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Inertial and Memory Effects in the Hydrodynamic Brownian Motion of Rouse and Zimm Polymer Coils

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Abstract

Traditional bead-spring models of the polymer dynamics are based on the Einstein theory of the Brownian motion (BM), valid only at the times much larger than the particle´s relaxation time. The reason is in neglecting the inertial and memory effects in the dynamics. In the present work we use a generalized theory of the BM to build models of the dynamics of flexible polymers in dilute solution. The equations of motion for the polymer segments include the friction force that follows from the linearized Navier-Stokes hydrodynamics. It has a form of a memory integral. To get a correct description of the short-time dynamics, inertial effects are included into the consideration. For negligible hydrodynamic interactions (HI) between the beads the motion of the polymer center of mass is not influenced by internal forces within the chain and has been considered exactly. Then we include the HI into the description of motion of chains, which are assumed Gaussian in equilibrium. Analytical solutions for the observable time correlation functions describing the movement of the polymer coils significantly differ from the classical results showing, in particular, algebraic long-time tails and ballistic motion at short times.

Keywords

Flexible polymers, coils, bead-spring models, hydrodynamic Brownian motion, memory effects

1. Introduction

The dynamics of a mesoscopic particle embedded in a viscous fluid is usually considered as being Markovian and described by the Einstein theory of the Brownian motion (BM) (see [1] and refs. therein). Recently, however, it has been proven in a number of experiments that this theory does not adequately describe the random motion of the particles. The reason is in neglecting the inertial and memory effects in the dynamics, which are connected to the fact that the thermal noise force driving the particles has a nonzero correlation time [2]. The

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necessary generalization of the Einstein and Langevin theory of the BM has been experimentally confirmed. This concerns also the dynamics of long polymer chains in a solvent. Exactly as in the theory of the BM, the classical bead-spring models of the polymer dynamics are expected to be valid only at the times much larger than the beads´ relaxation times. In the present work we use a generalized theory of the BM to build models of the dynamics of polymers in solution. Basic stochastic equations of motion for the polymer beads are established. We consider the models that naturally arise within the Navier-Stokes hydrodynamics. First, the Rouse model, in which the hydrodynamic interactions (HI) are screened out, is generalized. It is notable that the description of the motion of the polymer as a whole does not assume any concrete form of the interactions between the beads and the equilibrium conformation of the chain. In the original model the chains are Gaussian in equilibrium and only the nearest neighbors along the chain interact. To get a correct description of the short-time dynamics, inertial effects are included into the consideration. Then an attempt to include the HI into the consideration is presented. In both the cases the friction force has a form of a memory integral, so that mathematically the problem requires the solution of integro-differential stochastic equations.

2. Generalization of the Rouse bead-spring model

The details of the classical theories of the dynamics of large numbers of spherical beads forming chains in dilute solutions at θ conditions can be found in Ref. [3]. For more references and a generalization of the Rouse model to an exponentially correlated thermal noise see [4]. Here, to reveal the role of the inertial and memory effects we also begin with the Rouse theory as the simplest bead-spring model that even in its generalized form allows to obtain exact analytical solutions. The equation of motion along an axis, say x, for the nth bead ($n = 1, 2, ..., N \gg 1$) is

$$m\,\mathrm{d}^2 x_n / \mathrm{d}t^2 = f_n^{fr} + f_n^{ch} + f_n, \tag{1}$$

where x_n is the projection of the radius vector $\vec{r}_n$ of a particle of mass m, $\vec{f}_n^{fr}$ is the friction force, $\vec{f}_n^{ch}$ is the force by other particles in the chain, and $\vec{f}_n$ is the random force due to the chaotic motion of the molecules of solvent. The force $\vec{f}_n^{ch}$ can be expressed through the total energy of interaction between the particles, given by their equilibrium distribution in the chain [3]. In the original model this distribution is assumed Gaussian, and the monomers interact only with their nearest neighbors. The friction force is the Stokes one (then, due to the fluctuation-dissipation theorem, the random force is delta-correlated in the time), the inertial term is neglected, and the continuum approximation in n is used. Then Eq. (1) is transformed to a diffusion-type equation with the diffusion coefficient $D = k_B T/N\gamma$ ($\gamma = 6\pi\eta R$ is the friction factor for a particle with radius R in a fluid with viscosity η). Below this model is generalized in all the mentioned points. We do no assumption on the forces $\vec{f}_n^{ch}$. Instead of the Stokes friction, the resistance force naturally arises from the linearized Navier-Stokes and continuity equations for incompressible fluids as a memory force [5, 6]

$$\vec{f}_n^{fr}(t) = -\gamma\vec{\upsilon}_n(t) - m_s\dot{\vec{\upsilon}}_n(t) - 6\left(m_s\gamma/2\pi\right)^{1/2}\int_0^\infty \dot{\vec{\upsilon}}_n\left(t-\beta^2\right)\mathrm{d}\beta, \tag{2}$$

where $\upsilon_n = \mathrm{d}x_n/\mathrm{d}t$ is the bead velocity and m_s is the mass of the solvent displaced by the bead. The model can be modified by inclusion of the solvent viscosity independent internal friction

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[7], however, it does not affect the center of mass motion of the chain considered here, and we will not take it into account.

2. Center of mass motion of Rouse polymers

Let us sum up all equations of motion (1) from $n = 1$ to N. It is important that independently of a concrete model for the internal forces their sum is zero. The resulting equation will be

$$MN\frac{\mathrm{d}\upsilon_T}{\mathrm{d}t} + \gamma N\upsilon_T + 6NR^2(\pi\rho\eta)^{1/2}\int_{-\infty}^{t}\frac{\mathrm{d}\upsilon_T(\tau)}{\mathrm{d}\tau}\frac{\mathrm{d}\tau}{\sqrt{t-\tau}} = f\,, \tag{3}$$

where $M = m + m_s/2$, $f = \sum f_n$, and $\upsilon_T = \sum \upsilon_n / N$ is the velocity of the polymer center of inertia (CI). Using the approach presented in [5, 6], one can write down solutions for all relevant time correlation functions describing the motion of the polymer CI. So, its velocity autocorrelation function (VAF) $\Phi_T(t) = \langle \upsilon_T(0)\upsilon_T(t)\rangle$ exactly corresponds to the VAF of a Brownian particle with the mass MN:

$$\Phi_T(t) = \frac{k_BT}{MN(\lambda_2-\lambda_1)}\left\{\lambda_2\exp(\lambda_2^2 t)\mathrm{erfc}\left(-\lambda_2\sqrt{t}\right) - \lambda_1\exp(\lambda_1^2 t)\mathrm{erfc}\left(-\lambda_1\sqrt{t}\right)\right\}. \tag{4}$$

This result can be obtained also as a particular case of a more general problem considered in the next section, if the HIs are absent; due to this we omit here the details of its calculation. In Eq. (4) $\lambda_{1,2} = -(\tau_R^{1/2}/2\tau)[1 \mp \sqrt{1-4\tau/\tau_R}]$, where the time $\tau_R = R^2\rho/\eta$ characterizes the loss of memory in the dynamics (ρ is the density of the solvent). At $t \to \infty$ the VAF contains a long-time tail $\sim t^{-3/2}$: $\Phi_T(t) \approx k_BT\tau\sqrt{\tau_R}\left[1-3\left(1/2-3\tau/\tau_R\right)\tau_R/t+...\right]/2\sqrt{\pi}Mt^{3/2}$ ($\tau = M/\gamma$ is the usual Brownian relaxation time). In experiments, the mean square displacement (MSD) $X_T(t) = \langle[x_T(t) - x_T(0)]^2\rangle$ is measured. It is calculated according to the formula $X_T(t) = 2\int_0^t (t-s)\Phi_T(s)\mathrm{d}s$ [5] and, in addition to the classical result, at long times it contains a $t^{1/2}$ term: $X_T(t) \approx (2k_BTt/N\gamma)[1 - 2(\tau_R/\pi t)^{1/2} + ...]$. At short times that cannot be described by the original model, $X_T(t) \approx (k_BT/MN)t^2$. The velocity autocorrelation function, $\Phi_T(t) = \langle \upsilon_T(0)\upsilon_T(t)\rangle = (\mathrm{d}^2/2\mathrm{d}t^2)\,X_T(t)$, was zero in the original model; now it contains long-time tails, the longest-lived of which decays as $\sim t^{-3/2}$.

3. The model with hydrodynamic interactions

The inclusion of HI brings serious difficulties in the description of polymer dynamics [3, 7]. First, one has to calculate the velocity of the solvent in the place of nth bead due to the motion of other beads, $\upsilon(\vec{r}_n)$, and then to determine the friction force through $\mathrm{d}\vec{r}_n/\mathrm{d}t - \upsilon(\vec{r}_n)$. To do this, the hydrodynamic equations for the solvent must be solved. The Navier-Stokes equation contains an additional force density $\vec{\phi}(\vec{r}) = -\sum_n \vec{f}_n^{\,fr}(\vec{r}_n)\delta(\vec{r}-\vec{r}_n)$ reflecting the force from the beads on the solvent [8, 9]. The solution for $\vec{\upsilon}(\vec{r})$ is expressed through a nonstationary Oseen tensor $H_{\alpha\beta}(\vec{r},t)$ (see Appendix for its calculation). The incorporation of $H_{\alpha\beta}$ into the equations of motion makes the problem nonlinear, since the tensor depends on coordinates. A number of approximations, some of them hardly controllable, is thus needed to get analytical solutions of the generalized Zimm equation for the components of the beads´

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position vectors, $r_{n\alpha}$, $\alpha = x, y, z$. In the Fourier representation the equation for $r_{n\alpha} = \int_{-\infty}^{\infty} d\omega\, r_{n\alpha}^{\omega} \exp(-i\omega t)$ reads

$$-i\omega r_{n\alpha}^{\omega} = \psi_{n\alpha}^{\omega} (\gamma^{\omega})^{-1} + \sum_{\beta} \sum_{m \neq n} H_{\alpha\beta}^{\omega} (\vec{r}_n - \vec{r}_m) \psi_{m\beta}^{\omega}, \tag{5}$$

where $\psi_{n\alpha}^{\omega} = f_{n\alpha}^{ch,\omega} + f_{n\alpha}^{\omega} + m\omega^2 r_{n\alpha}^{\omega}$, $\gamma^{\omega} = \gamma[1 + \chi R + (\chi R/3)^2]$, and $\chi = \sqrt{-i\omega\rho/\eta}$ ($\mathrm{Re}\chi > 0$). It was used that the Fourier transform of the friction force (2) is $\vec{f}_n^{\,fr,\omega} = -\gamma^{\omega} \vec{\upsilon}_n^{\omega}$. Now we go to the continuum approximation, in which the internal forces, assuming Gaussian equilibrium distribution of the beads, become $\vec{f}_n^{\,ch} \to 3k_B T a^{-2} \partial^2 \vec{r}(t,n)/\partial n^2$ (a is the mean square distance between the neighboring beads along the chain). After the linearization of the problem by preaveraging of the Oseen tensor over this distribution, Eq. (5) contains only the diagonal terms with $\beta = \alpha$ and can be solved expanding the position vector in normal modes, $\vec{r}^{\,\omega}(n) = \vec{r}_T^{\,\omega} + 2\sum_{p=1}^{\infty} \vec{r}_p^{\,\omega} \cos(\pi np/N)$. The same expansion for the stochastic force is $f_{n\alpha}^{\omega} = f_{\alpha}^{\omega} + 2\sum_{p=1}^{\infty} f_{\alpha p}^{\omega} \cos(\pi np/N)$. Summing up equations (5) we obtain

$$\begin{aligned} -i\omega N \gamma^{\omega} r_{T\alpha} = {} & mN\omega^2 r_{T\alpha} + N f_{\alpha}^{\omega} + 2\sum_{n} \sum_{p=1}^{\infty} f_{\alpha p}^{\omega} \cos\frac{\pi np}{N} \\ & + \gamma^{\omega} \sum_{m \neq \tilde{n}} \sum_{p=1}^{\infty} h^{\omega}(n-m) \left[m\omega^2 r_{m\alpha}^{\omega} + f_{m\alpha}^{\omega} - \frac{6k_B T}{a^2} r_{\alpha p}^{\omega} \left(\frac{\pi p}{N} \right)^2 \cos\left(\frac{\pi pm}{N} \right) \right]. \end{aligned} \tag{6}$$

In the continuum approximation the sum over n is replaced by the integral $\int_0^N \mathrm{d}n(.)$. Let us denote $h_p^{\omega} = \int_0^N \mathrm{d}n \int_0^N \mathrm{d}m\, h^{\omega}(n-m)$. Then the equation for $r_{T\alpha}^{\omega}$ reads

$$-r_{T\alpha}^{\omega} \left[i\omega N + m\omega^2 \left(\frac{N}{\gamma^{\omega}} + h_0^{\omega} \right) \right] = \left(\frac{N}{\gamma^{\omega}} + h_0^{\omega} \right) f_{\alpha}^{\omega} + 2\sum_{p=1}^{\infty} f_{\alpha p}^{\omega} h_p^{\omega} + \sum_{p=1}^{\infty} r_{\alpha p}^{\omega} h_p^{\omega} \left[2m\omega^2 - \frac{6k_B T}{a^2} \left(\frac{\pi p}{N} \right)^2 \right]. \tag{7}$$

At this moment we neglect the small terms containing h_p^{ω} with $p > 0$. The possibility to do this was proven in Ref. [8] at $\omega = 0$. Here ω is nonzero but small since the long times are considered, which allows us to adopt this approximation. For h_0^{ω} an exact expression has been found, see (A11). We thus obtain the following equation that relates the coordinate of the CI to the random force:

$$r_{T\alpha}^{\omega} = \alpha(\omega) f_{\alpha}^{\omega} = -\left[m\omega^2 + i\omega \left(\frac{h_0^{\omega}}{N} + \frac{1}{\gamma^{\omega}} \right)^{-1} \right]^{-1} f_{\alpha}^{\omega}. \tag{8}$$

Now we can use the fluctuation-dissipation theorem to calculate the time correlation functions describing the motion of the polymer CI. For the diffusion, e.g., along the axis x, the MSD of

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the coil, $X_T(t) = 2\langle x_T(0)x_T(0) - x_T(0)x_T(t)\rangle$ ($x_T = r_{T\alpha}$) is determined through the susceptibility $\alpha(\omega)$ in Eq. (8) as [11]

$$X_T(t) = \frac{2k_BT}{\pi i}\int_{-\infty}^{\infty}\frac{\alpha(\omega)}{\omega}(1-\cos\omega\tau)\,d\omega = \frac{2k_BT}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Im}\,\alpha(\omega)}{\omega}(1-\cos\omega\tau)\,d\omega. \tag{9}$$

The calculation of this quantity, or the velocity autocorrelation function, is just a technical work. Here we give the long-time limit for the MSD, obtained as an asymptotic expansion of $X_T(t)$ for the Zimm polymers with strong HI ($h_0^0\gamma \gg N$)

$$X_T(t) \approx 2D_Z\left[t - \left(\frac{3N\rho}{32\eta}\right)^{1/2} t^{1/2} + \ldots\right] = 2D_Z t\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{\tau_R}{t}\right)^{1/2} + \ldots\right], \tag{10}$$

where $D_Z = k_BTh_0^0N^{-2} = 8k_BT/3\sqrt{6\pi^3N\eta a}$ is the diffusion coefficient known from the Zimm theory, and R in $\tau_R = R^2\rho/\eta$ is now the hydrodynamic radius of the coil [8, 9]. Similarly to the Rouse model with hydrodynamic memory, $X_T(t)$ at long times contains additional (to the Einstein term $\sim t$) contributions, the leading of which is $\sim t^{1/2}$. As illustrated in Fig. 1, the convergence to the classical result is very slow. For arbitrary strengths of the HI the diffusion coefficient of the coil contains both the Rouse and Zimm contributions, $D_C = D_Z + D_R$ [10], where $D_R = k_BT/N\gamma$.

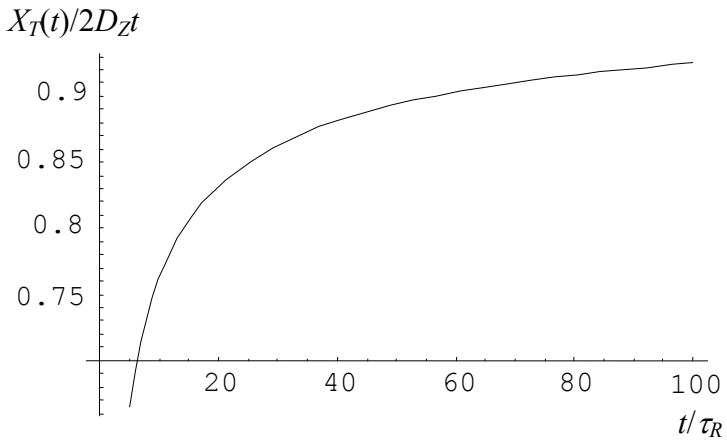

Fig. 1: MSD of a polymer coil calculated from Eq. (10) shows a slow convergence to the classical result from the Zimm theory, $X_T(t) = 2D_Zt$.

4. Discussion and Conclusions

This work deals with a generalization of the famous Rouse and Zimm models of polymer dynamics. It is shown how the inclusion of the inertial and memory effects that naturally arise within the nonstationary linearized Navier-Stokes hydrodynamics changes the description of the chaotic motion of polymer coils. Polymers interact with the fluid only through the friction force, which corresponds to theta conditions. The case of Rouse polymers when the hydrodynamic interactions are negligible has been considered exactly. It is notable that internal interactions within the polymer play no role in the motion of the polymer center of inertia. This could be used in possible computer simulations. For the description of real

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experiments the influence of hydrodynamic interactions should be taken into account. So far we can do it only after several approximations, such as the preaveraging of the Oseen tensor and the continuum limit. Nevertheless, the most peculiar results that distinguish our model from the classical Zimm theory, such as the appearance of the algebraic long-time tails in the velocity autocorrelation function of the coil, are in qualitative agreement with the computer experiments [12]. We have also given a calculation of the nonstationary Oseen tensor. It can be used for more detailed consideration of the Rouse-Zimm dynamics of polymers in solution, but also in other problems of the dynamics of suspensions.

The traditional approach to the polymer dynamics is based on the Einstein theory of the Brownian motion that is appropriate at "infinite" times. It might seem that the Langevin theory [13] that includes the inertial effects into the consideration can be used to describe the Brownian motion of particles (and the polymer dynamics) for any times. However, this theory, giving the same results as Einstein´s theory at long times, possesses good results at short times only when the density ρ_B of the particles is much larger than that of the surrounding fluid, ρ. This was shown in Ref. [14], where the hydrodynamic theory of the Brownian motion has been developed for the first time. The theory [14] constitutes the bases of the models presented in this paper. The inclusion of the inertial terms in the equations of motion for polymer segments allows describing the short time dynamics of the polymers with the characteristic time $\tau_B = m/\gamma$. The exponential relaxation of the Brownian particles would hardly be observable for such short times. However, the friction force in the form of the memory integral leads to a different relaxation due to which the Einstein diffusion regime is approached very slowly, with the characteristic time $\tau_R = R^2\rho/\eta = 9\rho\tau_B/2\rho_B$. As it is seen from Eq. (10), which has the same form for a Brownian particle and a polymer coil with R being its hydrodynamic radius, even for the times t as large as $100\,\tau_R$ the MSD constitutes only some 90% of the Einstein´s MSD. The dynamics differs also due to the increase of the effective mass of the particle, see Eq. (4). These features are present in the considered dynamics of the polymer chains as well.

Note that there are several other time scales inherent to the presented models. As in the Langevin theory of the Brownian motion, the time scale (~ 10^{-12} s) characterizing the collisions between the BP and the molecules of solvent must be much smaller than all other characteristic times. Then the collisions can be considered as a stochastic noise. The size of the beads R must be large enough to consider the solvent as a continuum. The solvent is described by the linearized hydrodynamic equations for incompressible fluids, so that we are restricted to the times much larger than the sound traversal time $\tau_s = R/c$, where c is the speed of sound. (For particles with R ~ 100 nm in water at room conditions, τ_s is less than 10^{-10} s.) The vorticity time $\tau_R = R^2\rho/\eta$ should be much larger than τ_c and τ_s. For a typical polymer coil with radius R ~ 100 nm this is well satisfied ($\tau_R \sim 10^{-8}$ s) but if R is a bead radius in the Rouse model, this phenomenological parameter can be so small that there will be no reason to consider the inertial and memory effects in the polymer dynamics. In a more general case with the hydrodynamic interactions, however, these effects seem to be accessible by various experimental methods. The presented model could be examined, e.g., by the technique of optical traps, using which the hydrodynamic approach to the Brownian motion that constitutes the basis of our approach has been recently confirmed [2].

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Appendix: Evaluation of the nonstationary Oseen tensor

To take the hydrodynamic interactions into account, the equation of motion (1) with the friction force (2) has to be solved together with the hydrodynamic (Navier-Stokes and continuity) equations for the macroscopic velocity of the liquid,

$$\rho\frac{\partial\vec{\upsilon}}{\partial t}=-\nabla p+\eta\Delta\vec{\upsilon}+\vec{\phi}\,,\qquad \mathrm{div}\,\vec{\upsilon}=0. \tag{A1}$$

Here p is the pressure. The quantity $\vec{\phi}$ has the meaning of an external force per unit volume [8]. Here

$$\vec{\phi}\left(\vec{r}\right)=-\sum_{n}\vec{f}_{n}^{\,fr}\left(\vec{r}_{n}\right)\delta\left(\vec{r}-\vec{r}_{n}\right). \tag{A2}$$

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

$$\vec{\upsilon}_{k}^{\omega}=\left(2\pi\right)^{-4}\int\mathrm{d}\vec{r}\mathrm{d}t\,\exp\left[i\left(\vec{k}\vec{r}+\omega t\right)\right]\vec{\upsilon}\left(\vec{r},t\right). \tag{A3}$$

The solution,

$$\vec{\upsilon}_{k}^{\omega}=\frac{1}{k^{2}\eta-i\omega\rho}\left[\vec{\phi}_{k}^{\omega}-\frac{\vec{k}}{k^{2}}\left(\vec{k}\vec{\phi}_{k}^{\omega}\right)\right], \tag{A4}$$

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

$$\upsilon_{\alpha}^{\omega}\left(\vec{r}\right)=\int\mathrm{d}\vec{r}'\sum_{\beta}H_{\alpha\beta}^{\omega}\left(\vec{r}-\vec{r}'\right)\phi_{\beta}^{\omega}\left(\vec{r}'\right). \tag{A5}$$

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The inverse transform, using (A2), is

$$\upsilon_\alpha\left(\vec{r},t\right)=-\frac{1}{2\pi}\sum_{m,\beta}\int_{-\infty}^{t}\mathrm{d}t'\,H_{\alpha\beta}\left(\vec{r}-\vec{r}_m,t-t'\right)f_{m\beta}^{fr}\left(\vec{r}_m\right). \tag{A6}$$

The Fourier transform of the Oseen tensor

$$H_{\alpha\beta}^{\omega}\left(\vec{r}\right)=\frac{1}{\left(2\pi\right)^3\eta}\int\frac{\mathrm{d}\vec{k}}{k^2-i\omega\rho/\eta}\left(\delta_{\alpha\beta}-\frac{k_\alpha k_\beta}{k^2}\right)\exp\left(-i\vec{k}\vec{r}\right) \tag{A7}$$

can be expressed as

$$H_{\alpha\beta}^{\omega}\left(\vec{r}\right)=A\delta_{\alpha\beta}+B\frac{r_\alpha r_\beta}{r^2}. \tag{A8}$$

After the integration in (A7) we obtain

$$A=\frac{1}{8\pi\eta\, r}\left[\exp(-y)-y\left(\frac{1-\exp(-y)}{y}\right)''\right],\qquad B=\frac{1}{8\pi\eta\, r}\left[\exp(-y)+3y\left(\frac{1-\exp(-y)}{y}\right)''\right]. \tag{A9}$$

Here $y=r\chi$, $\chi=\sqrt{-i\omega\rho/\eta}$ ($\mathrm{Re}\chi>0$), and the prime denotes the differentiation with respect to y. Equations (A8) and (A9) can be used also in different problems on the dynamics of suspensions.

If the equilibrium distribution of the beads is Gaussian,

$$P\left(r_{nm}\right)=\left(\frac{3}{2\pi a^2\left|n-m\right|}\right)^{3/2}\exp\left(-\frac{3}{2a^2}\frac{r_{nm}^2}{\left|n-m\right|}\right),\qquad \vec{r}_{nm}\equiv\vec{r}_n-\vec{r}_m, \tag{A10}$$

the preaveraging of the tensor (A8) consists in replacing it with the mean value over this distribution,

$$\left\langle H_{\alpha\beta nm}^{\omega}\right\rangle_0=\left\langle A\left(r_{nm}\right)\delta_{\alpha\beta}+B\left(r_{nm}\right)\frac{r_{nm\alpha}r_{nm\beta}}{r_{nm}^2}\right\rangle=\frac{\delta_{\alpha\beta}}{6\pi\eta}\left\langle\frac{1}{r_{nm}}\exp\left(-\chi r_{nm}\right)\right\rangle=\delta_{\alpha\beta}h^{\omega}\left(n-m\right). \tag{A11}$$

The result of integration is

$$h^{\omega}\left(n-m\right)=\left(6\pi^3\left|n-m\right|\right)^{-1/2}\left(\eta a\right)^{-1}\left[1-\sqrt{\pi}z\exp\left(z^2\right)\mathrm{erfc}\left(z\right)\right],\qquad z\equiv\chi a\sqrt{\left|n-m\right|/6}, \tag{A12}$$

where erfc (.) is the complementary error function. It is seen that the effective interaction between the beads decreases with the distance between the beads as

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

i.e., more rapidly than in the case without memory [3] when the function h at large $|n - m|$ behaves as $\sim |n-m|^{-1/2}$.

Using (A12), the integral $h_p^{\omega} = \int_0^N dn \int_0^N dm\, h^{\omega}(n-m)\cos(\pi pm/N)$ can be evaluated. Here we use it only at $p = 0$, when

$$h_0^{\omega} = \frac{2N}{\pi\eta a^2 \chi}\left\{1 - \frac{2}{\sqrt{\pi} R_g \chi} - \frac{1}{(R_g\chi)^2}\left[\exp\left(R_g^2\chi^2\right)\mathrm{erfc}\left(R_g\chi\right) - 1\right]\right\} \tag{A13}$$

($R_g = a(N/6)^{1/2}$ is the gyration radius connected to the hydrodynamic radius R as $Rg = 8R/(3\sqrt{\pi})$). At $\omega \to 0$ we have

$$h_0^{\omega} \approx \frac{8N^{3/2}}{3\eta a\sqrt{6\pi^3}}\left(1 - \frac{3\sqrt{\pi}}{8} R_g\chi + \ldots\right), \tag{A14}$$

and when $\omega \to \infty$,

$$h_0^{\omega} \approx \frac{2N}{\pi\eta a^2 \chi}\left(1 - \frac{2}{\sqrt{\pi} R_g\chi} + \frac{1}{(R_g\chi)^2} + \ldots\right). \tag{A15}$$

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