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325

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EFFECTS OF FLUID INERTIA
ON THE DYNAMICS OF POLYMERS
IN DILUTE SOLUTIONS

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2003

I. Introduction

Most of the theoretical investigations on the dynamic properties of flexible macromolecules performed so far are based on the Rouse-Zimm model [1 - 5]. In this model the polymer molecule is modeled as a chain of beads under Brownian motion. The bead participates in the interactions with solvent molecules. The solvent contributes a frictional force against the motion of a monomer and a random force to take into account the random collisions exerted on monomers. In the Rouse model, the solvent is considered as a continuum fluid. The Zimm theory incorporates a more refined hydrodynamic model, arguing that the motion of each monomer also affects other monomers, by way of the flow it induces in the ambient medium. It has been shown that the Zimm model predicts the correct dynamical behavior for dilute polymer solutions with substantial hydrodynamic interactions arising from solvents. The Rouse model is applicable for good solvents, where the corrections due to the hydrodynamic interactions and excluded volume effects to a large extent cancel each other [5]. It also gives a good description of the polymer dynamics in situations when the surrounding polymers screen out the hydrodynamic interactions [3, 4]. Both models assume Gaussian equilibrium distribution of the beads. This is important for the theory since the Gaussian chain is in most situations the only description of a polymer that can be manipulated analytically. Less convenient models provide the same macroscopic properties for a free chain in the limit of a large number of chain segments [6, 7]. Moreover, the Gaussian chain is the minimal model that adequately describes several polymeric properties using the smallest number of phenomenological parameters. Since the microscopic statistical behavior of monomeric units cannot be taken into account in an analytical theory because of the complicated interactions of their constituents, the description by a Gaussian function at least reproduces their qualitative behavior. This holds for polymer properties, which involve length scales that are large compared to monomer sizes. Although the Rouse-Zimm model has been proven as a universal theory well describing the long-time, long-range properties of the polymer macromolecules, there are still a number of unresolved problems in the understanding of the dynamics of flexible and semiflexible macromolecules in solution [8 - 10]. So, the q^3 dependence of the first cumulant in the intermediate scattering vector regime is well confirmed for synthetic polymers and DNA, however, the experimental values are about 25% smaller than the theoretical predictions. Systematic deviations from the theoretical behavior at large scattering vectors have been also found for various synthetic polymers using quasielastic neutron scattering. The diffusion coefficient calculated from the continuous Rouse-Zimm model deviates approximately 30% from the experimental value for both the natural and synthetic macromolecules. For a review of these and other difficulties of the Rouse-Zimm theory we refer to the works [8, 10] and an earlier paper [11]; comparing them, one can see that the situation has little changed during the decade. It can be concluded, that there is now evidence that the Rouse-Zimm model does not yield the correct static and dynamic properties for the same set of the model parameters, even for long flexible chains.

In the present work we propose a generalization of the Zimm model that could give a better understanding of the dynamical behavior of polymers in dilute solutions. We take into account the fluid inertia during the motion of the polymer in the solvent. The hydrodynamic interaction, i.e. the interaction between the beads mediated by the motion of the fluid, is considered solving the nonstationary Navier-Stokes equations. By this way the well-known Oseen tensor is generalized. Moreover, the resistance force on the moving bead will be assumed not the Stokes one, proportional to the velocity of the bead. We model this force by a more correct Boussinesq friction force [12] reflecting the fact that the force acting on the bead at a given time t is determined by the state of the bead motion in all the preceding moments of time. The use of the Stokes force assumes that we are interested only in the limit $t \rightarrow \infty$. Using the Boussinesq force and solving the nonstationary problem, we have a possibility to obtain solutions that are valid for almost arbitrary t (for incompressible fluids, of course, we cannot reach the exact limit $t \rightarrow 0$). The mentioned generalizations mean that we take into account the effects of hydrodynamic memory. These effects have been extensively studied in the physics of simple liquids and in the theory of Brownian motion (for a review see e.g. Ref. [13]) with very important consequences. In particular, the memory effects reveal in such interesting peculiarities like the famous "long-time tails" of the velocity autocorrelation function, first discovered by means of computer experiments [14, 15]. The concept of the Brownian motion lies in the basis of the Rouse-Zimm theory of polymer dynamics. It is thus natural to expect that the memory effects will be important for polymers as well. In the present communication we will show that the inclusion of the hydrodynamic memory into the classical Zimm model leads to an essentially different behavior of the time correlation functions describing the polymer motion in solution. It will be demonstrated by the appearance of long-time tails of these functions that reflect a strong persistence of the correlation with the initial state of the polymer. The relaxation of the mean square displacement of the whole polymer, as well as the decay of the polymer internal modes, are slower than in the original model. We have also shown how the tails are displayed in the long-time behavior of the Van Hove function used in the interpretation of quasielastic scattering of light and neutrons. We believe that the obtained results could contribute to the solution of some of the existing problems between the theory and experiment.

II. The Rouse-Zimm models and the effects of fluid inertia

Within the Zimm model the motion of the nth polymer segment (the bead) is described by the equation

$$M \frac{d^2 \vec{x}_n(t)}{dt^2} = \vec{f}_n^{fr} + \vec{f}_n^{ch} + \vec{f}_n.$$ (1)

Here $\vec{x}$ is the position vector of the nth bead, M is the mass of the bead, $\vec{f}_n^{ch}$ is the force with which the neighboring beads act on the nth bead, $\vec{f}_n$ is the random force due to the motion of the molecules of solvent, and $\vec{f}_n^{fr}$ is the friction force on the bead during its motion in the solvent. Within the Zimm model the latter force was the Stokes one,

$$\vec{f}_n^{fr} = -\xi \left[\frac{d\vec{x}_n}{dt} - \vec{v}(\vec{x}_n) \right],$$ (2)

with $\vec{v}(\vec{x}_n)$ being the velocity of the solvent in the place of the nth bead due to the motion of other beads. The friction coefficient for a spherical particle of radius b is $\xi = 6\pi\eta b$, where η is the solvent viscosity. However, this expression holds only in the case of steady flow. In the general case the resistance that a body feels during the motion in a liquid depends not only on the velocity that the body has at the given moment of time. It depends also on the whole history of the body motion, i.e. on velocities and accelerations in the preceding moments of time [12, 16]. At the translational motion of a rigid body in an incompressible viscous fluid this force, for any of the Cartesian components, has a form

$$f^{fr}(t) = -\xi v(t) - M' \dot{v}(t) - 6\sqrt{\frac{M'\xi}{\pi}} \int_0^\infty \dot{v}(t - \beta^2) d\beta, \qquad M' = \frac{2\pi b^3}{3} \rho,$$ (3)

where M' is the "effective hydrodynamic mass" ($= M_s/2$ with M_s being the mass of the solvent displaced by the bead), and ρ is the solvent density. Equations (1 – 3) have to be solved together with the hydrodynamic (Navier-Stokes and continuity) equations for the macroscopic velocity of the liquid,

$$\rho \frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta \Delta \vec{v} + \vec{\varphi}, \qquad \text{div} \vec{v} = 0.$$ (4)

Here p is the pressure. The quantity $\vec{\varphi}$ has the sense of an external force per unit volume [4, 17],

$$\vec{\varphi}(\vec{x}) = -\sum_n \vec{f}_n^{fr}(\vec{x}_n) \delta(\vec{x} - \vec{x}_n).$$ (5)

The hydrodynamic equations (4) are solved using the Fourier transformation (FT)

$$\vec{v}_k^\omega = \int \frac{dx dt}{(2\pi)^4} e^{i(\vec{k}\vec{x} + \omega t)} \vec{v}(\vec{x}, t).$$ (6)

The solution,

$$\vec{v}_k^\omega = \frac{1}{k^2 \eta - i\omega\rho} \left[\vec{\varphi}_k^\omega - \frac{\vec{k}}{k^2} (\vec{k} \vec{\varphi}_k^\omega) \right],$$ (7)

can be in the $\vec{x}$-representation, for any of the component α (x, y, or z), written in the form

$$v_\alpha^\omega(\vec{r}) = \int d\vec{r}' \sum_\beta H_{\alpha\beta}^\omega(\vec{r}-\vec{r}')\varphi_\beta^\omega(\vec{r}'). \tag{8}$$

The FT of the Oseen tensor

$$H_{\alpha\beta}^\omega(\vec{r}) = \frac{1}{(2\pi)^3\eta}\int \frac{d\vec{k}}{k^2 - i\omega\rho/\eta}\left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right)e^{-i\vec{k}\vec{r}} \tag{9}$$

can be expressed as

$$H_{\alpha\beta}^\omega(\vec{r}) = A\delta_{\alpha\beta} + B\frac{r_\alpha r_\beta}{r^2}. \tag{10}$$

After the integration in Eq. (9) we obtain

$$A = \frac{1}{8\pi\eta r}\left[e^{-y} - y\left(\frac{1-e^{-y}}{y}\right)''\right], \qquad B = \frac{1}{8\pi\eta r}\left[e^{-y} + 3y\left(\frac{1-e^{-y}}{y}\right)''\right]. \tag{11}$$

We have denoted here $y = r\chi$, $\chi = \sqrt{-i\omega\rho/\eta}$ (Re$\chi > 0$), and the prime ' means the differentiation with respect to y. Now we have to substitute φ_β^ω from the FT of Eq. (5) to v_α^ω from Eq. (8). The result will be substituted into the equation of motion (1), which in the FT is

$$-M\omega^2 x_{n\alpha}^\omega = -\xi^\omega\left[-i\omega x_{n\alpha}^\omega - v_\alpha^\omega(\vec{x}_n)\right] + f_{n\alpha}^{ch,\omega} + f_{n\alpha}^\omega. \tag{12}$$

We have used here the FT of the Boussinesq force (3)

$$f^{fr,\omega} = -\xi^\omega v^\omega, \qquad \xi^\omega = \xi\left[1 + \chi b + \frac{1}{9}(\chi b)^2\right]. \tag{13}$$

Up to this moment the consideration (within the formulation of the model) is strong. The obtained generalization of the Zimm equation is as follows:

$$-i\omega x_{n\alpha}^\omega = \frac{1}{\xi^\omega}\left(f_{n\alpha}^{ch,\omega} + f_{n\alpha}^\omega + M\omega^2 x_{n\alpha}^\omega\right) + \sum_\beta\sum_{m\neq n}H_{\alpha\beta}^\omega(\vec{x}_n - \vec{x}_m)\left[f_{m\beta}^{ch,\omega} + f_{m\beta}^\omega + M\omega^2 x_{m\beta}^\omega\right]. \tag{14}$$

In the sum entering this equation $m \neq n$, since the velocity field in the point n is created by all other beads except the nth one. The continuum approximation of Eq. (14) is

$$-i\omega x_{n\alpha}^\omega = \frac{1}{\xi^\omega}\left[f_\alpha^{ch,\omega}(n) + f_\alpha^\omega(n) + M\omega^2 x_\alpha^\omega(n)\right]$$

$$+ \int_0^N dm H_{\alpha\beta nm}^\omega\left[\frac{3k_BT}{a^2}\frac{\partial^2 x_\beta^\omega}{\partial m^2} + f_\beta^\omega(m) + M\omega^2 x_\beta^\omega(m)\right], \tag{15}$$

where a is the mean square distance between neighboring beads along the chain. We have used here that the force between the beads along the chain can be obtained from the effective potential u,

$$u = \frac{3k_BT}{2a^2}\sum_{n=2}^N(\vec{x}_n - \vec{x}_{n-1})^2, \tag{16}$$

which follows from the equilibrium (Gaussian) distribution of the beads [4],

$$P(r_{nm}) = \left(\frac{3}{2\pi a^2|n-m|}\right)^{3/2}\exp\left(-\frac{3}{2a^2}\frac{r_{nm}^2}{|n-m|}\right), \qquad \vec{r}_{nm} \equiv \vec{x}_n - \vec{x}_m, \tag{17}$$

so that in the continuum approximation

$$\vec{f}_n^{ch} \to \frac{3k_BT}{a^2}\frac{\partial^2\vec{x}(t,n)}{\partial n^2}. \tag{18}$$

Due to the dependence of the Oseen tensor on the difference $\vec{x}_n - \vec{x}_m$, the obtained generalized Zimm equation (15) is nonlinear and thus hardly solvable analytically. We shall use the common approximation of preaveraging of the tensor. It consists in replacing the tensor with its average over the equilibrium distribution (17). Using Eqs. (10), (11), and (17), we shall have

$$\left\langle H_{\alpha\beta nm}^\omega\right\rangle_0 = \left\langle A(r_{nm})\delta_{\alpha\beta} + B(r_{nm})\frac{r_{nm\alpha}r_{nm\beta}}{r_{nm}^2}\right\rangle = \frac{\delta_{\alpha\beta}}{6\pi\eta}\left\langle\frac{1}{r_{nm}}\exp(-\chi r_{nm})\right\rangle = \delta_{\alpha\beta}h^\omega(n-m). \tag{19}$$

The result of integration is

$$h^\omega(n-m) = \left(6\pi^3|n-m|\right)^{-1/2}(\eta a)^{-1}\left[1 - \sqrt{\pi}z\exp(z^2)\text{erfc}(z)\right], \qquad z \equiv \chi a\sqrt{\frac{|n-m|}{6}}. \tag{20}$$

In the case without memory [4] the function h at large $|n-m|$ behaves as $\sim|n-m|^{-1/2}$: the effective interaction between the beads slowly decreases when the distance between the beads increases. Here the correlation between the beads disappears more rapidly,

$$h^\omega(n-m) \approx \sqrt{\frac{3}{2\pi^2}}\frac{1}{-i\omega\rho a^2|n-m|^{3/2}}, \qquad |n-m| \to \infty. $$

Since Eq. (15) now contains only diagonal terms, in the continuum approximation it becomes

$$-i\omega\vec{x}^\omega(n) = \frac{1}{\xi^\omega}\left[\frac{3k_BT}{a^2}\frac{\partial^2\vec{x}^\omega(n)}{\partial n^2} + M\omega^2\vec{x}^\omega(n) + \vec{f}^\omega(n)\right]$$

$$+ \int_0^N dm\, h^\omega(n-m)\left[\frac{3k_BT}{a^2}\frac{\partial^2\vec{x}^\omega(m)}{\partial m^2} + M\omega^2\vec{x}^\omega(m) + \vec{f}^\omega(m)\right]. \tag{21}$$

This equation can be solved with the help of the FT in the variable n,

$$\bar{x}^{\omega}(n) = \bar{y}_0^{\omega} + 2\sum_{p=1}^{\infty} \bar{y}_p^{\omega} \cos\frac{\pi n p}{N}, \qquad \vec{f}_{\omega} = \vec{f}_0^{\omega} + 2\sum_{p=1}^{\infty} \vec{f}_p^{\omega} \cos\frac{\pi n p}{N}, \qquad (22)$$

where the boundary conditions at the ends of the chain have been taken into account [4],

$$\frac{\partial \bar{x}(t,n)}{\partial n} = 0 \text{ at } n = 0 \text{ and } n = N. \qquad (23)$$

The inverse FT yields the following equation for the Fourier components $\bar{y}_p^{\omega}$:

$$\bar{y}_p^{\omega} = \vec{f}_p^{\omega}\left[-i\omega\Xi_p^{\omega} - M\omega^2 + K_p\right]^{-1}, \qquad (24)$$

where we have denoted

$$\Xi_p^{\omega} = \xi^{\omega}\left[1 + (2-\delta_{p0})Nh_{pp}^{\omega}\right]^{-1}, \qquad K_p = \frac{3\pi^2 k_B T}{N^2 a^2}p^2, \qquad p = 0, 1, 2, \ldots \qquad (25)$$

The matrix h_{pp}^{ω} is defined by the expression

$$h_{pq}^{\omega} = \frac{1}{N^2}\int_0^N dn \int_0^N dm\, h^{\omega}(n-m)\cos\frac{\pi p n}{N}\cos\frac{\pi p m}{N}. \qquad (26)$$

In obtaining Eq. (25) we have already taken into account that the nondiagonal elements of the matrix are small in comparison with the diagonal ones and can be in the first approximation neglected. This "diagonalization approximation" has been proven in the case without memory [3, 4]. In our case it should be substantiated by numerical calculations. However, since we are interested in the long-time properties of the chain, only small ω corrections to the classical result for the Oseen tensor in the FT are expected to be the most important so that the approximation should possess at least qualitatively good results. The obtained equation (24) can be investigated as it is usually done in the theory of Brownian motion using the fluctuation-dissipation theorem (FDT) [18, 19] or the correlation properties of the forces $\vec{f}_p^{\omega}$ [20, 13]. The forces acting on different beads n and m are uncorrelated, so that their correlator is $\sim \delta_{nm}$. In going to the continuum approximation the Kronneker symbol δ_{nm} has to be replaced by the δ-function, $\delta(n-m)$, so that in the Fourier representation we obtain

$$\left\langle f_{p\alpha}^{\omega} f_{q\alpha}^{\omega}\right\rangle = \frac{k_B T}{(2-\delta_{p0})\pi N}\operatorname{Re}\Xi_p^{\omega}\delta_{\alpha\beta}\delta_{pq}\delta(\omega+\omega'). \qquad (27)$$

Equation (24) then yields the following expression for the time correlation function of the Fourier components $y_{\alpha p}$:

$$\psi_p(t) = \left\langle y_{\alpha p}(0)y_{\alpha p}(t)\right\rangle = \frac{k_B T}{(2-\delta_{p0})\pi N}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\frac{\operatorname{Re}\Xi_p^{\omega}}{\left|-i\omega\Xi_p^{\omega} - M\omega^2 + K_p\right|^2}, \qquad (28)$$

in agreement with the FDT [21]. The role of the generalized susceptibility is played by the quantity

$$\alpha_p(\omega) = \alpha_p'(\omega) + i\alpha_p''(\omega) = \left[(2-\delta_{p0})N\right]^{-1}\left[-i\omega\Xi_p^{\omega} - M\omega^2 + K_p\right]^{-1}, \qquad (29)$$

and the generalized forces corresponding to the coordinates $y_{p\alpha}^{\omega}$ are $Nf_{p\alpha}^{\omega}$. Then the FDT yields

$$\psi_p(t) = \frac{k_B T}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{\omega}e^{-i\omega t}\alpha_p''(\omega) = \frac{k_B T}{\pi i}\int_{-\infty}^{\infty}\frac{d\omega}{\omega}\alpha_p(\omega)\cos\omega t. \qquad (30)$$

It was used in the last equation that the real and imaginary parts of the susceptibility are the even and odd functions of ω, respectively. If we use also the Kramers-Kronig dispersion relation [21], the initial value of the function ψ_p at $t = 0$ follows immediately from Eq. (30):

$$\psi_p(0) = k_B T\alpha_p(0) = k_B T(2NK_p)^{-1}, \quad p > 0. \qquad (31)$$

Equation (30) gives the solution of the Rouse-Zimm model, within the approximations described, for the Fourier amplitudes of the correlation functions of the positions of beads. Knowing $\psi_p(t)$, other correlation functions of interest can be easily found from (30), e.g. the velocity autocorrelation function (VAF) or the mean square displacement (MSD),

$$\phi_p(t) = \left\langle v_\alpha(0)v_{\alpha p}(t)\right\rangle = -\frac{d^2\psi_p(t)}{dt^2}, \qquad \left\langle \Delta y_p^2(t)\right\rangle = 2\left[\psi_p(0) - \psi_p(t)\right]. \qquad (32)$$

III. The Rouse-Zimm limit without hydrodynamic memory

Consider first the case of the absence of hydrodynamic memory. In this approximation we simply put $\omega = 0$ in Eq. (25). For long-time properties we also neglect the inertial term in the equation of motion of the bead, so that $M = 0$. Since

$$\bar{y}_0(t) = \frac{1}{N}\int_0^N \bar{x}(t,n)dn, \qquad (33)$$

the mode y_0 describes the motion of the center of inertia of the coil. Equation (28) (or (30)) for this mode gives

$$\psi_0(0) - \psi_0(t) = \frac{2k_B T}{\pi N}\frac{1 + Nh_{00}^0}{\xi}\int_0^{\infty}d\omega\frac{1-\cos\omega t}{\omega^2} = \frac{k_B T}{N}\frac{1 + Nh_{00}^0}{\xi}t. \qquad (34)$$

The quantity h_{00}^0 is determined by Eq. (26). Hence, the diffusion coefficient of the whole coil is

$$D_C = k_B T \left(h_{00}^0 + \frac{1}{N\xi} \right), \tag{35}$$

and contains as special cases both the Zimm and Rouse limits,

$$D_C = k_B T h_{00}^0 = \frac{8 k_B T}{3\sqrt{6\pi^3 N} \eta a} \quad \text{(Zimm)}, \qquad D_C = \frac{k_B T}{N\xi} \quad \text{(Rouse)}. \tag{35a}$$

The internal modes ($p \neq 0$) relax exponentially,

$$\psi_p(t) = \frac{k_B T}{\pi N} \frac{1 + 2 N h_{pp}^0 \xi}{\xi} \int_0^\infty \frac{d\omega \cos \omega t}{\omega^2 + K_p^2 \left(1 + 2 N h_{pp}^0 \xi\right) \xi^{-2}} = \frac{k_B T}{2 N K_p} e^{-|t|/\tau_p}, \tag{36}$$

with the relaxation times τ_p,

$$\tau_p = \frac{\xi}{K\left(1 + 2 N h_{pp}^0 \xi\right)}, \qquad h_{pp}^0 = \frac{1}{\left(12\pi^3 N p\right)^{1/2} \eta a}. \tag{37}$$

IV. The "pure" Zimm model with hydrodynamic memory

Another important case is the Rouse limit. This limit assumes that the hydrodynamic interaction contribution to the quantity Ξ_p^ω from Eq. (25) is negligible for all ω. Accordingly, the subsequent equations change only by the substitution $\Xi_p^\omega \approx \xi^\omega$. The Rouse limit with memory is considered elsewhere [22]. Here we shall be interested in the "pure" Zimm model with memory. When the hydrodynamic interaction is strong for all frequencies that significantly contribute to the studied correlation functions, we have from Eq. (25)

$$\Xi_p^\omega \approx \left[\left(2 - \delta_{p0}\right) N h_{pp}^\omega\right]^{-1}. \tag{38}$$

However, the inertial effects of the viscous solvent are still included into the consideration. The Oseen matrix (26) can be calculated with arbitrary degree of precision, e.g. for $p = 0$ we have the exact result

$$h_{00}^\omega = \frac{3\sqrt{\pi}}{4\tilde{z}} h_{00}^0 \left[1 - \frac{2}{\sqrt{\pi}\tilde{z}} - \frac{1}{\tilde{z}}\left(e^{\tilde{z}^2} \text{erfc}\tilde{z} - 1\right)\right], \qquad \tilde{z} \equiv \sqrt{\frac{N}{6}} \chi a. \tag{39}$$

Then the susceptibility (29) may be written as a fraction of two polynomials of the small variable $(-i\omega)^{1/2}$. Since the polynomial in the denominator is of a higher order, the susceptibility can be represented as a sum of simple fractions $A_l / [(-i\omega)^{-1/2} - \alpha_l]$, where α_l are the simple roots of the polynomial in the denominator. The correlation functions can be then in

the t-representation expressed through the error functions. Their asymptotic expansions allow us to find the main contributions to the long-time behavior of the functions of interest. Here we shall not give this cumbersome procedure and show only the main terms of the asymptotic expansion of the time correlation functions.

In the case of the diffusion of the coil as a whole we obtain

$$\psi_0(0) - \psi_0(t) \approx D_C \left[t - \left(\frac{3N\rho}{32\eta}\right)^{1/2} t^{1/2} + \ldots\right] = D_C \left[t - \frac{2}{\sqrt{\pi}}\left(\tau_R t\right)^{1/2} + \ldots\right], \tag{40}$$

where D_C is the Zimm diffusion coefficient determined in Eq. (35). The second equality is written exactly in the form familiar in the theory of Brownian motion of rigid particles. The characteristic time $\tau_R = R^2 \rho / \eta$ is expressed through the hydrodynamic radius of the Zimm coil, determined from the relation $D_C = k_B T / 6\pi R \eta$. In the standard model of Gaussian chains the radius R coincides with the expression [10] (note the incorrect determination of R and D_C, Eq. (15a), in Ref. [4])

$$R^{-1} = N^{-2} \left\langle \sum_{n=1}^N \sum_{m=1, m\neq n}^N r_{nm}^{-1} \right\rangle \approx \sqrt{\frac{2}{3\pi N}} \frac{8}{a}, \tag{41}$$

valid for $N \gg 1$, when the summation can be replaced by integration. Consider now the internal modes of the polymer, $p \geq 1$. The calculation of the Oseen matrix is now more complicated but for our purposes the corresponding integral in Eq. (26) simplifies to [4]

$$h_{pp}^\omega \approx \frac{1}{N} \int_0^N h^\omega(s) \cos \frac{\pi p s}{N} ds, \tag{42}$$

and can be expressed through special functions [23], so that its expansion is known to any desired power of $(-i\omega)^{1/2}$. The first correction to the results of the model without memory is determined by the coefficient at the term $\sim (-i\omega)$. The first nonvanishing correction to the susceptibility $\alpha_p(\omega)$ from Eq. (29) is given by the term $\sim (-i\omega)^{5/2}$. The coefficient at this term is determined only by the expansion coefficients of the terms proportional to $(-i\omega)$ and $(-i\omega)^{3/2}$ in the expansion of h_{pp}^ω. Using any of Eqs. (30), we thus find for the correlation function $\psi_p(t)$

$$\frac{\psi_p(t)}{\psi_p(t)} \approx -\frac{2^9}{45\pi^3} \sqrt{\frac{2}{\pi}} \left(1 + \frac{16}{3\pi^2 p} \frac{\tau_R}{\tau_p}\right) \frac{1}{p^3} \frac{\tau_p}{\tau_R} \left(\frac{\tau_R}{t}\right)^{5/2}, \qquad \tau_p = \frac{\left(N^{1/2} a\right)^3 \eta}{\left(3\pi p^3\right)^{1/2} k_B T}, \tag{43}$$

where $p \geq 1$, $t \gg \tau_R$, and τ_p is the Zimm relaxation time (37).

Finally, we give here the result for the Van Hove function that is used in the description of the dynamic light or neutron scattering from a polymer coil,

$$G(\vec{k}, t) = \frac{1}{N} \sum_{m,n} \left\langle \exp\left\{i\vec{k}\left[\vec{x}_n(t) - \vec{x}_m(0)\right]\right\}\right\rangle. \tag{44}$$

Here $\vec{k}$ is the change of the wave vector at the scattering. Acting in a similar way as in Ref. [3] but taking into account that our solutions are obtained for large t, Eq. (44) can be approximated by the expression

$$G(k,t) \approx N \exp\{-k^2[\psi_0(0) - \psi_0(t)]\} \exp\left[-\frac{Na^2k^2}{36}\left(1 - \frac{8}{3\pi^6}\sum_{p=2,4,...}^{\infty}\frac{\psi_p(t)}{\psi_p(0)}\frac{1}{p^6}\right)\right], \qquad (45)$$

valid for $kR \ll 1$ (in the opposite case the Van Hove function becomes very small at large times). One can see from this equation that the contribution of the internal modes is small and thus hardly detectable in experiments. However, our predictions concerning the diffusion of the coil as a whole, could be directly measured in the scattering experiments. The diffusion contribution dominates at the times $t \gg \tau_D$, where the characteristic time for the diffusion is $\tau_D = R^2/D_C$ (see Eqs.(35a) and (41)).

V. Conclusion

We can conclude that in the generalized Zimm model, when the inertia of the viscous solvent is taken into account, the relaxation of the correlation functions that describe the polymer motion essentially differs from the original model. The diffusion of the polymer coil as a whole is described by the mean square displacement that, similarly to the Rouse model with hydrodynamic memory [22], at long times contains additional (to the Einstein term $\sim t$) contributions, the leading of which is $\sim t^{1/2}$. The internal modes of the polymer motion now do not relax exponentially. As distinct from the Brownian motion of one rigid particle, as well as from the motion of Rouse polymers with the memory, the longest-lived contribution to the correlation function of the bead displacement in the Fourier representation is $\sim t^{-5/2}$, while in the former cases it was $\sim t^{-3/2}$. We believe that it would be interesting to investigate the found peculiarities in the behavior of the time correlation functions experimentally, e.g. by the dynamic light or neutron scattering. Due to the long-range character of the hydrodynamic field, the characteristic time of the model, $\tau_R = R^2\rho/\eta$, connected with the size of the whole polymer coil, is for many macromolecules [8] sufficiently large from the point of view of the experiments. The differences from the original Zimm model thus seem to be experimentally accessible. This could help to solve the existing "puzzles" in the description of the dynamic scattering experiments on polymers [8, 10, 11]. The obtained theoretical results can be also tested using the methods of computer simulations.

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