{\partial}{\partial s_1} f_t = -a^2 \frac{\partial^2}{\partial r_1^2} f_t, \quad s_1 = 0; \qquad \frac{\partial}{\partial s_2} f_t = a^2 \frac{\partial^2}{\partial r_2^2} f_t, \quad s_2 = N. \tag{3.6}$$

A solution of this equation can be written in the form

$$f_t\begin{pmatrix} \mathbf{r}_1 & \mathbf{r}_2 \\ s_1 & s_2 \end{pmatrix} = \int ds_1'\, ds_2' \int d^d r_1'\, d^d r_2' \times K_t\left(\begin{array}{cc|cc} \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}_1' & \mathbf{r}_2' \\ s_1 & s_2 & s_1' & s_2' \end{array}\right) f_0\begin{pmatrix} \mathbf{r}_1' & \mathbf{r}_2' \\ s_1' & s_2' \end{pmatrix} \tag{3.7}$$

[the integration over s_1' and s_2' is carried out in the region $N \geqslant s_2' \geqslant s_1' \geqslant 0$; a corresponding integration region, $N \geqslant s_2 \geqslant s_1 \geqslant 0$, is understood in (3.2)]. The last unknown function in (3.2),

$$F_t\left(\begin{array}{ccc|c} \mathbf{r}' & \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}'' \\ s' & s_1 & s_2 & s \end{array}\right),$$

is the probability density for link s' to be at point $\mathbf{r}'$ at time t, for s_1 to be at point $\mathbf{r}_1$, and for s_2 to be at point $\mathbf{r}_2$—under the condition that link s is initially pinned at point $\mathbf{r}''$ and that during the interval from 0 to t the macromolecule moves in a reptation fashion in the absence of molecular fields (we are assuming that the distribution with respect to conformations of the macromolecule is Gaussian at $t = 0$).

Using Fourier-Laplace transforms and making use of the obvious symmetry of all of the functions with respect to a renumbering of the links in the opposite order (i.e., with respect to the substitution $s \to N - s$), we can put (3.2) in the form

$$\begin{aligned} P_N(\mathbf{q}) = {} & g(\mathbf{q}, N) - 2vD_\parallel \int_{-i\infty}^{i\infty} \frac{dp}{2\pi i} \int \frac{d^d q'}{(2\pi)^d} \\ & \times \int_0^N ds \int ds_1\, ds_2 K\left(0 \left| \begin{array}{cc} \mathbf{q} & -\mathbf{q} \\ s_1 & s_2 \end{array}\right.\right) \Lambda(-p, \mathbf{q}') \\ & \times \left(\frac{\partial}{\partial s_1} + \frac{\partial}{\partial s_2}\right) F\left(\begin{array}{ccc|c} \mathbf{q}' & \mathbf{q} & -\mathbf{q} & s; p \\ 0 & s_1 & s_2 & \end{array}\right) - 2v^2 D_\parallel^2 \left(\frac{\partial}{\partial s}\bigg|_{s=0} \right. \\ & \left. - \frac{\partial}{\partial s}\bigg|_{s=N}\right) \int_{-i\infty}^{i\infty} \frac{dp}{2\pi i} \int \frac{d^d q'}{(2\pi)^d} \int ds_1\, ds_2 K\left(0 \left| \begin{array}{cc} \mathbf{q} & -\mathbf{q} \\ s_1 & s_2 \end{array}\right.\right) \\ & \times G(-p, \mathbf{q}') \left(\frac{\partial}{\partial s_1} + \frac{\partial}{\partial s_2}\right) F\left(\begin{array}{ccc|c} \mathbf{q}' & \mathbf{q} & -\mathbf{q} & s; p \\ 0 & s_1 & s_2 & \end{array}\right), \end{aligned} \tag{3.8}$$

where $P_N(\mathbf{q})$ is the Fourier transform of the function $P_N(\mathbf{r})$,

$$g(\mathbf{q}, N) = \exp(-Nq^2a^2) \tag{3.9}$$

is the Fourier transform of the function $g_N(\mathbf{r})$,

$$\Lambda(p, \mathbf{q}) = 1 - v\varkappa(p, \mathbf{q}); \tag{3.10}$$

$$K\left(p \left| \begin{array}{cc} \mathbf{q}_1 & \mathbf{q}_2 \\ s_1 & s_2 \end{array}\right.\right) = \int_0^\infty dt\, e^{-pt} \int d^d r_1\, d^d r_2 \exp(-i\mathbf{q}_1\mathbf{r}_1 - i\mathbf{q}_2\mathbf{r}_2) \times K_t\left(\begin{array}{cc|cc} 0 & 0 & \mathbf{r}_1 & \mathbf{r}_2 \\ 0 & N & s_1 & s_2 \end{array}\right), \tag{3.11}$$

and

$$F\left(\begin{array}{ccc|c} \mathbf{q}_0 & \mathbf{q}_1 & \mathbf{q}_2 & s; p \\ s_0 & s_1 & s_2 & \end{array}\right) = \int_0^\infty dt e^{-pt} \int d^d r_0\, d^d r_1\, d^d r_2 \exp(-i\mathbf{q}_0\mathbf{r}_0 - i\mathbf{q}_1\mathbf{r}_1 - i\mathbf{q}_2\mathbf{r}_2) \cdot \times F_t\left(\begin{array}{ccc|c} \mathbf{r}_0 & \mathbf{r}_1 & \mathbf{r}_2 & 0 \\ s_0 & s_1 & s_2 & s \end{array}\right). \tag{3.12}$$

The functions F and K are calculated in the Appendix. Substituting (A9) and (A16) into (3.8), and using relation (A8), we find

$$\begin{aligned} P_N(\mathbf{q}) = \exp(-Nq^2a^2) \bigg\{ 1 + v \int_0^N ds \int d^d q' (2\pi)^{-d} \\ \times (N - s) \Lambda(0, \mathbf{q}) \exp(-sq'^2a^2) [1 - \exp(-2sqq'a^2)] \bigg\}. \end{aligned} \tag{3.13}$$

We thus have

$$\begin{aligned} R^2 = -\left[\frac{\partial^2 P_N(\mathbf{q})}{\partial \mathbf{q}^2}\right]_{q=0} = 2dNa^2 \bigg[1 + \frac{2v}{Nd} \int_0^s ds \int \frac{d^d q'}{(2\pi)^d} \\ \times (N - s) s^2 q'^2 a^2 \exp(-sq'^2a^2) \Lambda(0, \mathbf{q}') \bigg]. \end{aligned} \tag{3.14}$$

The final expressions, (3.13) and (3.14), contain only the static susceptibility $\varkappa(0,\mathbf{q})$ [see (3.10)]. This is the result which we would have expected since the quantities of interest here, R^2 and $P_N(\mathbf{q})$, characterize the system in the equilibrium state.

Substituting (2.16) into (3.10), we find

$$\Lambda(0, \mathbf{q}) = (1 + 2c_0 v/q^2a^2)^{-1}, \quad q^2a^2 \gg 1/N. \tag{3.15}$$

Finally substituting (3.15) into (3.14) and evaluating the integrals, we find

$$2 < d < 4, \tag{3.16}$$

where K_d is the ratio of the surface area of a unit sphere to $(2\pi)^d$:

$$K_d = 2^{1-d} \pi^{-d/2} / \Gamma(d/2).$$

In particular, for $d = 3$ we have the expression

$$R^2 = 6Na^2 [1 + (2^{1/2}/6\pi)(v/c_0)^{1/2} a^{-3}], \tag{3.17}$$

which agrees with the well-known result found by Edwards.[14]

Let us discuss expression (3.17) briefly. Its derivation used the assumption that (in the absence of volume interactions) the conformations of the polymer chain in the equilibrium state obey Gaussian statistics. For real polymers this assumption is valid only at length scales much greater than a. It is easy to see that the basic component of the fluctuation correction (the second term in square brackets) corresponds to wave vectors $q \sim (c_0 v/a^2)^{1/2}$, i.e., to length scales $\lambda = 1/q$ on the order of the static correlation length $\xi = a(2c_0 v)^{-1/2}$. Consequently, expression (3.17) can be valid only under the condition $\xi \gg a$ or

$$c_0 \ll 1/v. \qquad (3.18)$$

Another restriction stems from the circumstance that only the leading fluctuation correction, i.e., only the first term in the expansion in the parameter $z = (v/c_0)^{1/2}\alpha^{-3}$ was calculated. In general, expression (3.17) should be rewritten as[5)]

$$R^2 = 6Na^2\chi(v^{1/2}c_0^{-1/2}a^{-3}), \qquad (3.19)$$

where

$$\chi(z) = 1 + (2^{1/2}/6\pi)z + O(z^2), \quad z \ll 1.$$

In the analysis below we will be interested in length scales much greater than the correlation length ξ. At such scales the effect of fluctuations on equilibrium conformations of the macromolecule obviously reduces to simply a renormalization of the characteristic size of a unit, a: $a \to a^* = a[\chi(z)]^{1/2}$. It is assumed below that this renormalization has already been carried out, and the asterisk will be omitted from a.

We conclude this section of the paper with one more comment, which concerns the role played by the individual components h_0, $h_{\mathrm{rand}'}$, and h_{ind} of the molecular field [see (2.9)] in forming the fluctuation correction. If we take only the intrinsic field h_0 into account, i.e., if we discard the third term in (3.2) and the second term in (3.4), we find the following expression in place of (3.17):

$$R^2 = 6Na^2[1 + 6^{-1}\pi^{-3/2}N^{1/2}v/a^3]. \qquad (3.20)$$

This is the same as the well-known result for the swelling of an isolated polymer chain with volume interactions (in first-order perturbation theory). If, on the other hand, we take only the random molecular field h_{rand} into account, i.e., if we discard the second term in (3.2), we find that again the result is changed substantially:

$$R^2 = 6Na^2[1 - 0.0373(N/c_0v)^{1/4}v/a^3]. \qquad (3.21)$$

The random field h_{rand} thus gives rise to an effective attraction between the units of the macromolecule. The physical meaning of result (3.21) can be explained in the following way. We know that the dimensions of an ideal chain in a static random field $h_{\mathrm{rand}}(\mathbf{r})$ are smaller than the Gaussian dimensions.[16] At an accuracy to within the first correction, the mean square distance between the ends of the chain is

$$R^2 = 6Na^2[1 - \mathrm{const}\cdot\Delta(\tilde{q})N^{1/2}a^{-3}], \qquad (3.22)$$

where

$$\Delta(\mathbf{q}) \equiv T^{-2}\int d^3r e^{-i\mathbf{qr}}\langle h_{rand}(0)h_{rand}(\mathbf{r})\rangle \qquad (3.23)$$

[we are assuming $\langle h_{\mathrm{rand}}(\mathbf{r})\rangle = 0$] and $\tilde{q} \sim N^{-1/2}a^{-1}$ is a characteristic wave vector.

We now consider an ideal macromolecule in a variable random field $h_{\mathrm{rand}}(\mathbf{r},t)$. We assume that the macromolecule initially (at $t = 0$) has a Gaussian conformation. After this time, the conformation of the molecule changes by virtue of the reptation motion. We consider the time t, at which g units have "crept out" of the original tube ($N_e < g < N$). Here we evidently have

$$t \sim g^2/D_{\|}. \qquad (3.24)$$

Clearly, if the characteristic time $\tau_*(\tilde{q})$, of the relaxation of fluctuations of the random field with a wave vector $\tilde{q}(g) \sim g^{-1/2}a^{-1}$, exceeds t, then the deviation of the spatial size of the region which has crept out from the ideal size can be estimated from (3.22); i.e.,

$$R^2(g) = 6ga^2[1 - \mathrm{const}\cdot\Delta(\tilde{q})g^{1/2}a^{-3}]. \qquad (3.25)$$

Substituting (2.10) into (3.23), we find

$$\Delta(\tilde{q}) \approx v^2G_{t'}(\tilde{q}), \quad t' \sim t. \qquad (3.26)$$

Using (2.15) and (2.28), and recognizing that $\tau_* \gg t \gg \tau_c$, and $\tilde{q} \ll N_e^{-1/2}a^{-1}$, we can put expression (3.26) in the form

$$\Delta(\tilde{q}) \approx v^2(v^*/v)^2\varkappa_{rept}(0, \tilde{q}|v^*) \approx v^*. \qquad (3.27)$$

From (2.15) and (2.28) we again find the characteristic time of the rotation relaxation.[13]

$$\tau_*(q) \sim \begin{cases} t^*/(c_0v^*N), & q \leqslant a^{-1}(N/c_0v^*)^{-1/4} \equiv q^*, \\ (q/q^*)^4t^*/c_0v^*N, & q \geqslant q^*. \end{cases} \qquad (3.28)$$

The condition $\tau_*(\tilde{q}) \sim t$ gives the maximum size of a region which has crept out (the size of a blob), for which expression (3.25) again is valid. Using (3.24) and (3.28) we find

$$g_{max} \sim (N/c_0v^*)^{1/2}, \quad t_{max} \sim g_{max}^2/D_{\|} \sim t^*/c_0v^*N. \qquad (3.29)$$

At times $t \gg t_{\max}$ the fluctuations of the field h_{rand} which dominate the changes in the dimensions of the sections of the macromolecule have already undergone relaxation. Consequently, the conformations of various $g_{\max}$ blobs must be essentially independent; (i.e., over scales $g \gg g_{\max}$ the macromolecule must constitute a Gaussian chain of $g_{\max}$ blobs. The overall size of the macromolecule should thus be

$$R^2 = (N/g_{max})R^2(g_{max}). \qquad (3.30)$$

Substituting (3.25), (3.27), and (3.29) into (3.30), we finally find

$$R^2 = 6Na^2[1 - \mathrm{const}(v^*/a^3)(N/c_0v^*)^{1/4}] \qquad (3.31)$$

in complete agreement with expression (3.21).

Comparing (3.17), (3.20), and (3.21), we conclude that the effect of the field h_{rand} is, on the one hand, far weaker (in the sense of the dependence on N) than the effect of the intrinsic repusion between units (the field h_0) but, on the other, far stronger than the resultant effect of all three fields $h_0 + h_{\mathrm{ind}} + h_{\mathrm{rand}}$ taken together.

4. FLUCTUATION CORRECTION TO THE SELF-DIFFUSION COEFFICIENT

We turn now to the central part of this study: the calculation of the self-diffusion coefficient of a macromolecule,

D_s. We assume that each unit of some selected polymer chain is acted upon by a weak external field with a potential

$$h_{ext}(\mathbf{r}) = -\beta T, \tag{4.1}$$

where $\beta \to 0$ is a parameter. An external force causes the center of mass of the selected macromolecule to move along the z axis. By virtue of the Einstein relation, the average velocity u_z of this displacement must be proportional to the self-diffusion coefficient D_s:

$$u_z = \beta N D_s + O(\beta^2). \tag{4.2}$$

On the other hand, because of the reptation nature of the motion of the macromolecule [see (2.5)], this velocity can be written

$$u_z = (D_{\|}/NT)\langle (z_N - z_0)[h_{tot}(\mathbf{r}_0) - h_{tot}(\mathbf{r}_N)]\rangle, \tag{4.3}$$

where $\mathbf{r}_0$ and $\mathbf{r}_N$ are the positions of the beginning and end of the polymer chain at the same instant, and

$$h_{tot}(\mathbf{r}) = h(\mathbf{r}) + h_{ext}(\mathbf{r}) \tag{4.4}$$

is the resultant field acting on the units of the macromolecule. Substituting (4.4) and (4.1) into (4.3), and comparing the result with (4.2), we find

$$D_s = D_{s0}(1+\Delta), \tag{4.5}$$

where

$$D_{s0} = 2a^2 D_{\|}/N \tag{4.6}$$

is the classical result of reptation theory (Ref. 3, for example), and

$$\Delta = \lim\{(2a^2\beta T)^{-1}\langle (z_N - z_0)[h(\mathbf{r}_0) - h(\mathbf{r}_N)]\rangle\} \tag{4.7}$$

is a correction for the fluctuations in molecular field h.

Making use of the obvious symmetry of the problem, we can simplify expression (4.7):

$$\Delta = \lim_{\beta\to 0}\{(a^2\beta T)^{-1}\langle (z_N - z_0) h(\mathbf{r}_0)\rangle\}. \tag{4.8}$$

Below we calculate Δ in the lowest-order perturbation theory.

Using the method described in Sec. 2, we can take the average on the right side of expression (4.8). In the leading order in h, the result is [cf. (3.2)]

$$\Delta = \frac{vD_{\|}}{Na^2}\int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int d^d r\, d^d r_1\, d^d r_2\, d^d r'\, d^d r'' \int_0^N ds \int ds_1\, ds_2 z' z$$
$$\times K_{t-t'}\left(\begin{array}{cc|cc} 0 & \mathbf{r} & \mathbf{r}_1 & \mathbf{r}_2 \\ 0 & N & s_1 & s_2 \end{array}\right) \Lambda_{t-t''}(\mathbf{r}'')\left(\frac{\partial}{\partial s_1} + \frac{\partial}{\partial s_2}\right)$$
$$\times\left\{ F_{t'-t''}\left(\begin{array}{ccc|c} \mathbf{r}' & \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}'' \\ N & s_1 & s_2 & s \end{array}\right) - F_{t'-t''}\left(\begin{array}{ccc|c} \mathbf{r}' & \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}'' \\ 0 & s_1 & s_2 & s \end{array}\right)\right\}$$
$$-\frac{v^2 D_{\|}^2}{Na^2}\left(\frac{\partial}{\partial s}\bigg|_{s=0} - \frac{\partial}{\partial s}\bigg|_{s=N}\right)$$
$$\times\int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int d^d r\, d^d r_1\, d^d r_2\, d^d r'\, d^d r'' \int ds_1\, ds_2 z' z\cdot$$
$$\times K_{t-t'}\left(\begin{array}{cc|cc} 0 & \mathbf{r} & \mathbf{r}_1 & \mathbf{r}_2 \\ 0 & N & s_1 & s_2 \end{array}\right) G_{t-t''}(\mathbf{r}'')\left(\frac{\partial}{\partial s_1} + \frac{\partial}{\partial s_2}\right)$$
$$\times\left\{ F_{t'-t''}\left(\begin{array}{ccc|c} \mathbf{r}' & \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}'' \\ N & s_1 & s_2 & s \end{array}\right) - F_{t'-t''}\left(\begin{array}{ccc|c} \mathbf{r}' & \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}'' \\ 0 & s_1 & s_2 & s \end{array}\right)\right\}. \tag{4.9}$$

The first term here corresponds to the fields h_0 and $h_{\text{ind}'}$, and the second to $h_{\text{rand}'}$.

After some manipulations [in which we use (A8)–A10)], expression (4.9) becomes

$$\Delta = \frac{v}{N}\int_{-i\infty+0}^{i\infty+0} \frac{dp}{2\pi i p}\int \frac{d^d q}{(2\pi)^d}[\Lambda(-p,\mathbf{q}) - \Lambda(0,\mathbf{q})]W(p,\mathbf{q}), \tag{4.10}$$

where

$$W(p,\mathbf{q}) = \frac{D_{\|}}{a^2}\int d^d R'\, d^d R_1\, d^d R_2 \exp(-i\mathbf{q}\mathbf{R}_1)\int_0^N ds \int ds_1\, ds_2$$
$$\times\left\{\left(\frac{\partial}{\partial s_1} + \frac{\partial}{\partial s_2}\right)\left[\Phi\left(\begin{array}{ccc|c} \mathbf{R}' & \mathbf{R}_1 & \mathbf{R}_2 & 0 \\ N & s_1 & s_2 & s \end{array}\right)\right.\right.$$
$$\left.\left. -\Phi\left(\begin{array}{ccc|c} \mathbf{R}' & \mathbf{R}_1 & \mathbf{R}_2 & 0 \\ 0 & s_1 & s_2 & s \end{array}\right)\right]\right\}$$
$$\times R_z'\left(R_{2z} - R_{1z} - i\frac{\partial}{\partial q_z}\right) K\left(p\left|\begin{array}{cc} \mathbf{q} & 0 \\ s_1 & s_2 \end{array}\right.\right). \tag{4.11}$$

Analysis of expressions (4.10) and (4.11) shows that the quantity Δ is dominated by the region

$$pt^* \gg 1, \quad qR \gg 1, \tag{4.12}$$

which corresponds to times much shorter than the reptation time t^* and to length scales much smaller than the size R, of a macromolecule. Under the condition $pt^* \gg 1$ the second term in (A15) is exponentially small. Substituting (A15) without this second term into (4.11), and evaluating the integrals over the spatial variables, we find

$$W(p,\mathbf{q}) = D_{\|}\int dl\, ds_1\, ds'\, ds \exp(-s' q^2 a^2)\rho(p; l, s_1, s')$$
$$\times\frac{\partial}{\partial s_1}\varphi(l, s_1, s', s), \tag{4.13}$$

where

$$\varphi(l, s_1, s', s) = 2\exp(-q^2 a^2 |s - s_1|)$$
$$\times[N - l - 2q_z^2 a^2 (s - s_1) B], \tag{4.14}$$

and

$$B = \begin{cases} s', & s < s_1, \\ s - s_1 + s', & s_1 < s < N - l + s_1, \\ N - l + s', & s > N - l + s_1, \end{cases}$$

Substituting (A11) into (4.13), using $\sigma = (pt^*)^{1/2} \gg 1$, and also using $u = q^2 a^2 N/2 \gg 1$, we find

$$W(p,\mathbf{q})={}^1/_2N^3(\sigma+u)^{-2}. \tag{4.15}$$

From (2.28) to (3.4) we find, under the conditions $\sigma\gg 1$ and $u\gg 1$,

$$\Lambda(-p,\mathbf{q})=\left(\frac{v^*}{v}\right)\left[1+Nc_0v^*\frac{i\sigma-2u}{2i\sigma(u-i\sigma)^2}\right]^{-1},$$

$$p=\frac{\sigma^2}{t^*},\quad \operatorname{Im}\sigma>0. \tag{4.16}$$

Finally substituting (4.15) and (4.16) into (4.10), making the substitutions

$$u\equiv q^2a^2N/2=(Nc_0v^*/2)^{1/2}x,\quad \sigma=(Nc_0v^*/2)^{1/2}iy \tag{4.17}$$

and deforming the contour of the integration over p in the appropriate way, we find

$$\Delta=-I_d(v^*/a^d)N^{2-d/2}(c_0v^*N)^{d/4-1},\quad 0<d<4, \tag{4.18}$$

where

$$I_d=\pi^{-1}2^{1+d/4}K_d\int_0^\infty dx\,x^{d/2}\int_0^\infty dy\,(x^2+y^2)^{-2}\left[1+\frac{2x+y}{y(x+y)^2}\right]^{-1}. \tag{4.19}$$

In particular, for $d=3$ we find

$$\Delta=-0.0780(v^*/a^3)(N/c_0v^*)^{1/4}. \tag{4.20}$$

Fluctuation effects thus lead to a decrease in the self-diffusion coefficient D_s; this decrease can be quite substantial.

It follows from (4.17) that the characteristic values of the variables p and q which dominate the value of Δ in (4.10) are

$$\tilde{p}\sim c_0v^*N/t^*,\quad \tilde{q}\sim(c_0v^*N)^{1/4}R^{-1}.$$

Consequently, strong inequalities (4.12) are indeed satisfied under the condition $c_0v^*N\gg 1$, i.e., for polymer chains which are sufficiently long [this condition is actually equivalent to the condition $N\gg N_e$; see (2.24)]. The quantities $\tilde{p}$ and $\tilde{q}$ correspond to a characteristic time $\tilde{t}\equiv 1/\tilde{p}\sim t^*/c_0v^*N$ and a characteristic length $\tilde{\lambda}\equiv 1/\tilde{q}\sim R(c_0v^*N)^{-1/4}$ (the relationship between $\tilde{t}$ and $\tilde{\lambda}$ is extremely simple in meaning: $\tilde{\lambda}$ is the distance an end of the macromolecule moves over a time on the order of $\tilde{t}$).

Fluctuations in the molecular field with characteristic times $t\gg\tilde{t}$ do not have any significant effect on the reptation motion of macromolecules. Consequently, the creeping of a macromolecule along a tube is of a diffusive nature at $t\gg\tilde{t}$. The effect of fluctuations reduces to one of simply renormalizing the diffusion coefficient for diffusion along the tube:

$$D_\parallel\to D_\parallel^*.$$

All the classical predictions of reptation theory for characteristic times $t\gg\tilde{t}$ and characteristic distances $\lambda\gg\tilde{\lambda}$ thus remain in force when we make the single substitution $D_\parallel\to D_\parallel^*$. In particular, we have

$$t_r=\frac{N^2}{4D_\parallel^*},\quad \eta=\frac{G_0t_r}{3}=\frac{c_0T}{3N_e}\frac{N^2}{4D_\parallel^*},\quad D_s=\frac{2a^2D_\parallel^*}{N} \tag{4.21}$$

[cf. (4.21) with (2.18), (1.2), and (4.6)]. Comparing the last of expressions (4.21) with (4.5), and using (4.20), we find

$$D_\parallel^*=D_\parallel(1+\Delta)\approx D_\parallel[1-0.078(v^*/a^3)(N/c_0v^*)^{1/4}]. \tag{4.22}$$

The expression on the right side of (4.22) is invariant under link-enlargement transformations (transformations in which g original links are combined into a single renormalized link), for which we have

$$N\to N/g,\quad a\to ag^{1/2},\quad c_0\to c_0/g,\quad v\to vg^2.$$

What is the physical meaning of (4.22)? Let us consider the motion of some selected macromolecule (in a concentrated system in the equilibrium state). We call the tube which contains the macromolecule at the initial time, $t=0$, the "seed" tube. The concentration of the links of the surrounding polymer chains near the axis of this tube must obviously be slightly lower than the average concentration, since the total concentration of all of the links, including the links of the selected chain, must be approximately constant in the equilibrium state. Consequently, the surrounding chains create a potential well (or cavity) for our selected macromolecule; the shape of this well corresponds to that of the seed tube.

The state of our selected chain after a time t is shown in Fig. 2a. The chain has moved a distance $n=s_2'-s_1'$ along the tube:

$$n\sim(D_\parallel t)^{1/2}. \tag{4.23}$$

The chain has moved out of end regions AC and $A'C'$ of the seed tube, having created some new end regions, BC and $B'C'$. We will show that an effective restoring force acts on the molecule in this position.

The situations near points C and C' are different, since near point C there is a region of the seed tube (AC) which has been left empty (in a qualitative analysis, we can ignore the shorter region $A'C'$). Region AC is of course soon filled by links of surrounding chains by virtue of the rapid deformation of the network of entanglements (Sec. 2). It is not difficult to show, however, that the links of the surrounding chains fill cavity AC only partially: A part of size v^*/v remains effectively empty [see (2.23)]. Consequently, the average concentration of units in spherical region Ω, which includes regions AC and BC, nevertheless does not reach an equilibrium value. It remains smaller by an amount

$$\Delta c\sim(v^*/v)n/R_\Omega^3\sim(v^*/v)n^{-1/2}a^{-3},$$

where $R_\Omega\sim s_1^{1/2}a\sim n^{1/2}a$ is a characteristic dimension of region Ω (Fig. 2a). Consequently, molecular field h, which is exerted on point B by the surrounding chains, must be, on the average, weaker than the field h' which acts on point B'. The difference, $f=h'-h$ is, in order of magnitude,

$$f\sim Tv\Delta c\sim Tv^*/n^{1/2}a^3. \tag{4.24}$$

In this situation, the macromolecule is thus acted upon by an effective force f which tends to move the molecule in the opposite direction along the tube. Obviously, the effect of force f must be to effectively reduce the diffusion coefficient $D_{\|}$. It is easy to show that the relative change in this coefficient, $\Delta D_{\|}/D_{\|} \equiv \Delta$, must be proportional to the height of the potential barrier associated with force f:

$$|\Delta| = \text{const}\cdot U/T, \tag{4.25}$$

where

$$U = \int f\, dn, \tag{4.26}$$

and the integral is evaluated from 0 to $\tilde{n}$, where $\tilde{n}$ is the characteristic distance (expressed as a number of links) a macromolecule can move along the tube over the lifetime ($\tilde{\tau}$) of cavity AC.

Substituting (4.24) into (4.26), we find

$$U/T = \text{const}\cdot (v^*/a^3)\tilde{n}^{1/2}, \tag{4.27}$$

where $\tilde{n} \sim (D_{\|}\tilde{t})^{1/2}$ [see (4.23)].

The time $\tilde{t}$, over which the force f persists, is obviously equal in order of magnitude to τ_*, the relaxation time of concentration fluctuations with a wavelength on the order of the size of region Ω, i.e., with a wave vector $\tilde{q} \sim \tilde{n}^{-1/2}a^{-1}$. Using (3.28) and the relation $\tilde{n} \sim (D_{\|}\tilde{t})^{1/2}$, we find the following from the condition $\tilde{t} \sim \tau_*(\tilde{q})$:

$$\tilde{n} \sim (N/c_0 v^*)^{1/2}. \tag{4.28}$$

Substituting (4.28) into (4.27) and (4.25), we find

$$|\Delta| = \text{const}\cdot (v^*/a^3)(N/c_0 v^*)^{1/4}, \tag{4.29}$$

in complete agreement with exact expression (4.20).

5. CONCLUDING REMARKS

Expressions (4.20) and (4.22), the basic results of the preceding section of this paper, represent the fluctuation effects in the first order of a perturbation-theory expansion. They are valid under the condition $|\Delta| \ll 1$. In general, we should replace (4.22) by

$$D_{\|}^* = D_{\|}\zeta(\alpha), \quad \alpha = 0{,}078(\tilde{v}/a^3)(N/c_0 v^*)^{1/4}, \tag{5.1}$$

where

$$\zeta(\alpha) = 1 - \alpha + O(\alpha^2), \quad \alpha \ll 1. \tag{5.2}$$

The qualitative considerations expressed at the end of the preceding section make it possible to predict the behavior of the function $\zeta(\alpha)$ at $\alpha \gg 1$ also. In this case, expression (4.27) for the height of the potential barrier, U, obviously remains in force, since the only assumption which was made in the derivation of (4.27) was that the conformations of the sections of the macromolecule (sections AC and BC; Fig. 2a) obey Gaussian statistics. In particular, the sizes of these sections are $an^{1/2}$ in order of magnitude, and this is true regardless of the value of the parameter α (Sec. 1). The value of $\tilde{n}$ at $\alpha \gg 1$ can be estimated in the following way.

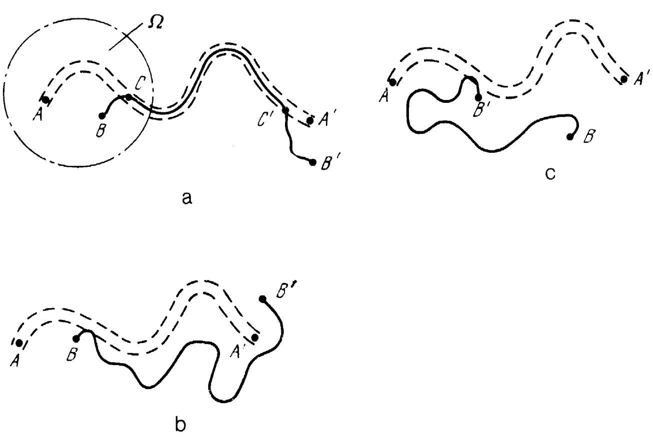

FIG. 2. a: Typical position of a macromolecule (solid line $BCC'B'$) with respect to the seed tube (dashed lines $ACC'A'$) at time t. The length of section AC is s_1, that of section BC is s_2, that of $A'C'$ is s_1' and that of $B'C'$ is s_2'. Here $s_1 + s_1' = s_2 + s_2' = l$, and Ω is the spherical region of minimum radius which contains sections AC and BC. b,c: Possible positions of the macromolecule at the time at which it finally escapes from the seed tube.

We recall that $\tilde{n}$ is that maximum displacement of the macromolecule (along the tube) over which the cavity corresponding to the liberated section of the seed tube (section AC) does not yet manage to relax. Let us consider a spherical region which contains section AC entirely, at the time of maximum displacement $\tilde{n}$. The size of this region is $a\tilde{n}^{1/2}$ in order of magnitude, and its volume is

$$\Omega \sim a^3\tilde{n}^{3/2}. \tag{5.3}$$

It is completely obvious that if region Ω does not contain a single end link (other than, of course, end B of our selected macromolecule) then the relaxation cannot occur in principle, since the action of the molecular field created by the cavity on the interior links (i.e., links other than the end links) of the polymer chains has no effect on their motion [see (2.5)]. On the other hand, if region Ω contains the end of at least one of the surrounding chains, then the relaxation will occur essentially instantaneously. The explanation is that region Ω corresponds to an effective potential well created by cavity AC, so this chain "is drawn into" region Ω quite rapidly[6] and thereby raises the effective potential of the molecular field in this region to the average value. Consequently, the maximum displacement $\tilde{n}$ must correspond to a region Ω which may or may not contain ends of chains, with a probability on the order of 1/2. This condition can obviously be written

$$\Omega c_0/N \sim 1, \tag{5.4}$$

where $2c_0/N$ is the concentration of the ends of polymer chains. Substituting (5.3) into (5.4), we find

$$\tilde{n} \sim (N/c_0 a^3)^{2/3}. \tag{5.5}$$

Note that with $\alpha \sim 1$ function (5.5) joins with (4.28), as it should.

Substituting (5.5) into (4.27), we find the height of the potential barrier to be

$$U/T=\text{const}\cdot(v^*/a^3)\,(N/c_0a^3)^{1/3}=\text{const}\cdot\alpha^{4/3},\quad \alpha\gg1. \tag{5.6}$$

As it moves along the tube, our macromolecule is thus obliged to overcome some very high potential barriers ($U/T\gg1$). This circumstance can of course lead to an exponential growth of the diffusion time and, correspondingly, an exponential decrease in the effective diffusion coefficient $D_\parallel^*$. Within a coefficient of the exponential function, we can write

$$D_\parallel^*\sim D_\parallel\exp(-U/T). \tag{5.7}$$

Substituting (5.6) into (5.7), and comparing the result with (5.2), we finally find

$$\zeta(\alpha)\propto\exp(-\text{const}\cdot\alpha^{4/3}),\quad \alpha\gg1. \tag{5.8}$$

The analysis above ignored random fluctuations in the molecular field, in particular, fluctuations in the effective depth of the potential well in region Ω. It can be shown, however, that incorporating these fluctuations with $d=3$ does not affect the final result (5.8); the only consequence is some change in the value of the const.

We can now formulate the final result regarding the dependence of the viscosity on the length of the macromolecules, N. Using (2.4), (2.19), (4.21), (5.1), (5.2), and (5.8), we find

$$\eta=AN^3\zeta^{-1}(\alpha),\quad \alpha=BN^{1/4}, \tag{5.9}$$

where

$$A=c_0T\tau_0/12N_e^2,\quad B=(0.078/c_0a^3)\,(\nu/N_e)^{3/4}, \tag{5.10}$$

$$\zeta^{-1}(\alpha)=\begin{cases}1+\alpha, & \alpha\ll1, \quad (5.11\text{a})\\ \propto\exp(\text{const}\cdot\alpha^{4/3}), & \alpha\gg1. \quad (5.11\text{b})\end{cases}$$

In deriving the second expression in (5.10) we noted that for real polymer systems the relation $c_0vN_e/v\gg1$ holds.

The classical reptation law $\eta\propto N^3$ is thus valid only for sufficiently low molecular weights of the polymer, under the condition $\alpha\ll1$. At large values of N (at $\alpha\gg1$) the viscosity increases exponentially,

$$\eta\propto\exp(\text{const}\cdot N^{1/3}). \tag{5.12}$$

An estimate of the parameter α for real polymer systems shows that even for the highest-molecular-weight synthetic polymers we have $\alpha\lesssim1$. It is thus not surprising that an exponential dependence of the type in (5.12) has not been observed experimentally.

Let us compare the theoretical behavior of the viscosity with experimental data for melts of polystyrene (PS).[4] From (5.9) and (5.11a) we find

$$\ln(\eta/M^3)\approx\text{const}+\alpha=\text{const}+0{,}013M^{1/4}, \tag{5.13}$$

where M is the molecular weight of the polymer. The derivation of the coefficient of $M^{1/4}$ in (5.13) made use of the relations

$$c_0=\rho/M_Lb,\quad N=M/M_Lb,\quad N_e=M_e/M_Lb,\quad a=b/6^{1/2},$$

where $\rho=0.97$ g/cm^3 is the density of the PS melt, $M_L=35$ Å^{-1} is the molecular weight of a unit length of a PS chain, $b=14\pm3$ Å is a Kuhn segment of PS, and $M_e=(17\pm1)\cdot10^3$. In addition, we have used the value[17] $\nu=6.5$. Figure 3 shows curves of $\ln(\eta/M^3)$ versus $M^{1/4}$: a theoretical curve calculated from (5.13) (curve 1) and an experimental curve (curve 2; Ref. 4). Each of the curves has been shifted an arbitrary distance along the ordinate, so one should compare the slopes of these curves, rather than absolute values. We see that at lower molecular weights the slope of the experimental curve is considerably higher than that of the theoretical curve. This result is completely understandable since in this region the ratio M/M_e is still not very large, so such intermediate effects as fluctuations in the contour length of the tube (which lead to a strengthening of the M dependence of η; see the Introduction) can play a significant role here. At larger values of M, on the other hand, the slope of the experimental curve approaches that of the theoretical curve.

For a more comprehensive test of the predictions of this study we would need data for even higher molecular weights. Such data could apparently be obtained from numerical simulations, particularly for two-dimensional polymer systems.

APPENDIX

We will first calculate the function F. We consider a macromolecule which is moving in a reptation fashion. It is not being acted upon by any external (including molecular) fields: $h=0$. We assume that at the initial time ($t=0$) unit s of the macromolecule is at point $\mathbf{r}$, while the distribution of the other units is an equilibrium (Gaussian) distribution. We denote the corresponding distribution with respect to conformations by $O_{\mathbf{r},s}\{\Gamma\}$, where Γ runs over all possible conformations of the polymer chain. The functional $O_{\mathbf{r},s}\{\Gamma\}$ is normalized by the condition

$$\int O_{\mathbf{r},s}\{\Gamma\}D\{\Gamma\}=1. \tag{A1}$$

The distribution with respect to conformations of this macromolecule at time t, $P_t\{\Gamma\}$, can obviously be written as a superposition of distributions of the type $O_{\mathbf{r}',s'}\{\Gamma\}$:

$$P_t\{\Gamma\}=\int d^d r'\,ds'\,\theta_t(\mathbf{r}'-\mathbf{r},s',s)\,O_{\mathbf{r}',s'}\{\Gamma\}, \tag{A2}$$

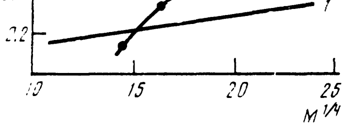

FIG. 3. Plot of $\ln(\eta/M^3)$, where η is the viscosity of the system and M the molecular weight of the polymer, versus $M^{1/4}$. 1—Theoretical, calculated from expression (5.13); 2—experimental (for a polystyrene melt[4]). Each curve has been displaced an arbitrary distance along the ordinate.

where the function $\theta_t(\mathbf{r},s,s')$ satisfies an equation which follows from (2.5),

$$D_{\parallel}^{-1}\partial\theta_t/\partial t=\partial^2\theta_t/\partial s^2, \tag{A3}$$

with the boundary conditions

$$\frac{\partial\theta_t}{\partial s}=-a^2\frac{\partial^2}{\partial\mathbf{r}^2}\theta_t,\quad s=0;\qquad \frac{\partial\theta_t}{\partial s}=a^2\frac{\partial^2}{\partial\mathbf{r}^2}\theta_t,\quad s=N \tag{A4}$$

and the initial condition

$$\theta_0(\mathbf{r},s,s')=\delta(\mathbf{r})\delta(s-s'). \tag{A5}$$

System of equations (A3)–(A5) can be solved by the standard methods.[2,9] Here is the explicit expression for the Fourier-Laplace transform of the function $\theta_t(\mathbf{r},s',s)$,

$$\theta(p,\mathbf{q},s',s)\equiv\int dt\,d^d r e^{-pt}e^{-i\mathbf{q}\mathbf{r}}\theta_t(\mathbf{r},s',s), \tag{A6}$$

in a form which has been made symmetric with respect to the substitution $s\rightarrow N\rightarrow -s$ (it is this combination which appears in all of the final expressions):

$$[\theta(p,\mathbf{q},s',s)+\theta(p,\mathbf{q},s',N-s)]/2=(t^*/N)\sigma^{-1}\operatorname{ch}(\sigma\gamma)$$
$$\times[(\sigma\operatorname{ch}\sigma+u\operatorname{sh}\sigma)\operatorname{ch}(\sigma\gamma')/(u\operatorname{ch}\sigma+\sigma\operatorname{sh}\sigma)-\operatorname{sh}(\sigma\gamma')], \tag{A7}$$

where

$$\sigma=(pt^*)^{1/2},\quad u=Nq^2a^2/2,\quad \gamma=\min[|2s/N-1|,\ |2s'/N-1|],$$
$$\gamma'=\max[|2s/N-1|,\ |2s'/N-1|].$$

The function $\theta(p,\mathbf{q},s',s)$ satisfies the following important relation, which follows directly from Eqs. (A3) and (A5):

$$\int ds\,\theta(p,\mathbf{q},s',s)+\frac{D_{\parallel}}{p}\left(\frac{\partial}{\partial s}\bigg|_{s=0}-\frac{\partial}{\partial s}\bigg|_{s=N}\right)\theta(p,\mathbf{q},s',s)=\frac{1}{p}. \tag{A8}$$

The expression for the function F which follows from relation (A2) as a particular case of the latter is

$$F\left(\begin{matrix}\mathbf{q} & \mathbf{q}_1 & \mathbf{q}_2\\ s & s_1 & s_2\end{matrix}\,\middle|\, s_0;p\right)$$
$$=\int ds'\theta(p,\mathbf{q}+\mathbf{q}_1+\mathbf{q}_2,s',s_0)\,\Phi\left(\begin{matrix}\mathbf{q} & \mathbf{q}_1 & \mathbf{q}_2\\ s & s_1 & s_2\end{matrix}\,\middle|\, s'\right), \tag{A9}$$

where

$$\Phi\left(\begin{matrix}\mathbf{q} & \mathbf{q}_1 & \mathbf{q}_2\\ s & s_1 & s_2\end{matrix}\,\middle|\, s'\right)=\int d^d r\,d^d r_1\,d^d r_2\exp(-i\mathbf{q}\mathbf{r}-i\mathbf{q}_1\mathbf{r}_1-i\mathbf{q}_2\mathbf{r}_2)$$
$$\times\Phi\left(\begin{matrix}\mathbf{r} & \mathbf{r}_1 & \mathbf{r}_2\\ s & s_1 & s_2\end{matrix}\,\middle|\,\begin{matrix}0\\ s'\end{matrix}\right). \tag{A10}$$

Here $\Phi(\mathbf{r}/s\ \mathbf{r}_1/s_1\ \mathbf{r}_2/s_2|0/s')$ is the equilibrium probability distribution that unit s of an ideal Gaussian chain will be at point $\mathbf{r}$, unit s_1 at point $\mathbf{r}_1$, and unit s_2 at point $\mathbf{r}_2$, under the condition that unit s' is at the origin of coordinates. We turn now to the calculation of the function K. For this purpose we first examine some general properties of the reptation motion (for $h=0$). We assume that the macromolecule is initially in a seed tube whose conformation we denote by Γ_0: $\Gamma_0=\{\mathbf{r}_s,\ 0\leqslant s\leqslant N\}$. Over a time t, the macromolecule can partially creep out of this tube (Fig. 2). The state of the macromolecule at time t is conveniently characterized by the following parameters: s_1, which is the "length" of the initial section of the seed tube which the macromolecule has left; s_2, which is the "length" of the new section of the tube which has appeared in place of section s_1; and $l=s_1+s_1'=s_2+s_2'$, which is the total "length" of the sections of the macromolecule from which the seed tube has escaped (Fig. 2a).

The probability that the parameters l, s_1, and s_2 assume certain given values at time t is obviously independent of the initial conformation Γ_0; i.e., the probability distribution of the quantities l, s_1, and s_2 is some universal function $\rho_t(l,s_1,s_2)$. This function can be calculated without difficulty by working from specifically the universal nature of this function (the calculation method is shown for a particular case in Ref. 18). The result is

$$\rho(p;l,s_1,s_2)\equiv\int_0^\infty dt\,e^{-pt}\rho_t(l,s_1,s_2)$$
$$=\begin{cases}0, & l<\max(s_1,s_2),\\ \dfrac{4t^*}{N^3}\dfrac{2\sigma}{\operatorname{sh}^2(2\sigma y)}\left\{\operatorname{sh}[2\sigma(x_1+x_2)]-\dfrac{2\operatorname{sh}(2\sigma x_1)\operatorname{sh}(2\sigma x_2)}{\operatorname{th}(2\sigma y)}\right\}, & \\ l>\max(s_1,s_2),\end{cases} \tag{A11}$$

where $y=l/N$, $x_1=s_1/N$, and $x_2=s_2/N$. It is not difficult to verify that at $t>0$ we have

$$\int\rho_t(l,s_1,s_2)\,dl\,ds_1\,ds_2<1. \tag{A12}$$

The reason for the disruption of the normalization is that the set of parameters (l,s_1,s_2) does not describe all possible states of the meacromolecule: Over the time t, the polymer chain can completely creep out of its seed tube. By the time at which it finally escapes from this tube the polymer chain may be in state $O_{\mathbf{r},0}$ (Fig. 2b) or $O_{\mathbf{r},N}$ (Fig. 2c), where $\mathbf{r}$ is any point of the seed tube It is easy to show that the rates at which states $O_{\mathbf{r},0}$ and $O_{\mathbf{r},N}$ are generated are, respectively,

$$D_{\parallel}\int ds\,\rho_t(N,s,0)\delta(\mathbf{r}-\mathbf{r}_s),\qquad D_{\parallel}\int ds\,\rho_t(N,s,N)\delta(\mathbf{r}-\mathbf{r}_s). \tag{A13}$$

Using (A2), we find $P_t^*\{\Gamma\}$, i.e., the distribution with respect to conformations of those macromolecules which have completely escaped from the seed tube by time t:

$$P_t^*\{\Gamma\}=D_{\parallel}\int_0^t dt'\int d^d r'\,ds\,ds'[\theta_{t'}(\mathbf{r}'-\mathbf{r}_s,s',0)\rho_{t-t'}(N,s,0)$$
$$+\theta_{t'}(\mathbf{r}'-\mathbf{r}_s,s',N)\rho_{t-t'}(N,s,N)]O_{\mathbf{r}'s'}\{\Gamma\}. \tag{A14}$$

Using (A1), we can verify that the following relation holds (as it should):

$$\int\rho_t(l,s_1,s_2)\,dl\,ds_1\,ds_2+\int P_t^*\{\Gamma\}D\{\Gamma\}=1.$$

The function K can be expressed directly in terms of the function ρ:

$$K\left(p\left|\begin{matrix}\mathbf{q}_1 & \mathbf{q}_2\\ s_1 & s_2\end{matrix}\right.\right)=\int ds'\,\rho(p;N+s_1-s_2,s_1,s')\,g(\mathbf{q}_1,s')\times g(\mathbf{q}_2,N+s_1-s_2-s')+D_{\parallel}\delta(s_2-s_1-0)\int ds'\{\theta(p,\mathbf{q}_1+\mathbf{q}_2,s',0)\rho(p;N,s_1,0)+\theta(p,\mathbf{q}_1+\mathbf{q}_2,s',N)\rho(p;N,s_1,N)\}g(\mathbf{q}_1,s')g(\mathbf{q}_2,N-s').\qquad(\mathrm{A15})$$

The first term here corresponds to those macromolecules which are partially in the seed tube, while the second term corresponds to those macromolecules which have completely crept out of this tube [cf. the second term in (A15) and expression (A14)]. In the important particular case $p\rightarrow0$, $\mathbf{q}_1=-\mathbf{q}_2$ the function K is given by

$$K\left(p\left|\begin{matrix}\mathbf{q} & -\mathbf{q}\\ s_1 & s_2\end{matrix}\right.\right)=\frac{t^*}{N^2}\{2g(\mathbf{q},N+s_1-s_2)+\delta(x_2-x_1-0)g(\mathbf{q},N)\times[\sigma^{-2}+{}^2/_3(3x_1^2-3x_1-1)]\}+O(p).\qquad(\mathrm{A16})$$

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[1] We wish to stress that the value $z=3.4$ is a nominal value: The experimental data (for various systems) correspond to values $z=3.1$–3.7 (Ref. 5).

[2] For example, these fluctuations reduce the parameter v [see (2.24)] by about 20% (Ref. 13).

[3] Equations (2.7) and (2.8) were derived in the case $h=0$ in Ref. 2 (see also Ref. 10).

[4] For an unstretchable filament, there is no intermediate Rouse stage of the relaxation.[13]

[5] Expression (3.19) is valid in the limit of very long polymer chains and under condition (3.18); see the review by Oono.[15]

[6] "Quite rapidly" because at $\alpha\gg1$ the effective potential energy of a section of a chain consisting of $\tilde{n}$ units in this well is large in absolute value: $|U|\gg T$ (more on this below).

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