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### **Long-time tails in the dynamics of polymers in dilute solutions with hydrodynamic memory**

The dynamics of polymers in dilute solutions is studied taking into account the hydrodynamic memory, as a consequence of fluid inertia. As distinct from the Rouse-Zimm (RZ) theory, the Boussinesq friction force acts on the monomers (beads) instead of the Stokes force, and the motion of the solvent is governed by the nonstationary Navier-Stokes equations. The obtained generalized RZ equation is solved in the continuum approximation. It is shown that the time correlation functions describing the polymer motion essentially differ from those in the RZ model. In particular, as  $t \rightarrow \infty$ , they contain long-time tails.

Most of the theoretical investigations on the dynamics of flexible polymers are based on the Rouse-Zimm (RZ) model [1 — 4]. In this theory the polymer molecule is modeled as a chain of beads under Brownian motion. The beads interact with the neighbors along the chain and with the solvent. The solvent contributes a frictional force against the motion of a monomer and a random force due to the random collisions exerted on monomers. In the Rouse model, the solvent is considered as nonmoving. Within the Zimm theory, the motion of each monomer also affects other monomers, by way of the flow it induces in the ambient medium. The Zimm model predicts the correct dynamical behavior for dilute polymer solutions in  $\theta$ -conditions. The Rouse model is applicable for good solvents, where the corrections due to the hydrodynamic interactions and excluded volume effects cancel each other to a large extent, or in situations when the surrounding polymers screen out the hydrodynamic interactions [3, 4]. Both models assume Gaussian equilibrium distribution of the beads. The models hold for polymer properties, which involve length scales large compared to monomer sizes. Although the RZ model has been proven as a universal theory well describing the long-time behavior of the polymer macromolecules, there is still a number of unresolved problems in the understanding of the polymer dynamics in solution [5 — 7]. For example, the diffusion coefficient calculated from the continuous RZ model systematically deviates from the experimental values for both the natural and synthetic macromolecules.

In the present work we propose a generalization of the RZ theory 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 is considered solving the nonstationary Navier-Stokes

equations. The resistance force on the moving bead is assumed not the Stokes one, proportional to the velocity of the bead. We model this force by the Boussinesq friction force [8], which, at a given time  $t$ , is determined by the state of the bead motion in all the preceding moments of time. We thus have a possibility to obtain solutions valid for almost arbitrary  $t$  (for incompressible fluids, however,  $t \gg b/c$ , where  $b$  is the monomer size and  $c$  the sound velocity). In other words, the effects of hydrodynamic memory are taken into account. Such effects have been extensively studied in the physics of simple liquids and in the theory of Brownian motion (see e.g. Ref. [9]) with very important consequences. In particular, the memory effects reveal in the famous long-time “tails” of the velocity autocorrelation function (VAF), first discovered by means of computer experiments [10, 11]. The concept of the Brownian motion lies in the basis of the RZ theory of polymer dynamics. It is thus natural to expect that the memory effects will be important for polymers as well.

Within the RZ model the motion of the  $n$ th polymer segment (the bead) is described by the equation

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

Here,  $\vec{x}$  is the position vector of the bead,  $M$  is its mass,  $\vec{f}_n^{ch}$  is the force from the neighboring beads along the chain,  $\vec{f}_n$  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. In the RZ model the latter force was

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

with  $\vec{v}(\vec{x}_n)$  being the velocity of the solvent in the place of the  $n$ th 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  $\eta$  is the solvent viscosity. However, this expression holds only in the case of steady-state flow. In the general case the resistance against a body depends on the whole history of its motion, i.e. on velocities and accelerations in the preceding moments of time. We use, for incompressible fluids, instead of Eq. (2) the Boussinesq force [8, 12, 13]. This means to replace, in the Fourier representation with respect to the time, the friction coefficient  $\xi$  with a frequency dependent quantity

$$\xi^\omega = \xi \left[ 1 + \chi b + \frac{1}{9} (\chi b)^2 \right], \quad (3)$$

where  $\rho$  is the solvent density and  $\chi = \sqrt{-i\omega\rho/\eta}$ ,  $\text{Re}\chi > 0$ . Equations (1 — 3) have to be solved together with the hydrodynamic equations for the velocity of the solvent,

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

Here  $p$  is the pressure. The quantity  $\bar{\varphi}$  is an external force per unit volume [4],

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

The solution of Eqs. (4) can be, for any of the Cartesian component  $\alpha$  ( $x$ ,  $y$ , or  $z$ ), written in the form

$$v_\alpha^\omega(\bar{r}) = \int d\bar{r}' \sum_\beta H_{\alpha\beta}^\omega(\bar{r} - \bar{r}') \varphi_\beta^\omega(\bar{r}'), \quad (6)$$

with the Fourier transformation (FT) of the Oseen tensor [15]

$$H_{\alpha\beta}^\omega(\bar{r}) = A \delta_{\alpha\beta} + B \frac{r_\alpha r_\beta}{r^2}, \quad (7)$$

$$A = (8\pi\eta r)^{-1} \left\{ e^{-y} - y \left[ (1 - e^{-y}) y^{-1} \right]'' \right\},$$

$$B = (8\pi\eta r)^{-1} \left\{ e^{-y} + 3y \left[ (1 - e^{-y}) y^{-1} \right]'' \right\}. \quad (8)$$

Here  $y = r\chi$  (3) and the prime ' denotes the differentiation with respect to  $y$ . Substituting  $\varphi_\beta^\omega$  from the FT of Eq. (5) to  $v_\alpha^\omega$  from (6), and the result into the FT of equation of motion (1), we obtain a generalization of the RZ equation, which in the continuum approximation reads

$$-i\omega x_{n\alpha}^\omega = \frac{1}{\xi^\omega} \left[ f_\alpha^{ch,\omega}(n) + f_\alpha^\omega(n) + M\omega^2 x_\alpha^\omega(n) \right] + \int_0^N dm H_{\alpha\beta nm}^\omega \left[ \frac{3k_B T}{a^2} \frac{\partial^2 x_\beta^\omega}{\partial m^2} + f_\beta^\omega(m) + M\omega^2 x_\beta^\omega(m) \right]. \quad (9)$$

Here  $a$  is the mean square distance between neighboring beads along the chain. We have used that the force between the beads can be obtained from the effective potential  $u = (3k_B T / 2a^2) \sum_{n=2}^N (\bar{x}_n - \bar{x}_{n-1})^2$ , which follows from the equilibrium distribution of the beads [4],  $P(r_{nm}) = (2\pi a^2 |n-m|/3)^{-3/2} \exp[-3r_{nm}^2 / (2a^2 |n-m|)]$ . Due to the dependence of the Oseen tensor on the difference  $\vec{r}_{nm} \equiv \bar{x}_n - \bar{x}_m$ , Eq. (9) is nonlinear

and thus hardly solvable analytically. We use the common approach, preaveraging the Oseen tensor over  $P(r_{nm})$  that gives:

$$\langle H_{\alpha\beta nm}^\omega \rangle_0 = \delta_{\alpha\beta} h^\omega(n-m), \quad (10)$$

$$h^\omega(n-m) = (6\pi^3 |n-m|)^{-1/2} (\eta a)^{-1} [1 - \sqrt{\pi} z \exp(z^2) \operatorname{erfc}(z)],$$

with  $z \equiv \chi a (|n-m|/6)^{1/2}$ . In the case without memory [4] the function  $h$  at large  $|n-m|$  behaves as  $\sim |n-m|^{-1/2}$ ; now the effective interaction between the beads disappears more rapidly,  $\sim |n-m|^{-3/2}$ . Since Eq. (9) contains only the diagonal terms, it can be solved using the FT in the variable  $n$ ,  $\bar{x}^\omega(n) = \bar{y}_0^\omega + 2 \sum_{p \geq 1} \bar{y}_p^\omega \cos(\pi np/N)$ , where the boundary conditions at the ends of the chain have been taken into account [4],  $\partial \bar{x}(t, n)/\partial n = 0$  at  $n = 0, N$ . The inverse FT then yields the following equation for the Fourier components  $\bar{y}_p^\omega$ :

$$\bar{y}_p^\omega = \bar{f}_p^\omega [-i\omega \Xi_p^\omega - M\omega^2 + K_p]^{-1}, \quad (11)$$

where  $\Xi_p^\omega = \xi^\omega [1 + (2 - \delta_{p0}) N h_{pp}^\omega]^{-1}$ , and  $K_p = 3\pi^2 p^2 k_B T / (Na)^2$ ,  $p = 0, 1, 2, \dots$ . The matrix  $h_{pp}^\omega$  is defined by the expression

$$h_{pq}^\omega = \frac{1}{N^2} \int_0^N dn \int_0^N dm h^\omega(n-m) \cos \frac{\pi pn}{N} \cos \frac{\pi pm}{N}. \quad (12)$$

In obtaining Eq. (11) it has been 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; the substantiation of this is the same as in Ref. [3, 4]. Equation (11) can be investigated as it is usually done in the theory of Brownian motion using the fluctuation-dissipation theorem (FDT) [14] or the properties of the forces  $\bar{f}_p^\omega$  [9]. 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 Kronecker symbol  $\delta_{nm}$  has to be replaced by the  $\delta$ -function,  $\delta(n-m)$ . Thus, in the Fourier representation we have

$$\langle f_{p\alpha}^\omega f_{q\alpha}^\omega \rangle = \frac{k_B T}{(2 - \delta_{p0}) \pi N} \operatorname{Re} \Xi_p^\omega \delta_{\alpha\beta} \delta_{pq} \delta(\omega + \omega'). \quad (13)$$

Equation (11) then yields the following expression for the time correlation function  $\psi_p(t) = \langle y_{\alpha p}(0) y_{\alpha p}(t) \rangle$ :

$$\psi_p(t) = \frac{k_B T}{(2 - \delta_{p0}) \pi N} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \frac{\text{Re} \Xi_p^\omega}{|-i\omega \Xi_p^\omega - M\omega^2 + K_p|^2}, \quad (14)$$

in agreement with the FDT [13, 14]. The generalized susceptibility is  $\alpha_p(\omega) = [(2 - \delta_{p0})N]^{-1} \times [-i\omega \Xi_p^\omega - M\omega^2 + K_p]^{-1}$ , and the forces corresponding to the coordinates  $y_{p\alpha}^\omega$  are  $Nf_{p\alpha}^\omega$ . Using the Kramers-Kronig dispersion relation [13], the same initial value of the function  $\psi_p$  at  $t = 0$  as in the RZ theory is immediately obtained:  $\psi_p(0) = k_B T \alpha_p(0) = k_B T (2NK_p)^{-1}$ ,  $p > 0$ . Equation (14) gives the solution of the model, for the Fourier amplitudes of the correlation functions of the positions of beads. Knowing  $\psi_p(t)$ , other correlation functions of interest can be found, e.g. the VAF  $\phi_p(t) = \langle v_\alpha(0)v_{\alpha p}(t) \rangle = -d^2\psi_p(t)/dt^2$ , or the mean square displacement (MSD),  $\langle \Delta y_p^2(t) \rangle = 2[\psi_p(0) - \psi_p(t)]$ . The previous RZ results are obtained putting  $\omega = 0$  in  $\Xi_p^\omega$ , Eq. (11), and neglecting the inertial term in the equation of motion of the bead, so that  $M = 0$ . The mode  $y_0$  describes the motion of the center of inertia of the coil [4]. In the RZ case one obtains  $\psi_0(0) - \psi_0(t) = D_C t$ . The diffusion coefficient  $D_C = k_B T (h_{00}^0 + 1/N\xi)$  contains the Zimm ( $D_C = k_B T h_{00}^0 = 8k_B T (3\sqrt{6\pi^3 N\eta a})^{-1}$ ) and Rouse ( $D_C = k_B T/N\xi$ ) limits. The internal modes ( $p \neq 0$ ) relaxed exponentially,  $\psi_p(t) = (k_B T/2NK_p) \exp(-t/\tau_p)$ , with the relaxation times  $\tau_p$ ,  $\tau_p = \xi / [K_p (1 + 2Nh_{pp}^0 \xi)]$ , where  $h_{pp}^0 = (12\pi^3 Np)^{-1/2} (\eta a)^{-1}$ .

For the solution of the Rouse case with memory (when the hydrodynamic interaction contribution in Eq. (11) is negligible for all  $\omega$ ) we refer to our recent work [16]. In the Zimm model, when the hydrodynamic interaction is strong for all frequencies that significantly contribute to the studied correlation functions, we have in Eq. (11)  $\Xi_p^\omega \approx [(2 - \delta_{p0})Nh_{pp}^\omega]^{-1}$ . The Oseen matrix (12) can be calculated with arbitrary degree of precision, e.g. for  $p = 0$  we have the exact result

$$h_{00}^\omega = \frac{3\sqrt{\pi}}{4\tilde{z}} h_{00}^0 \left[ 1 - \frac{2}{\sqrt{\pi}\tilde{z}} - \frac{1}{\tilde{z}} (e^{-\tilde{z}^2} \text{erfc}\tilde{z} - 1) \right], \quad (15)$$

where  $\tilde{z} \equiv (N\chi a/6)^{1/2}$ . Then the correlation functions can be in the  $t$ -representation calculated using the standard methods of the theory of Brownian motion [9]. Here we show the main terms of the asymptotic expansion of the time correlation functions that

can be obtained also using the expansion of the susceptibility  $\alpha_p(\omega)$  in small  $(-i\omega)^{1/2}$ . In the case of the diffusion of the coil as a whole we obtain the expression

$$\psi_0(0) - \psi_0(t) = D_C \left[ t - \frac{2}{\sqrt{\pi}} (\tau_R t)^{1/2} + \dots \right], \quad (16)$$

where  $D_C$  is the Zimm diffusion coefficient. The characteristic time  $\tau_R = R^2\rho/\eta$  is expressed through the hydrodynamic radius of the coil [3, 4]. Consider now the internal modes of the polymer,  $p \geq 1$ . The components of the matrix (12) are calculated as in Ref. [4], and can be expressed through special functions, so that their 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  $\alpha_p(\omega)$  is given by the term  $\sim (-i\omega)^{5/2}$ . The coefficient at this term is determined by the expansion coefficients of the terms proportional to  $(-i\omega)$  and  $(-i\omega)^{3/2}$  in the expansion of  $h_{pp}^{\omega}$ . Using Eq. (15), we thus find for the correlation function  $\Psi_p(t)$

$$\frac{\Psi_p(t)}{\Psi_p(0)} \approx -\frac{2^9}{45\pi^3} \sqrt{\frac{2}{\pi}} \left( 1 + \frac{16}{3\pi^2} \frac{\tau_R}{p \tau_p} \right) \frac{1}{p^3} \frac{\tau_p}{\tau_R} \left( \frac{\tau_R}{t} \right)^{5/2}, \quad (17)$$

where  $p \geq 1$ ,  $t \gg \tau_R$ , and  $\tau_p = (N^{1/2}a)^3(\eta/k_B T)/(3\pi p^3)^{1/2}$  is the Zimm relaxation time.

Finally, we give the result for the intermediate scattering function  $G(\vec{k}, t)$  that is used in the description of the dynamic light or neutron scattering from a polymer coil [3] ( $\vec{k}$  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  $t$ , it can be approximated by the expression

$$G(k, t) \approx N \exp\{-k^2 [\psi_0(0) - \psi_0(t)]\} \times \exp\left[-\frac{Na^2k^2}{36} \left( 1 - \frac{8N^2a^4k^4}{3\pi^6} \sum_{p=2,4,\dots}^{\infty} \frac{\Psi_p(t)}{\Psi_p(0)} \frac{1}{p^6} \right)\right] \quad (18)$$

valid for  $kR \ll 1$  (in the opposite case the function  $G(k, t)$  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 against the diffusion term given by the first exponent. 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  $\tau_D = R^2/D_C$ .

We conclude that in the generalized RZ model, when the memory of the viscous solvent is taken into account, the relaxation of the correlation functions describing the polymer motion essentially differs from the original theory. The MSD at small times

is  $\sim t^2$  (instead of  $\sim t$ ). At long times it contains additional (to the Einstein term) contributions, the leading of which is  $\sim t^{1/2}$ . The internal modes of the polymer motion now do not relax exponentially. The longest-lived contribution to the correlation function of the bead displacement is  $\sim t^{-3/2}$  in the Rouse case [16], and  $\sim t^{-5/2}$ , when the hydrodynamic interaction is strong. The found peculiarities can be investigated 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 Zimm model,  $\tau_R = R^2\rho/\eta$  is connected with the size of the whole polymer coil and sufficiently large from the point of view of the experiments. The differences from the original model thus seem to be experimentally accessible. As seen from Eq. (17) and (18), the tails in the MSD lead to a slower decay of the scattering function. This corresponds to diffusion with an effectively smaller diffusion coefficient than predicted by the previous theory. This was one of the unresolved “puzzles” between the theory and experiments. We believe that the presented theory could help to solve this and other existing problems in the interpretation of the dynamic scattering experiments on polymers [5 — 7] and thus to contribute to a deeper understanding of the dynamical properties of polymers.

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**Долговременные хвосты в динамике полимеров в разбавленных растворах с гидродинамической памятью**

**АННОТАЦИЯ**

Изучается динамика полимеров в разбавленных растворах с учетом гидродинамической памяти как следствия инерционных свойств жидкости. В отличие от теории Рауза-Зимма, вместо Стоксовой силы на мономеры (бусинки) действует сила трения Буссинэ, а движение растворителя описывается нестационарным уравнением Навье-Стокса. Получено обобщенное уравнение Рауза-Зимма для векторов положений полимерных звеньев. В континуальном приближении найдены временные корреляционные функции, описывающие движение полимера. Показано, что инерционные свойства вязкого растворителя существенно влияют на поведение этих функций. Релаксация внутренних мод полимера отличается от традиционной экспоненциальной, а диффузия клубка как целого не эйнштейновская. Это демонстрируется асимптотикой среднеквадратичного смещения клубка, которое при  $t \rightarrow \infty$  содержит дополнительный "хвост"  $\sim t^{1/2}$ . В корреляционных функциях внутренних мод также появляются хвосты, из которых наиболее долго живущий пропорционален  $t^{-5/2}$ . В пределе больших времен найден динамический структурный фактор рассеяния Ван Хофа.

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**Довгочасові хвости у динаміці полімерів разбавлених розчинів з гідродинамічною пам'яттю**

**АННОТАЦІЯ**

Вивчається динаміка полімерів у разбавлених розчинах з врахуванням гідродинамічної пам'яті як наслідка інерційних властивостей рідини. На відміну від теорії Рауза-Зімма, замість сили Стокса на бусинки діє сила тертя Бусинє, а рух розчинника підкоряється нестационарним рівнянням Нав'є-Стокса. Одержано узагальнене рівняння Рауза-Зімма для векторів положення ланки полімера. У континуальному наближенні знайдені часові кореляційні функції, які описують рух полімера. Показано, що інерційні властивості в'язкого розчинника суттєво впливають на поведінку цих функцій. Релаксація внутрішніх мод полімера відрізняється від традиційної експоненти, а дифузія клубка як цілого не ейнштейнова. Це демонструється асимптотикою середньоквадратичного зміщення клубка, яке при  $t \rightarrow \infty$  має додатковий "хвіст"  $\sim t^{1/2}$ . Вивчена також часова асимптотика динамічного структурного фактора розсіювання Ван Хофа.