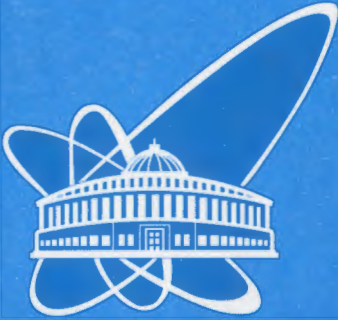


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J. Tothova<sup>1</sup>, V. Lisy<sup>1</sup>, A. V. Zatovsky<sup>2</sup>

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LONG-TIME TAILS  
IN THE DYNAMICS OF ROUSE POLYMERS

<sup>1</sup>Permanent address: Institute of Physics, P. J. Safarik University,  
041 54 Kosice, Slovakia

<sup>2</sup>Permanent address: Department of Theoretical Physics,  
I. I. Mechnikov Odessa National University, 65026 Odessa, Ukraine

Fifty years after the appearance of the famous work by P.E. Rouse<sup>1</sup> his model continues to play an important role in investigations of the dynamics of polymers. There are several reasons why this model is still so popular. From the methodological point of view, it can be easily shown that the model is universal in the sense that it describes the long-time motion of ideal phantom polymers in nonmoving solvent independently on the details of their structure.<sup>2,3</sup> This is not so easy to prove for more sophisticated models, e.g. the Zimm model<sup>4</sup> that includes the hydrodynamic interaction. The Zimm model predicts the correct dynamical behavior for dilute polymer solutions in  $\theta$ -conditions. However, 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<sup>5</sup>. The dynamical behavior of macromolecules in semidilute solutions and polymer melts is also better described by the Rouse theory, since there the hydrodynamic interactions are screened out by the surrounding polymers. It is also very important that the model is analytically tractable and open for various generalizations. During the passed years much effort has been devoted to improve the classical Rouse and Zimm models. Despite this, still some problems in the polymer dynamics remain unsolved (for good reviews on the development of the Rouse-Zimm theory and existing problems we refer to the recent works<sup>6-8</sup>).

In the present communication we propose a generalization of the original Rouse model, that takes into account the viscous aftereffect during the motion of the polymer monomers (modeled by spherical beads) in the viscous incompressible fluid. In other words, we include into the consideration the hydrodynamic memory. It reflects the fact that the force on the bead at a given moment of time depends not only on the bead velocity at the same moment of time, but is influenced by the state of its motion in all the preceding times. This is a consequence of fluid inertia and its possible importance for the Rouse model has been already mentioned in Ref.<sup>9</sup> but, to our knowledge, such a generalization did not appear in the literature so far. It is well known that in the theory of Brownian motion the hydrodynamic memory leads to interesting peculiarities, such as the famous long-time tails of the velocity autocorrelation function, with a very important impact on the physics of liquids.<sup>10</sup> Since the Brownian motion lies in the basis of the Rouse-Zimm theory of polymer dynamics, it is natural to expect that the mentioned generalization will be important for polymers as well.

Within the Rouse model of flexible polymer in solution the equation of motion for the  $n$ th bead of the coil consisting of  $N$  beads is

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

Here  $M$  is the mass of the bead,  $\bar{f}_n^{fr}$  is the resistance force on the bead during its motion in

the solvent - the Stokes force that is proportional to the velocity of the bead,  $\bar{f}_n^{ch}$  describes the influence of other beads, and  $\bar{f}_n$  is the random force due to the chaotic motion of the molecules of solvent. The effective potential of interaction between the beads follows from their equilibrium (Gaussian) distribution, so that<sup>3</sup>

$$u = \frac{3k_B T}{2a^2} \sum_{n=2}^N (\bar{x}_n - \bar{x}_{n-1})^2, \quad (2)$$

thus the neighboring beads along the chain act on the  $n$ th bead with the force

$$\bar{f}_n^{ch} = -\frac{\partial u}{\partial \bar{x}_n} = \frac{3k_B T}{2a^2} (\bar{x}_{n+1} - 2\bar{x}_n + \bar{x}_{n-1}). \quad (3)$$

The quantity  $a$  has the sense of the mean square distance between the neighbors along the chain. For long-wave processes the continuum approximation in the variable  $n$  is used,  $\bar{x}_n(t) \rightarrow \bar{x}(t, n)$ ,  $\bar{x}_{n\pm 1}(t) \rightarrow \bar{x}(t, n) \pm \partial \bar{x} / \partial n + (1/2) \partial^2 \bar{x} / \partial n^2$ . The force  $\bar{f}_n^{ch}$  in this approximation reads

$$\bar{f}_n^{ch} \rightarrow \frac{3k_B T}{a^2} \frac{\partial^2 \bar{x}(t, n)}{\partial n^2}. \quad (4)$$

The Rouse equation (1) must be in the continuum limit supplemented by boundary conditions. They follow from the modification of the force  $\bar{f}_n^{ch}$  due to the fact that at the ends of the chain the beads have only one neighboring bead:<sup>3</sup>

$$\frac{\partial \bar{x}(t, n)}{\partial n} = 0 \text{ at } n = 0, n = N. \quad (5)$$

In the original Rouse model (if the inertial term in Eq. (1) is neglected) we come to a diffusion-type equation for the vector  $\bar{x}_n(t)$  with the boundary conditions (5).

In our approach we use as the resistance force on the particle (a rigid sphere) moving in an incompressible fluid, instead of the Stokes force in Eq. (1), a more correct Boussinesq force. For any of the Cartesian components, e.g.,  $x$ , this force can be written in the form:<sup>11</sup>

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

where  $M'$  is the "effective hydrodynamic mass" ( $= M_s/2$  with  $M_s$  being the mass of the solvent with the same volume as the bead),  $\rho$  is the solvent density,  $\eta$  its viscosity,  $b$  the radius of the bead, and its friction coefficient is  $\xi = 6\pi\eta b$ . The Fourier transform (FT) of this

force in the time ( $f^{fr, \omega} = (1/2\pi) \int_{-\infty}^{+\infty} f^{fr}(t) \exp(i\omega t) dt$ ) is

$$f^{fr, \omega} = -\xi^\omega v^\omega, \quad \xi^\omega = \xi \left[ 1 + \chi b + \frac{1}{9} (\chi b)^2 \right], \quad \chi = \sqrt{-i\omega/\nu}. \quad (7)$$

Here  $\text{Re} \chi \geq 0$  is the inverse penetration depth of the shear wave and  $\nu = \eta/\rho$  is the kinematic viscosity of the solvent. Using Eq. (7), the modified Rouse equation in the FT for every of the Cartesian components of the position vector  $\bar{x}$  in the continuum approximation becomes

$$x^\omega(n) (-i\omega \xi^\omega - M\omega^2) = \frac{3k_B T}{a^2} \frac{\partial^2 x^\omega(n)}{\partial n^2} + f^\omega(n). \quad (8)$$

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

$$x^\omega(n) = y_0^\omega + 2 \sum_{p=1}^{\infty} y_p^\omega \cos \frac{\pi p n}{N}, \quad f^\omega = f_0^\omega + 2 \sum_{p=1}^{\infty} f_p^\omega \cos \frac{\pi p n}{N}. \quad (9)$$

In this representation we obtain the following equations for the Fourier components  $y_p^\omega$ :

$$y_p^\omega = (-i\omega \xi^\omega - M\omega^2 + K_p)^{-1} f_p^\omega, \quad p = 0, 1, 2, \dots \quad (10)$$

Here it is denoted

$$K_p = \frac{3\pi^2 k_B T}{N^2 a^2} p^2. \quad (11)$$

Consider separately the equations for  $p = 0$  and  $p \geq 1$ . In the first case, since from Eq. (9)

$$y_0(t) = \frac{1}{N} \int_0^N x(t, n) dn, \quad (12)$$

Equation (10) determines the FT of the coordinate of the center of inertia of the polymer coil. In the absence of the hydrodynamic memory the mean square displacement (MSD) of the Rouse coil as a whole is given by the Einstein relation

$$\langle \Delta y_0^2(t) \rangle = \langle [y_0(0) - y_0(t)]^2 \rangle = 2D_C t, \quad (13)$$

where  $D_C$  is the diffusion coefficient of the coil,  $D_C = D/N$ , and  $D = k_B T/\xi$  is the diffusion coefficient for one bead.

Equation (10) at  $p \geq 1$  determines internal modes of the polymer motion. Within the model without memory the time correlation functions of the Rouse modes relax exponentially with the relaxation times  $\tau_p$ ,

$$\psi_p(t) = \langle y_p(0)y_p(t) \rangle = D_C \tau_p e^{-t/\tau_p}, \quad \tau_p = \frac{N^2 a^2 \xi}{3\pi^2 k T p^2} = \frac{\xi}{K_p}, \quad p \geq 1. \quad (14)$$

To find the time correlation functions of the position of center of inertia and the internal modes of the polymer, one can use the correlation properties of the random force  $\bar{f}_n$  in its Fourier  $p$ -representation. The correlation functions of the Langevin forces for one Brownian particle are well known. They have been proven, for instance, in the work<sup>12</sup>, and are a consequence of the fluctuation-dissipation theorem.<sup>13</sup> For different components of the force we have in the Fourier representation

$$\langle f_\alpha^\omega f_\beta^{\omega'} \rangle = \frac{k_B T}{\pi} \text{Re} \xi^\omega \delta_{\alpha\beta} \delta(\omega - \omega'). \quad (15)$$

Since the forces acting on different beads  $n \neq m$ , are independent, their correlator is  $\sim \delta_{nm}$ . In the continuum limit the Kronecker symbol has to be replaced by the delta function,  $\delta_{nm} \rightarrow \delta(n-m)$ . Then, after the transition to the  $p$ -representation, one obtains

$$\langle f_{p\alpha}^\omega f_{q\beta}^{\omega'} \rangle = \frac{k_B T}{(2 - \delta_{p0}) \pi N} \text{Re} \xi^\omega \delta_{\alpha\beta} \delta_{pq} \delta(\omega - \omega'). \quad (16)$$

Now it is easy to find from Eq. (10) expressions for the desired correlation functions  $\langle \Delta y_0^2(t) \rangle$ ,  $\psi_p(t)$ , or for the velocity autocorrelation function (VAF) that is often used in the description of experiments or in computer simulations,

$$\phi_p(t) = \langle v_p(0)v_p(t) \rangle = \frac{1}{2} \frac{d^2}{dt^2} \langle \Delta y_p^2(t) \rangle. \quad (17)$$

For the function  $\psi_p(t)$  we find from Eq. (10),

$$\psi_p(t) = \frac{k_B T}{(2 - \delta_{p0}) \pi N} \int_{-\infty}^{+\infty} d\omega \frac{\text{Re} \xi^\omega}{|-i\omega \xi^\omega - M\omega^2 + K_p|^2} \cos \omega t. \quad (18)$$

Equation (18) represents the fluctuation-dissipation theorem<sup>13</sup> for the Rouse chain of  $N$  beads. The integral in this equation is often encountered in the theory of translational Brownian motion of one particle: in the case  $p = 0$  the particle is free, and if  $p \neq 0$ , it is in a harmonic field with the force constant  $K_p$ . Such problems for a particle in incompressible fluid were solved in a number of investigations beginning from the work<sup>14</sup> where the first hydrodynamic theory of the Brownian motion has been developed. Adopting the known solutions for our functions describing the Rouse polymer, we have for the MSD of the polymer coil the

following asymptotic expression:

$$\langle \Delta y_0^2(t) \rangle = 2D_C t \left[ 1 - \frac{2}{\sqrt{\pi}} \left( \frac{\tau_b}{t} \right)^{1/2} + \frac{2}{9} \left( 4 - \frac{M}{M_s} \right) \frac{\tau_b}{t} - \frac{1}{9\sqrt{\pi}} \left( 7 - 4 \frac{M}{M_s} \right) \left( \frac{\tau_b}{t} \right)^{3/2} + \dots \right], \quad (19)$$

$t \gg \tau_b$ , where  $\tau_b = b^2 \rho / \eta$  defines the time for passing the distance  $b$  by the shear wave, and  $D_C$  is defined after Eq. (13). For small times we have

$$\langle \Delta y_0^2(t) \rangle \approx \frac{k_B T}{N(M + M_s/2)} t^2, \quad (20)$$

where, however,  $t \gg b/c$  ( $c$  is the velocity of sound); the condition is due to the fluid incompressibility. The physically correct limiting value  $k_B T^2 / NM$  can be obtained only if the compressibility is taken into account, as discussed already in Ref.<sup>14</sup> (for a detailed solution of this "hydrodynamic paradox" see Ref.<sup>10</sup>). The long time asymptote for the VAF of the polymer is

$$\phi_0(t) = \frac{D_C}{2\sqrt{\pi}} \left[ \left( \frac{\tau_b}{t^3} \right)^{1/2} - \frac{1}{6} \left( 7 - 4 \frac{M}{M_s} \right) \left( \frac{\tau_b^3}{t^5} \right)^{1/2} + \dots \right]. \quad (21)$$

Here it should be noted that based on the model of a polymer as a porous particle penetrable by the solvent (the Debye-Brinkmann-Bueche model), the similar long-time tails of the VAF for the polymer have been already derived in the work<sup>15</sup>. The diffusion coefficient was however  $N$  times larger than in the Rouse model. Although the dependence  $D_C \sim 1/N$  is specific for the Rouse model, the diffusion coefficient for the coil should be in general smaller than for one bead. Assuming that the diffusion coefficients in both the models<sup>1,15</sup> are the same, the friction coefficient for the whole coil in the model<sup>15</sup> would be as for one bead only.

The case  $p \neq 0$  ( $K_p \neq 0$ ) is solved in Ref.<sup>10</sup>. The integral in Eq. (18) can be represented through the inverse Laplace transform. The integrand is then expanded into a sum of elementary fractions, for which the Laplace transforms are known. This allows one to express the searched integral in a closed form through the error function. The asymptotic expansions are then derived using known properties of these functions. (The leading terms in these large  $t$  asymptotes can be also easily obtained by simple expansions of the integrand in Eq. (18) for small  $\omega$ ). The long-time asymptote for the function  $\psi_p(t)$  has the form

$$\psi_p(0) - \psi_p(t) = \frac{k_B T}{2NK_p} \left\{ 1 + \frac{1}{2\sqrt{\pi}} \frac{\tau_p}{\tau_b} \left[ \left( \frac{\tau_b}{t} \right)^{3/2} + 3 \frac{\tau_p}{\tau_b} \left( \frac{\tau_b}{t} \right)^{5/2} + \dots \right] \right\}. \quad (22)$$

The dependence on the bead mass  $M$  appears only in the small  $\sim t^{-7/2}$  term.<sup>10</sup> The longest-lived contribution to the function  $\phi_p(t) = -d^2 \psi(t)/dt^2$  is  $\sim t^{-7/2}$ .

Comparing these formulas with the results of the theory by Rouse, it is seen that for internal modes ( $p \geq 1$ ) the value  $\psi_p(0) = k_B T / 2NK_p$  is the same as in the original model. The MSD of the whole coil at small times is different, now it is  $\sim t^2$  (instead of  $\sim t$ ). The diffusion coefficient of the coil,  $D_C$ , is the Rouse one. At large times, in addition to the Einstein term in the MSD, there are other contributions, the leading of which is  $\sim t^{1/2}$ . A difference reveals also in the long-time dependence of other time correlation functions of the coordinates and velocities of the polymer segments in the Fourier representation. The inclusion of the hydrodynamic memory leads to the relaxation of the internal modes that now essentially differs from the traditional exponential decay of the correlation functions  $\psi_p(t)$  and  $\phi_p(t)$ . This is reflected in the long-time tails of these functions. The discovery of the tails of the molecular VAF in simple liquids more than three decades ago (first by means of computer experiments) has led to enormous number of investigations in the field of the statistical theory of liquids and in the theory of Brownian motion.<sup>10</sup> We believe that similar peculiarities found here for the Rouse polymers could stimulate new studies in the dynamics of polymers.

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