Relaxation of long-wavelength density fluctuations in a concentrated polymer solution

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The temporal correlation function $G_q(t)$ of the concentration fluctuations in a solution of linear macromolecules is investigated. It is shown that there exist three characteristic long-wavelength regions, differing in the behavior of this function: $R \equiv N^{1/2}a \ll 2\pi/q \ll \lambda_1$, $\lambda_1 \ll 2\pi/q \ll \lambda_2$, and $2\pi/q \gg \lambda_2$, with $\lambda_1 \sim N^{1/2}R$ and $\lambda_2 \sim NR$, where N is the number of links in one polymer chain. In the first region the correlation function is described by two exponentials with substantially different relaxation times. In the second region the term corresponding to the slower relaxation becomes essentially nonexponential. In the third region the dependence $G_q(t)$ again becomes exponential, with one relaxation time.

1. INTRODUCTION

A solution of flexible-chain linear macromolecules is said to be connected if the volume fraction Φ of polymer in it is not small in comparison with unity. The spatial size R of the polymer coils in a concentrated solution is close to the "ideal" size: $R = N^{1/2}a$ (Ref. 1), where N is the number of links in the chain and a is the length of one link.

A large number of both theoretical and experimental papers[1–7] have been devoted in recent years to the study of the dynamical and equilibrium behavior of polymer-concentration fluctuations $c(q)$ with wavelength $2\pi/q$ considerably greater than the length of one link. In the case of long-wavelength fluctuations (with wavelength $2\pi/q \gg R$) the main attention has been paid to the study of the dependence of the cooperative-diffusion coefficient D_c on the concentration and other characteristics of the solution.[1,4–7] In the present paper it is shown theoretically that the relaxation of very long-wavelength concentration fluctuations is far from always described by a single coefficient D_c. On the contrary, the relaxation of these fluctuations in the general case has a complicated, nonexponential character.

In the first part of the next section we describe the traditional version of the theory, and an analysis of its applicability is concluded by the construction of a more complete system of dynamical equations. The third section is devoted to an investigation of these equations and to a description of the results.

2. HYDRODYNAMIC DESCRIPTION OF CONCENTRATION FLUCTUATIONS IN A POLYMER SOLUTION

The temporal correlation function of the concentration fluctuations in the **q**-representation is defined as

$$G_q(t) = \int e^{-i\mathbf{q}\mathbf{r}} \langle \delta c(0,0)\, \delta c(t,\mathbf{r}) \rangle\, d^3r. \qquad (2.1)$$

For the calculation of this function it is convenient to use the fluctuation-dissipation theorem. Let an external field $h(t,\mathbf{r})$ act on each link of the macromolecule. The response of the system can be represented in the form

$$\delta c_q(t) = -\int_0^\infty d\tau\, \varkappa_q(\tau)\, h_q(t-\tau), \qquad (2.2)$$

where $\varkappa_q(\tau)$ is the generalized susceptibility, and $\delta c_q(t)$ and $h_q(t)$ are the Fourier transforms of the functions $\delta c(t,\mathbf{r})$ and $h(t,\mathbf{r})$, respectively. The relationship between the correlation function and the generalized susceptibility in the nonquantum case has the form[8]

$$T\varkappa_q(t) = -dG_q(t)/dt, \quad t > 0. \qquad (2.3)$$

Thus, to determine $G_q(t)$ it is sufficient to calculate the generalize susceptibility $\varkappa_q(t)$.

In the limit of very large wavelengths the concentration change induced by the action of an external field can be described by the diffusion equation

$$\partial c/\partial t = -\nabla \mathbf{J}, \qquad (2.4)$$

$$\mathbf{J} = -c\beta^{-1}\nabla(\mu + h), \qquad (2.5)$$

where β^{-1} is the effective mobility of a link, and $\mu = \mu(c)$ is the chemical potential of a link. The expression found from Eqs. (2.3)–(2.5) for $G_q(t)$ for small q can be called the traditional expresssion[1]:

$$G_q(t) = \left(\frac{1}{T} \frac{\partial \mu}{\partial c} \right)^{-1} \exp(-D_c q^2 t). \qquad (2.6)$$

The cooperative-diffusion coefficient D_c is equal to

$$D_c = c \frac{\partial \mu}{\partial c} \beta^{-1} = \frac{\partial \Pi}{\partial c} \beta^{-1}, \qquad (2.7)$$

where Π is the osmotic pressure. The expression (2.6) is not specific to polymers, inasmuch as the dependences $\beta(c)$ and $\mu(c)$ in a concentrated polymer solution have the same character as for a system of broken links.

An important feature specific to polymer systems is the fact that the region of applicability of the law (2.6) should be limited to extremely small q. For $q \neq 0$ the chains move with different phases, i.e., each distinct chain should be displaced relative to the polymer matrix that surrounds this chain. This displacement is strongly impeded by the meshing effect,[9] which reflects the fact that a given chain in motion cannot intersect the contours of other chains. As a result, as shown below, the law (2.6) can be violated even for $q \ll 2\pi/R$ (i.e., for wavelengths considerably greater than the size of one molecular coil).

We turn to the construction of a more complete system of equations describing the dynamics of concentration fluctuations with $q \ll 2\pi/R$ in a polymer solution. Following the general scheme of Ref. 10 for the description of hydrodynamic fluctuations, besides the concentration field $c(t,\mathbf{r})$ we also introduce the field $\mathbf{v}(t,\mathbf{r})$ of the macroscopic velocities of the polymer links. Strictly speaking, a complete description of the solution should include two more fields: the total density $\rho(t,\mathbf{r})$ and the mass flux $\mathbf{j}(t,\mathbf{r})$, related by the continuity equation

$$\partial\rho/\partial t + \nabla\mathbf{j} = 0.$$

However, if we assume that the solution as a whole is incompressible, i.e., $\rho = \text{const}$, the flux $\mathbf{j}$ will not affect the concentration fluctuations; therefore, we can set $\mathbf{j} = 0$.

The linarized equations of motion in an external field h have the form

$$mc\partial\mathbf{v}/\partial t = -\nabla\Pi - c\nabla h - c\beta\mathbf{v} + \eta\nabla^2\mathbf{v} + (\zeta+\eta/3)\nabla(\nabla\mathbf{v}), \quad (2.8)$$

$$\partial c/\partial t = -\nabla\mathbf{J}, \qquad \mathbf{J} = c\mathbf{v} - c(ND_s/T)[\beta\mathbf{v} + \nabla(\mu+h)], \quad (2.9)$$

where m is the mass of one line, η and ζ are the viscosities of the solution, and D_s is the self-diffusion coefficient of the macromolecules in the solution. Equation (2.8) differs from the usual Navier-Stokes equation only in the term $-c\beta\mathbf{v}$, which is the density of the force exerted on the polymer by the solvent. In view of the large dissipation caused by the friction between the polymer and the solvent, we can neglect the inertial term $mc\partial\mathbf{v}/\partial t$ in Eq. (2.8). The flux $\mathbf{J}$ of polymer links in the second formula of (2.9) consists of two terms: a hydrodynamic term $c\mathbf{v}$, and a diffusion term, which corresponds to the flux arising from the self-diffusion of the macromolecules in the matrix of the surrounding chains under the influence of the external force $-N(\beta\mathbf{v} + \nabla\mu + \nabla h)$.

For a low-molecular-weight solution, the last two terms in Eq. (2.8), which are due to the viscosity, would be negligibly small in comparison with the frictional force $-c\beta\mathbf{v}$. Omitting these terms, after simple transformations we can reduce the system of equations (2.8), (2.9) to the system (2.4), (2.5). In the case of a polymer solution the "viscous" terms cannot be discarded, since the viscosity of the solution is anomalously large.[9]

The viscosity of the polymer solution and the self-diffusion coefficient of the macromolecules have been calculated on the basis of the reptation model of Ref. 11:

$$\eta_0 = \frac{\pi^2}{12}G_0T_d, \quad D_s = \frac{1}{3\pi^2}\frac{R^2}{T_d} = \frac{1}{3\pi^2}\frac{Na^2}{T_d}, \quad (2.10)$$

$$G_0 = cT/N_e, \quad T_d = \tau_0N^3/N_e, \quad (2.11)$$

where G_0 is the characteristic shear modulus of the system, T_d is the characteristic relaxation time, and N_e and τ_0 are phenomenological parameters: N_e has the meaning of the average number of links between meshings along the chain (usually, $N_e \sim 10^2$); the parameter τ_0 is of the order of the time taken by one link to diffuse over a distance a. The formulas (2.10), (2.11) are correct for sufficiently long macromolecules with $N \gg N_e$. Such a strong dependence of the viscosity on the number of links in the polymer chain ($\eta_0 \propto N^3$, which follows from the reptation theory) is due precisely to the meshing effect mentioned above.

In Ref. 11 it was found that the viscosity of a polymer solution has considerable dispersion:

$$\eta(\omega) = \eta_0\frac{96}{\pi^4}\sum_n\frac{1}{n^2(n^2+i\omega T_d)}, \quad (2.12)$$

where the sum is taken over odd positive n. Using the method of Ref. 11, it is not difficult to show that the second viscosity ζ of the polymer solution is proportional to the first viscosity:

$$\zeta(\omega) = {}^2/_3\,\eta(\omega). \quad (2.13)$$

Introducing the Laplace parameter $p = i\omega$, we can transform the expression (2.12) to the form

$$\eta(p) = \eta_0\nu(s), \quad (2.14)$$

where

$$\nu(s) = \frac{3}{s^2}\left(1 - \frac{\operatorname{th} s}{s}\right), \quad s = \left(\frac{\pi^2pT_d}{4}\right)^{1/2}.$$

After Fourier transformation with respect to the spatial variables and Laplace transformation with respect to the time, the system of equations (2.8), (2.9) is reduced to the form

$$i\gamma_0\mathbf{q}c + \beta c_0\mathbf{v} + \eta(p)q^2\mathbf{v} + [\zeta(p) + \eta(p)/3]\mathbf{q}(\mathbf{qv}) + i\mathbf{q}c_0h = 0, \quad (2.15)$$

$$pc + i\mathbf{q}c_0\mathbf{v} + (ND_s/T)[q^2(\gamma_0c + hc_0) - i\mathbf{qv}c_0\beta] = 0, \quad (2.16)$$

where $c = c(p,\mathbf{q})$ and $\mathbf{v} = \mathbf{v}(p,\mathbf{q})$ are the Fourier-Laplace transforms of the corresponding functions, c_0 is the average concentration of the solution, and $\gamma_0 = (\partial\Pi/\partial c)_{c=c_0}$ is the inverse compressibility of the polymer component.

3. RESULTS

From the quantities appearing in Eqs. (2.15), (2.16) we can construct the dimensionless parameter $\varepsilon = \beta ND_s/T \sim N_e/N$, which is small by virtue of the inequality $N_e \ll N$. Solving Eqs. (2.15), (2.16) in leading order in ε, we find

$$\varkappa^{-1} = (\gamma_0/c_0)[1 + \tau_cp + \varphi(p)], \quad (3.1)$$

$$\tau_c = (D_cq^2)^{-1}, \quad \varphi(p) = \frac{pT}{ND_s\gamma_0q^2}\left[1 + \frac{c_0T}{2q^2ND_s\eta(p)}\right]^{-1}. \quad (3.2)$$

We introduce one further important dimensionless parameter:

$$\alpha = 2G_0/c_0\gamma_0 = 2T/\gamma_0N_e. \quad (3.3)$$

Depending on the structure of the polymer, the quantity α can take any value; for polymers with a chain of not very high rigidity, $\alpha \sim 0.1$–0.01.

Using the relations (3.1), (3.2), and (2.3), it is not difficult to find the correlation function $G_{\mathbf{q}}(t)$. Depending on the wavelength $2\pi/q$, three different relaxation laws are possible. If

$$N^{1/2}a \ll 2\pi/q \ll Na/N_e^{1/2} \equiv \lambda_1,$$

then

$$G_{\mathbf{q}}(t)=\frac{c_0T}{\gamma_0(1+\alpha)}[\exp(-\tilde{D}_cq^2t)+\alpha\exp(-D_2q^2t)], \tag{3.4}$$

where

$$\tilde{D}_c=(1+\alpha)\gamma_0/\beta=(1+\alpha)D_c, \qquad D_2=2ND_sG_0/c_0T=D_c\varepsilon\alpha.$$

Thus, the relaxation consists of two stages: a rapid stage, which is characterized by a diffusion coefficient $\tilde{D}_c$ (this coefficient does not depend on the number N of links in the macromolecule), and a slow stage, which is characterized by a much smaller diffusion coefficient $D_2 \propto 1/N$.

For

$$Na/N_e^{1/2} \equiv \lambda_1 \ll 2\pi/q \ll aN^{3/2}N_e^{-1/2}[\gamma_0\tau_0(1+\alpha)/\beta a^2]^{1/2} \equiv \lambda_2$$

the correlation function has the form

$$G_{\mathbf{q}}(t)=\frac{c_0T}{\gamma_0(1+\alpha)}[\exp(-\tilde{D}_cq^2t)+\alpha\psi(t/T_d)], \tag{3.5}$$

where

$$\psi(x)=\frac{8}{\pi^2}\sum_n\frac{1}{n^2}\exp(-n^2x), \tag{3.6}$$

in which n are odd positive numbers. Consequently, the slow stage of relaxation in this regime is found to be essentially nonexponential, with a characteristic time T_d.

Finally, for very large wavelengths $2\pi/q \gg \lambda_2$ the relaxation occurs in accordance with the law (2.6), corresponding to pure diffusion.

As follows from (3.4)–(3.6), at the largest times the relaxation is always exponential:

$$G_{\mathbf{q}}(t) \propto e^{-\Gamma t}, \quad t\to\infty,$$

where the characteristic relaxation rate Γ depends on q in a highly distinctive way:

$$\Gamma(q)=\begin{cases} D_2q^2, & R \ll 2\pi/q \ll \lambda_1, \qquad (3.7\text{a}) \\ T_d^{-1}, & \lambda_1 \ll 2\pi/q \ll \lambda_2, \qquad (3.7\text{b}) \\ D_cq^2, & \lambda_2 \ll 2\pi/q. \qquad (3.7\text{c}) \end{cases}$$

We shall discuss the physical meaning of the results obtained, drawing attention principally to the dependence of the relaxation rate Γ on N and q. The increment in the free energy of the system on account of a small change δc in the concentration is equal to $\delta F = \frac{1}{2}A(\delta c)^2$ per unit volume, where A is a coefficient that does not depend on N. The relaxation rate at large times can be found by equating $\delta\dot{F} = A\delta c\delta\dot{c}$ to the dissipation rate W. If the main relaxation mechanism is diffusion of macromolecules in the matrix of the surrounding chains, then

$$W \sim TD^{-1}nv^2, \tag{3.8}$$

where D is the diffusion coefficient, which depends on N in accordance with the law $D \sim D_0/N^2$ (see (2.10)), $n = c_0/N$ is the concentration of macromolecules, and v is their characteristic velocity, which can be determined from the continuity equation:

$$\delta\dot{c}=-\nabla(c_0\mathbf{v})\sim qc_0v. \tag{3.9}$$

Substituting (3.8) and (3.9) into the equation

$$\delta\dot{F}=W, \tag{3.10}$$

we find

$$\Gamma=\delta\dot{c}/\delta c \sim AD_0c_0q^2/TN=\text{const}\cdot q^2/N,$$

where const does not depend on N. Thus, the regime considered corresponds to formula (3.7a).

For large wavelengths $2\pi/q$, a relaxation mechanism competing with the diffusion is the coherent motion of the macromolecules, in which the dissipation is due to the viscosity $\eta \sim \eta_0N^3$ of the polymer solution (see (2.10)):

$$W \sim \eta(\nabla\mathbf{v})^2 \sim \eta q^2v^2. \tag{3.11}$$

Comparing (3.8) and (3.11), we find that coherent motion becomes more favored if

$$\lambda \equiv 2\pi/q > \lambda_1 \sim (D_0\eta_0/Tc_0)^{1/2}N=\text{const}\cdot N. \tag{3.12}$$

Substituting (3.11) into (3.10), we obtain

$$\Gamma=\delta\dot{c}/\delta c \sim Ac_0^2/\eta_0N^3=\text{const}\cdot N^{-3},$$

which agrees with (3.7b).

Finally, for still larger wavelengths the rate $W = TD_0^{-1}c_0v^2$ of dissipation on account of friction between the polymer and the solvent becomes more important than the "viscous" dissipation. This occurs at

$$\lambda=2\pi/q>\lambda_2 \sim (D_0\eta_0/Tc_0)^{1/2}N^{3/2}=\text{const}\cdot N^{3/2}.$$

In this case,

$$\Gamma=\delta\dot{c}/\delta c \sim AD_0c_0q^2/T=\text{const}\cdot q^2,$$

which corresponds to the regime (3.7c).

Thus, the three long-wavelength regimes (a, b, c) considered above correspond to: a) dissipation primarily on account of diffusion of macromolecules through the polymer matrix; b) hydrodynamic flow of the polymer component as a viscous liquid; c) friction with the solvent during the motion of segments of the macromolecules. We note that the characteristic wavelength λ_1 corresponds, in its geometrical meaning, to the total length of the "tube" introduced in the reptation model[9]; at the same time, the other characteristic length λ_2 cannot be interpreted geometrically.

Thus, in this paper we have shown that the relaxation even of very long-wavelength fluctuations of the concentration of a polymer solution is not described by simple diffusion. This effect is connected with the presence of topological restrictions—meshings that strongly affect the motion of the macromolecules. It might appear that topological restrictions could not influence the relaxation of concentration fluctuations, inasmuch as these fluctuations are most often formed with no change of the "topology." This argument, however, is incorrect, since the fact that fluctuations with a change of "topology" arise rarely is compensated by the fact that they take a long time to relax.

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