Rotational Brownian motion of axisymmetric particles in a Maxwell fluid

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A theory of non-Markovian rotational Brownian motion is developed for axisymmetric particles moving in a Maxwell fluid in the presence of an external field. Both the inertial and viscoelastic effects are taken into account. A kinetic equation for the joint probability distribution of orientation, angular velocity, and acceleration of a particle without spin is derived starting from the rotational Langevin equation with relaxed hydrodynamic and random torques. A third-order stochastic differential equation for the particle orientation vector is also derived. Directly from this equation, the set of nonlinear evolution equations for one-time moments is derived in a noninertial approximation. The expressions for a linear response to a time-dependent external field and dynamic susceptibility of particle are obtained by direct averaging of particle orientation equation. Appendices derive the rotational mobility of axisymmetric particles in a general linear viscoelastic fluid, and the evolution equations for one-time moments of the orientation vector for axisymmetric particles moving in a Maxwell fluid in the presence of an external field.

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I. INTRODUCTION

The theory of Brownian motion plays an important role in many parts of modern physics. It also has a wide variety of applications. Debye [1] who first analyzed the rotational Brownian motion of a sphere in viscous fluid adopted Einstein's approach to the translational Brownian motion, neglecting the effects of the fluid's inertia and elasticity. Several statistical approaches developed recently for studying the rotational Brownian motion in viscous liquids (see reviews [2–5]). An interest emerged recently in Brownian motion in viscoelastic fluids [6–12]. Evidently, viscoelastic properties of a carrier fluid may significantly affect the statistical characteristics of Brownian motion. The simplest, Maxwell model of viscoelastic fluid is characterized by two parameters: a single relaxation time and viscosity. Due to memory effects in viscoelastic liquids, the stochastic motion of a Brownian particle in these fluids represents a non-Markov process, even if the inertia of the particle and fluid are negligible. Wang and Uhlenbeck [13] first analyzed the non-Markov properties in translational Brownian motion of a simple harmonic oscillator in viscous fluid. They reduced a non-Markov process described by a stochastic second-order differential equation for the position of Brownian particle, to a higher-dimension Markov process containing velocity as an extra variable. Using a similar idea, a theory of translation Brownian motion in a Maxwell fluid was recently developed [8,9]. In this theory, the non-Markov process described by a third-order stochastic equation for the position of a Brownian particle, was reduced to a higher dimension Markov process by introducing the velocity and acceleration as two new independent extra variables. Using this technique, a universal kinetic equation for the distribution function of position, velocity, and acceleration was obtained for translation Brownian motion in Maxwell fluid [9] that provided a complete statistical description of the non-Markov stochastic process.

Papers [10,11] have recently studied a two-dimensional (2D) rotational Brownian motion in Maxwell fluid. This rotational Brownian motion was found to be equivalent to the Brownian translation of a particle on a circular track. To study this simplest non-Markov Brownian rotational motion, the authors of paper [10] adopted the approach [8] developed for analysis of translation Brownian motion in a Maxwell fluid. The rotational Bwnian motion for anisotropic particles is highly simplified when the particles have a shape of a flat circular disk. In this case, the stochastic equations for angular velocity are linear and therefore the process is Gaussian. However, even in this case, the equations for particle orientation that relate the orientation vector and angular velocity, are nonlinear. To analyze 3D rotational Brownian motions of any nonspherical particle one has to overcome some fundamental difficulties [3], since statistical characteristics of these motions are always non-Gaussian.

The present paper studies 3D rotational motion of Brownian axisymmetric particles in Maxwell fluid. The particles are assumed to have an arbitrary shape of a body of revolution, such as spheroids, rods, disks, etc. When assuming that the spin, i.e., the rotation around the axis of particle symmetry is absent (or dynamically negligible) the random torque in stochastic equations for the angular velocity and orientation vector are proven to be Gaussian. Using this ''spinless'' assumption, we analyze the motion of a Brownian particle with permanent dipole moment affected by an external (electric or magnetic) field. This creates an opportunity for direct studies of orientation and rotation of Brownian axisymmetric particles in various complex fluids.

II. BROWNIAN DYNAMICS WITH RELAXED TORQUE

We consider the rotational Brownian motion of a nonspherical, axisymmetric particle represented as a body of

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revolution, in a quiescent Maxwell fluid with a single relaxation time τ. The general stochastic equations describing the inertial rotations of such a particle are

$$\frac{dL_i}{dt}=M_i+M_i^e+M_i^r. \quad (1)$$

Here L_i is the angular moment relative to an arbitrary point O within the particle body,

$$L_i=I_{ij}\Omega_j, \quad (2)$$

Ω_i is the angular velocity of the particle, I_{ij} is the anisotropic inertia tensor of an axisymmetric particle,

$$I_{ij}=I_{\parallel}e_ie_j+I_{\perp}(\delta_{ij}-e_ie_j), \quad (3)$$

and $\mathbf{e}=\{e_i\}$ is the unit vector that describes the orientation of the symmetry axis. The particle rotation is induced by the hydrodynamic, $M_i(t,\mathbf{e})$, external, $M_i^e(t,\mathbf{e})$, and random, $M_i^r(t,\mathbf{e})$, torques; the random torque $M_i^r(t,\mathbf{e})$ resulting from bombarding a Brownian particle by molecules of environmental liquid.

The hydrodynamic torque $M_i(t)$ acting on the Brownian particle from the Maxwell fluid, is defined by Eq. (A8) from Appendix A as

$$\tau\frac{dM_i}{dt}+M_i=-\zeta_{ij}^r(\mathbf{e})\,\Omega_j. \quad (4)$$

The anisotropic properties of the Brownian motion are caused by the rotational friction tensor ζ_{ij}^r that for axisymmetric particles has the uniaxial form, depending on the particle orientation:

$$\zeta_{ij}^r=\zeta_{\parallel}^r e_ie_j+\zeta_{\perp}^r(\delta_{ij}-e_ie_j). \quad (5)$$

Along with randomly changed orientation, the Brownian particle may also rotate around its axis of symmetry. Thus the angular velocity for such a particle can be decomposed into components parallel, $\Omega_i^{\parallel}$, and perpendicular, $\Omega_i^{\perp}$, to the particle axis of symmetry:

$$\Omega_i=\Omega_i^{\parallel}+\Omega_i^{\perp},\ \ [\Omega_i^{\parallel}=\Omega_e e_e e_i,\ \ \Omega_i^{\perp}=\Omega_e(\delta_{ei}-e_e e_i)]. \quad (6)$$

The evident kinematic relation,

$$\frac{de_i}{dt}=\varepsilon_{ijk}\Omega_j e_k, \quad (7)$$

where ε_{ijk} is the antisymmetrical unit tensor, describes the rate of change in particle orientation. Combining Eqs. (6) and (7), one can see that a random rotation around the particle symmetry axis does not change the particle orientation.

We consider below an important particular case of a particle motion without inner rotation (spin). In this case the angular velocity vector is normal to the orientation vector, i.e., $\Omega_e e_e=0$, and Eq. (1) becomes

$$I_{\perp}\frac{d\Omega_i}{dt}=M_i+M_i^e+M_i^r. \quad (8)$$

The hydrodynamic torque for the spinless rotation of an axisymmetric particle in a Maxwell fluid is determined from the relaxation equation:

$$\tau\frac{dM_i}{dt}+M_i=-\zeta_{\perp}^r\Omega_i. \quad (9)$$

When $\Omega_e e_e=0$, the terms involving $I_{\parallel}$ and $\zeta_{\parallel}^r$ in Eqs. (3) and (5) vanish, and the friction coefficient $\zeta_{\perp}^r$ represents the rotation resistance in the direction perpendicular to the particle symmetry axis.

The external torque M_i^e could arise from various sources, such as the interactions of electric, magnetic, or gravitational fields with, respective, electric particle dipole, magnetic moment of ferromagnetic particle, and a gravitational dipole of a particle. In all these cases, the external torque has the form

$$M_i^e=\varepsilon_{ijk}p_jH_k, \quad (10)$$

where p_i is the dipole moment of the particle, and H_k is an external field. In the following we restrict ourselves to studying either constant or long-wave oscillating external fields, when the wavelength is considerably more than the largest particle size. In this case, the external field can be considered as uniform, generally time dependent, i.e., $H_k=H_k(t)$. In Eq. (10), the permanent dipole moment p_i is assumed to be oriented parallel to the symmetry axis,

$$p_i=\mu e_i, \quad (11)$$

with the constant magnitude of dipole moment μ.

The correlation properties of the random torque are determined by the form of the stochastic equation for rotational particle motion. The statistical properties of the random torque $M_i^r(t)$ for a non-Markovian rotational Langevin equation with frictional relaxation equations (8) and (9) can be found by a method used before for the translational Brownian motion in a Maxwell fluid [9]. In the case under study, this method gives

$$\langle M_i^r(t)\rangle=0, \quad (12)$$

$$\langle M_i^r(t)M_k^r(0)\rangle=T\frac{\zeta_{\perp}^r}{\tau}e^{-|t|/\tau}\delta_{ik}.$$

Equation (12) demonstrates that the random torque $M_i^r(t)$ is represented by a Markov process, and can be regarded as the solution of the first-order stochastic differential equation

$$\tau\frac{dM_i^r}{dt}+M_i^r=\xi_i^r(t). \quad (13)$$

Here $\xi_i^r(t)$ is the delta-correlated random torque,

$$\langle\xi_i^r(t)\xi_k^r(0)\rangle=2T\zeta_{\perp}^r\delta(t)\delta_{ik}, \quad (14)$$

and $\delta(t)$ is the delta function. Equation (13) shows that the memory effect in the random torque originates from a fluctuating environment. Equations (13) and (14) result from the solution of an inverse problem [9] for restoring the white noise for a random function with a given correlation function. These equations with arbitrary initial conditions may be considered as a most general form of the fluctuation-dissipation theorem for non-Markovian rotational Langevin equations (8) and (9).

Using the relaxation equations for systematic (9) and random (13) torques allows us to represent the set of stochastic equation (8) and (9) in the equivalent form with a δ-function-correlated random torque $\xi_i^r(t)$:

$$\frac{de_i}{dt}=\varepsilon_{ijk}\Omega_j e_k, \quad \frac{d\Omega_i}{dt}=\dot{\Omega}_i, \tag{15a}$$

$$\tau I_\perp \frac{d}{dt}\dot{\Omega}_i + I_\perp \dot{\Omega}_i = -\zeta_\perp^r \Omega_i + \tau \dot{M}_i^e + M_i^e + \xi_i^r. \tag{15b}$$

Hereafter the overdots denote the time derivatives. According to Eqs. (10) and (11), the rate of change in M_i^e is given by

$$\dot{M}_i^e = -m_{ij}\Omega_j - \alpha_{ij}e_j, \quad m_{ij}=\mu(e_e H_e \delta_{ij} - e_i H_j),$$
$$\alpha_{ij}=\mu\varepsilon_{ikj}\dot{H}_k. \tag{16}$$

Equation (15b) with the use of Eq. (16) takes the form

$$\tau I_\perp \frac{d}{dt}\dot{\Omega}_i + I_\perp \dot{\Omega}_i = -\zeta_{ij}\Omega_j - \beta_{ij}e_j + \xi_i^r. \tag{17}$$

Here, the following notations have been used:

$$\zeta_{ij}=\zeta_\perp^r \delta_{ij} + \tau m_{ij}, \quad \beta_{ij}=\mu\varepsilon_{ikj}h_k, \quad h_i = H_i + \tau \dot{H}_i. \tag{18}$$

According to Eq. (17), the angular velocity $\mathbf{\Omega}$ is a non-Markov process. As shown before, it can be reduced to a Markov process defined by the extended dynamic set of equations (15a) and (15b), affected by a delta-correlated random torque. This set defines a multidimensional Markovian process $\{\mathbf{e},\mathbf{\Omega},\dot{\mathbf{\Omega}}\}$.

It should be noted that not every random process could be reduced to a Markovian one, even in the most general sense. For instance, this is impossile when significant residual effects are associated with inertia of liquid.

III. ROTATIONAL FOKKER-PLANCK EQUATION

Using the Klyatskin-Tatarskii method [14] we directly derive from the stochastic equations of motion a kinetic equation for the join probability density of orientation, angular velocity, and acceleration of an axisymmetric Brownian particle moving in a Maxwell fluid.

The distribution function for the solution of the set (15) is defined as

$$f(\mathbf{e},\mathbf{\Omega},\dot{\mathbf{\Omega}})=\langle \delta[\mathbf{e}-\mathbf{e}(t)]\delta[\mathbf{\Omega}-\mathbf{\Omega}(t)]\delta[\dot{\mathbf{\Omega}}-\dot{\mathbf{\Omega}}(t)]\rangle. \tag{19}$$

Here $\mathbf{e}$, $\mathbf{\Omega}$, and $\dot{\mathbf{\Omega}}$ are the solution of Eqs. (15a) and (15b) corresponding to a certain realization of the random torque $\xi_i^r(t)$ in Eq. (15b). The angular brackets in Eq. (19) define the average of the variables over the set of all realizations. Taking the time derivative of Eq. (19) and using Eqs. (15a) and (15b) yields

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial e_i}(\varepsilon_{ijk}\Omega_j e_k f) + \dot{\Omega}_i \frac{\partial f}{\partial \Omega_i} - \frac{\zeta_{ij}\Omega_j + \beta_{ij}e_j}{\tau I_\perp}\frac{\partial f}{\partial \dot{\Omega}_i}$$
$$= \frac{1}{\tau}\frac{\partial}{\partial \dot{\Omega}_i}(\dot{\Omega}_i f) - \frac{1}{\tau I_\perp}\frac{\partial}{\partial \dot{\Omega}_i}\langle \xi_i^r(t) R[\xi]\rangle,$$
$$\mathbf{R}[\xi]=\delta[\mathbf{e}-\mathbf{e}(t)]\delta[\mathbf{\Omega}-\mathbf{\Omega}(t)]\delta[\dot{\mathbf{\Omega}}-\dot{\mathbf{\Omega}}(t)]. \tag{20}$$

Here $\mathbf{R}[\xi]$ is a nonlinear random functional of the Gaussian stochastic process $\xi(t)$ with zero average. To close Eq. (20) we express the average value $\langle \xi_i^r(t)\mathbf{R}[\xi]\rangle$ in terms of f, using the Furutsu-Novikov formula [15]. This formula, in our case, is of the form

$$\langle \xi_i^r(t)\mathbf{R}[\xi]\rangle = \int_0^t \langle \xi_i^r(t)\xi_j^r(s)\rangle \left\langle \frac{\partial \mathbf{R}[\xi]}{\delta \xi_j^r(s)}\right\rangle ds. \tag{21}$$

Calculating the functional derivatives with the use of Eqs. (15a) and (15b),

$$\frac{\delta e_i(t)}{\delta \xi_j^r(t)}=0, \quad \frac{\delta \Omega_i(t)}{\delta \xi_j^r(t)}=0, \quad \frac{\delta \dot{\Omega}_i(t)}{\delta \xi_j^r(t)}=\frac{1}{\tau I_\perp}\delta_{ij}, \tag{22}$$

and employing the fluctuation-dissipation relation (14), yields

$$\langle \xi_i^r(t)\mathbf{R}[\xi]\rangle = -\frac{T\zeta_\perp^r}{\tau I_\perp}\frac{\partial f}{\partial \dot{\Omega}_i}. \tag{23}$$

Using Eq. (23) and the evident relation, $\partial e_i/\partial e_j = \delta_{ij} - e_i e_j$, results in the closed form of the equation for the distribution function:

$$\frac{\partial f(\mathbf{e},\Omega,\dot{\Omega})}{\partial t} + \varepsilon_{ijk}e_j \frac{\partial}{\partial e_k}(\Omega_i f) + \dot{\Omega}_i \frac{\partial f}{\partial \Omega_i} - \frac{\zeta_{ij}\Omega_j + \beta_{ij}e_i}{\tau I_\perp}\frac{\partial f}{\partial \dot{\Omega}_i}$$
$$= \frac{\partial}{\partial \dot{\Omega}_i}\left(\frac{\dot{\Omega}_i}{\tau} + D_{\dot{\Omega}}\frac{\partial}{\partial \dot{\Omega}_i}\right) f. \tag{24}$$

The diffusion coefficient in the space of angular acceleration is represented as

$$D_{\dot{\Omega}} = \frac{D_\perp}{(\tau \tau_I)^2}. \tag{25}$$

Here $D_\perp = T/\zeta_\perp^r$ is the transverse diffusion constant and $\tau_I = I_\perp/\zeta_\perp^r$ is the inertial relaxation time.

The joint distribution function $f(\mathbf{e},\mathbf{\Omega},\dot{\mathbf{\Omega}})$ of orientation, angular velocity, and acceleration is a solution of Eq. (24) for a given initial distribution $f_0 = f(\mathbf{e},\mathbf{\Omega},\dot{\mathbf{\Omega}},t_0)$. Additionally, one can obtain the distribution function for orientation and angular velocity, $f(\mathbf{e},\mathbf{\Omega},t) = \int f(\mathbf{e},\mathbf{\Omega},\dot{\mathbf{\Omega}},t)\,d\dot{\mathbf{\Omega}}$. However, the function $f(\mathbf{e},\mathbf{\Omega},t)$ cannot be found from the rotational Fokker-Planck equation since the stochastic process $\{\mathbf{e}(t),\mathbf{\Omega}(t)\}$ is non-Markovian.

For the free spinless rotational Brownian motion of axisymmetric particle in a Maxwell fluid, Eq. (24) takes the form

$$\frac{\partial f(\mathbf{e},\mathbf{\Omega},\dot{\mathbf{\Omega}})}{\partial t} + \nabla_i^r(\Omega_i f) + \dot{\Omega}_i\frac{\partial f}{\partial \Omega_i} - \frac{\Omega_i}{\tau\tau_I}\frac{\partial f}{\partial \dot{\Omega}_i} = \frac{\partial}{\partial \dot{\Omega}_i}\left(\frac{\dot{\Omega}_i}{\tau} + D_{\dot{\Omega}}\frac{\partial}{\partial \dot{\Omega}_i}\right) f. \tag{26}$$

Here the rotational operator ∇_i^r, defined as

$$\nabla_i^r = \varepsilon_{ijk} e_j \frac{\partial}{\partial e_k}, \tag{27}$$

is equivalent to the orbital angular momentum operator in quantum mechanics [5].

Equation (26) has the stationary solution,

$$f_s(\mathbf{\Omega},\dot{\mathbf{\Omega}}) = C \exp\left[-\frac{I_\perp(\mathbf{\Omega}_e\cdot\mathbf{\Omega}_e + \tau\tau_I\dot{\mathbf{\Omega}}_e\cdot\dot{\mathbf{\Omega}}_e)}{2T}\right], \tag{28}$$

where C is a normalization constant. Equation (28) is an extension of the Maxwell distribution, which includes the new dependence on the angular accelerations. Using Eq. (28), the equilibrium moments are defined as follows:

$$\langle \Omega_i\Omega_k\rangle_0 = \frac{T}{I_\perp}\delta_{ik}, \quad \langle \dot{\Omega}_i\dot{\Omega}_k\rangle_0 = \frac{T}{I_\perp\tau\tau_I}\delta_{ik}, \quad \langle \Omega_i\dot{\Omega}_k\rangle_0 = 0. \tag{29}$$

The second formula in Eq. (29) demonstrates that the equilibrium value of the second one-time moment of the angular acceleration depends on the rheological properties of carrier fluid. This formula shows that the unphysical singularity, characterizing the classical model of rotational Brownian motion in a viscous fluid, where $\tau = 0$, vanishes in the case of the Maxwell fluid model. The first relation in Eq. (29) corresponds to the familiar equipartition distribution of kinetic and thermal energy over the degrees of freedom:

$$\frac{1}{2}I_\perp\langle\Omega_i^2\rangle_0 = \frac{1}{2}T.$$

Here the temperature T is expressed in energy units. Thus as $t\to\infty$, the Brownian particles comes into the thermodynamic equilibrium with the viscoelastic environment.

IV. ORIENTATION DYNAMICS

According to Eq. (7), the random angular velocity drives the random orientational motion. In order to find the equation defining the orientation of a particle we make the vector multiplication of Eq. (17) by $\mathbf{e}$ and using after that Eq. (7), obtain

$$\tau I_{ik}^\perp\frac{d^3e_k}{dt^3} + I_{ik}^\perp\frac{d^2e_k}{dt^2} + [\zeta_\perp^r + \tau(\mu e_k H_k + I_\perp\dot{e}_k\dot{e}_k)]\frac{de_i}{dt} = \mu(h_i - e_ie_nh_n) + \varepsilon_{ijk}\xi_j^r e_k, \tag{30}$$

$$I_{ik}^\perp = I_\perp(\delta_{ik} - e_ie_k).$$

The orientation of a Brownian particle described by these equations is a non-Gaussian, non-Markovian stochastic process, with Eq. (30) defining the inertial nonlinear transformation of white noise.

To simplify the problem we neglect the inertia effects on orientation dynamics of nanosize particles, excluding from analysis very short-time processes. According to Eq. (30) the stochastic equation for the orientation of an noninertial Brownian particle in a Maxwell fluid has the form

$$(\zeta_\perp^r + \tau\mu e_kH_k)\frac{de_i}{dt} = \mu(h_i - e_ie_nh_n) + \varepsilon_{ijk}\xi_j^e e_k. \tag{31}$$

Equation (31) describes the noninertial nonlinear transformation of white noise and shows that in a noninertial approximation, the orientation of a particle is still the non-Gaussian Markov process. Also, Eq. (31) formally corresponds to the limit $I_\perp/\zeta_\perp^r \to 0$. This limit should be considered more carefully for large values of relaxation times τ when the inertial effects might be coupled with viscoelasticity. For viscoelastic carrier fluid under study, the external field H_i plays a double role, orienting a particle, and also hindering its rotation. This hindrance to rotation introduces an additional friction coefficient, which depends on the relaxation time τ of the fluid, and the alignment energy $\mu e_k H_k$. We neglect, for simplicity below, the fluctuations of the friction coefficient. Then Eq. (31) becomes

$$\zeta_r\frac{de_i}{dt} = \mu(h_i - e_ie_nh_n) + \varepsilon_{ijk}\xi_j^a e_k \quad (\zeta_r = \zeta_\perp^r + \tau\mu\langle e_k\rangle H_k). \tag{32}$$

Here ζ_r is the mean friction coefficient.

According to the fluctuation-dissipation theorem, the random torque $\xi_i^e(t)$ for the noninertial rotational Brownian motion has the following properties:

$$\langle\xi_i^e(t)\rangle = 0, \;\; \langle\xi_i^e(t)\xi_j^e(0)\rangle = 2T\zeta_r\delta(t)\delta_{ij}. \tag{33}$$

The evolution equations for one-time moments of various orders can then be derived from the rotational Langevin equation (32) by averaging procedures. Due to the quadratic nonlinearity in Eq. (32), these equations form an infinite (nonclosed) chain. These equations, whose derivation is presented in Appendix B, are shown below up to the fourth-order moment equation:

$$\nu(t)\frac{d\langle e_i\rangle}{dt}=-\frac{1}{\tau_1}\langle e_i\rangle+\lambda(h_i-\langle e_ie_k\rangle h_k), \tag{34}$$

$$\nu(t)\frac{d\langle e_ie_k\rangle}{dt}=-\frac{1}{\tau_2}\left(\langle e_ie_k\rangle-\frac{1}{3}\delta_{ik}\right)+\lambda[\langle e_i\rangle h_k+\langle e_k\rangle h_i-2\langle e_ie_ke_j\rangle h_j], \tag{35}$$

$$\nu(t)\frac{d\langle e_ie_ke_j\rangle}{dt}=-\frac{1}{\tau_3}\left[\langle e_ie_ke_j\rangle-\frac{1}{6}(\delta_{ik}\langle e_j\rangle+\delta_{ij}\langle e_k\rangle+\delta_{kj}\langle e_i\rangle)\right]+\lambda[\langle e_ie_k\rangle h_j+\langle e_ie_j\rangle h_k+\langle e_ke_j\rangle h_i-3\langle e_ie_ke_je_n\rangle h_n], \tag{36}$$

$$\nu(t)\frac{d\langle e_ie_je_ke_l\rangle}{dt}=-\frac{1}{\tau_4}\left[\langle e_ie_je_ke_l\rangle-\frac{1}{10}(\delta_{ij}\langle e_ke_l\rangle+\delta_{ik}\langle e_je_l\rangle+\delta_{ie}\langle e_ke_j\rangle+\delta_{jk}\langle e_ie_l\rangle+\delta_{jl}\langle e_ie_k\rangle+\delta_{kl}\langle e_ie_j\rangle)\right]+\lambda[\langle e_ie_je_k\rangle h_l+\langle e_ie_je_l\rangle h_k+\langle e_ie_ke_l\rangle h_j+\langle e_je_ke_l\rangle h_i-4\langle e_ie_je_ke_le_n\rangle h_n]. \tag{37}$$

In Eqs. (34)–(37), the rotational relaxation times τ_α, the parameter λ, and function $\nu(t)$ are defined as

$$\tau_\alpha=\zeta_\perp^r/[\alpha(\alpha+1)T],\quad \lambda=\mu/\zeta_\perp^r,$$
$$\nu(t)\equiv\zeta_r(t)/\zeta_\perp^r=1+\lambda\tau\mu H_k(t)\langle e_k(t)\rangle. \tag{38}$$

We now consider the case of a stationary external field H_i, when $h_i=H_i$, and the constant unit vector n_i in the direction of the field, is defined as $H_i=n_iH$. Then the nondimensional parameter $\kappa=\mu H/T$, characterizing the strength of the external field relative to the thermal energy, is naturally introduced in Eqs. (34)–(37) in the products $\lambda\tau_kH$ in these equations.

There are two physically important cases when it is possible to find asymptotic solutions of the nonlinear relaxation equations (34)–(37) for the one-time moments of various orders. We will present below only the analytical results of steady analyses for thermal equilibrium of the moments in a constant field. The same procedure for nonsteady situations might also be developed but will need a numerical analysis. It should be noted that formulas obtained below for the stationary case are identical for both the viscous and viscoelastic carrier liquids.

(i) In the case of a *weak external field*, when $\kappa=\mu H/T\ll1$, the steady solution of Eqs. (34)–(37) is of the form

$$\langle e_i\rangle_e=\frac{\kappa}{3}\left(1-\frac{\kappa^2}{15}+O_i(\kappa^4)\right)n_i,$$

$$\langle e_ie_k\rangle_e=\frac{1}{3}\delta_{ik}+\frac{1}{15}\kappa^2\left(n_in_k-\frac{1}{3}\delta_{ik}\right)+O_{ik}(\kappa^4), \tag{39}$$

$$\langle e_ie_ke_j\rangle_e=\frac{1}{15}\kappa(\delta_{ik}n_j+\delta_{ij}n_k+\delta_{kj}n_i)-\frac{\kappa^3}{45}n_in_kn_j+O_{ikj}(\kappa^5),$$

$$\langle e_ie_je_ke_m\rangle_e=\frac{1}{15}I_{ijkm}+\frac{\kappa^2}{315}[3(\delta_{ik}n_jn_m+\delta_{ij}n_kn_m+\delta_{im}n_kn_j+\delta_{kj}n_in_m+\delta_{km}n_in_j+\delta_{jm}n_in_k)-2I_{ijkm}]+O_{ijkm}(\kappa^4).$$

Here $I_{ijkm}=\delta_{ij}\delta_{km}+\delta_{ik}\delta_{jm}+\delta_{im}\delta_{jk}$, and $O_{ik\ldots}$ are the order functions of various tensor dimensionalities.

(ii) In the case of a *strong external field*, when $\kappa=\mu H/T\gg1$, the stationary asymptotic solution of Eqs. (34)–(37) is of the form

$$\langle e_i\rangle_e=(1-\kappa^{-1})n_i+O_i(\kappa^{-2}),$$

$$\langle e_ie_k\rangle_e=\kappa^{-1}\delta_{ik}+(1-3/\kappa)n_in_k+O_{ik}(\kappa^{-2}),$$

$$\langle e_ie_ke_j\rangle_e=n_in_kn_j+\kappa^{-1}(\delta_{ik}n_j+\delta_{ij}n_k+\delta_{kj}n_i-6n_in_kn_j)+O_{ikj}(\kappa^{-2}), \tag{40}$$

$$\langle e_ie_je_ke_m\rangle_e=n_in_jn_kn_m+\kappa^{-1}(\delta_{ik}n_jn_m+\delta_{ij}n_kn_m+\delta_{im}n_kn_j+\delta_{kj}n_in_m+\delta_{km}n_in_j+\delta_{jm}n_in_k-10n_in_jn_kn_m)+O_{ijkm}(\kappa^{-2}).$$

In finding the form of the terms in Eqs. (39) and (40), the evident properties for the second, third, and fourth moments $\delta_{ik}\langle e_ie_k\rangle=1$, $\delta_{ik}\langle e_ie_ke_j\rangle=\langle e_j\rangle$, and $\delta_{ik}\langle e_ie_ke_je_m\rangle=\langle e_je_m\rangle$ have also been used. Formulas (39) and (40) demonstrate the general fact that the polyadic one-time moment tensors of different orders, formed of the unit orientation vector e_i, depend only on all possible symmetrical combinations of the unit tensor δ_{ik} and the unit vector n_i describing the orientation of the external field, with coefficients depending only on parameter κ. The same is true for the nonstationary case, where the coefficients of these symmetrical tensors will also depend on time.

V. DYNAMIC SUSCEPTIBILITY

The orientation of a particle can be experimentally investigated by measuring the mean dipole moment

$$P_i=\mu\langle e_i\rangle. \tag{41}$$

In this regard, the theory developed above allows for interpretation of these experiments when the time-dependent solution of a linear problem for the mean dipole moment is available. We consider below the linear noninertial response of a Brownian axisymmetric particle suspended in Maxwell liquid to an external field $\mathbf{H}(t)$. In this case, the terms of the order $(\mu H/T)^2$ and higher in Eq. (34) can be neglected. Using Eqs. (41) and (34), yields the linear equation for the mean dipole moment

$$\tau_1 \frac{dP_i}{dt} + P_i = \chi_0 \left(H_i + \tau \frac{dH_i}{dt} \right), \quad \chi_0 = \mu^2/3T. \tag{42}$$

Here χ_0 is the static susceptibility of particle. The orientation relaxation time τ_1 is defined in Eq. (34). Equation (34) was lianearized with replacing unknown first and second moments by their equilibrium values $\langle e_i \rangle_0 = 0$ and $\langle e_i e_k \rangle_0 = 1/3\delta_{ik}$ in the absence of an applied field. The solution of Eq. (42) is of the form

$$P_i = \int_0^\infty \chi(s) H_i(t-s)\, ds, \tag{43}$$

where the response function $\chi(t)$ is

$$\chi(t) = \frac{\chi_0}{\tau_1} \left[\tau\delta(t) + \left(1 - \frac{\tau}{\tau_1} \right) e^{-t/\tau_1} \right]. \tag{44}$$

For the oscillating external field,

$$H_i = H_i^m \operatorname{Re}(e^{-i\omega t}) \tag{45}$$

with a constant amplitude H_i^m, the mean dipole moment is defined by

$$P_i = H_i^m \operatorname{Re}[\chi(\omega) e^{-i\omega t}]. \tag{46}$$

The steady-state response is described by the dynamic susceptibility of particle $\chi(\omega)$ depending on frequency ω:

$$\chi(\omega) = \frac{1 - i\omega\tau}{1 - i\omega\tau_1}. \tag{47}$$

For a viscous carrier fluid ($\tau = 0$) Eq. (47) reduces to the well-known expression for the Debye susceptibility [1]. The reduced real and imaginary parts of dynamic susceptibility are

$$\chi_R' = \frac{1 + \alpha\omega_R^2}{1 + \omega_R^2}, \quad \chi_R'' = \frac{(1-\alpha)\omega_R}{1 + \omega_R^2}, \tag{48}$$

where

$$\chi_R' = \chi'/\chi_0, \;\; \chi_R'' = \chi''/\chi_0, \;\; \alpha = \tau/\tau_1, \;\; \omega_R = \omega\tau_1. \tag{49}$$

Here the parameter α characterizes the effect of viscoelasticity, and ω_R is a nondimensional frequency of field oscillation. Figures 1 and 2 demonstrate the plots of reduced components of dynamic susceptibility versus the dimensionless frequency. The dashed and solid lines, respectively, represent the predictions of the Debye theory ($\alpha = 0$) and the present theory with $\alpha = 0.2$. Figure 1 shows that the real part has the nonvanishing limit at large values of $\omega\tau_1$. According to Eq. (48), the limiting values of the real part of dynamic susceptibility at small and large values of ω_R are, respectively, defined as

$$\chi_0' = \chi, \quad \chi_\infty' = \chi\tau/\tau_1. \tag{50}$$

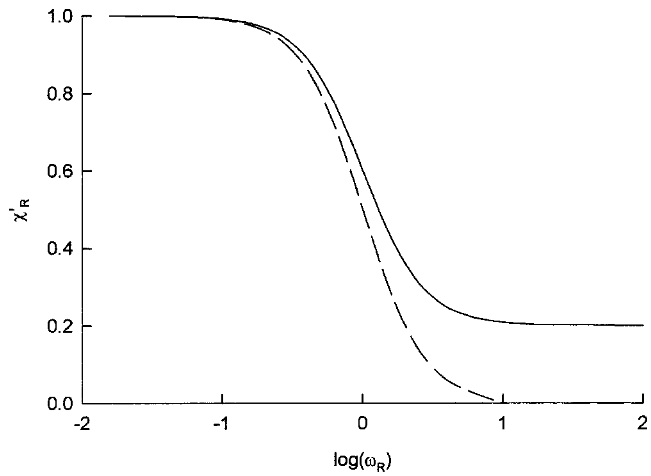

FIG. 1. Frequency dependence of the real part of dynamic susceptibility for $\alpha = 0$ (dashed lines) and $\alpha = 0.2$ (solid lines).

Equation (50) shows that in the viscous case where $\tau = 0$, the Debye theory predicts $\chi_\infty' = 0$. In contrast, in the viscoelastic liquid, the relative limiting susceptibility χ_∞'/χ_0' is nonzero and increases with increasing the relaxation time of the fluid.

VI. CONCLUSIONS

This paper studied the rotational Brownian motion of axisymmetric particles in Maxwell viscoelastic fluid with one relaxation time. This type of Brownian motion is described by the nonlinear stochastic equations (1) and (7) with viscoelastic torque (4), which depends on the orientation of the particle. The solution of this equation represents a non-Gaussian, non-Markov process.

In the important special case when the rotation around the symmetry axis of the particle is dynamically negligible, the random torque in stochastic equations for rotational motion is a Gaussian stochastic process. Its stochastic properties are defined by Eqs. (12). The non-Markov stochastic process, defined by the stochastic equations (7)–(9), was analyzed by increasing the dimensionality of space of dynamic variables.

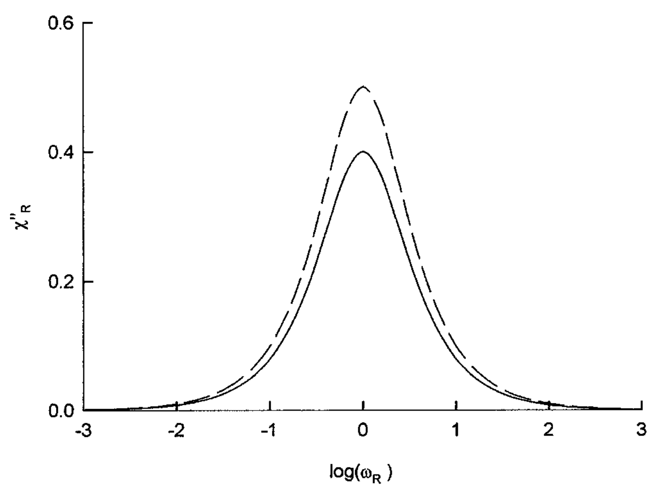

FIG. 2. Frequency dependence of the imaginary part of dynamic susceptibility for the same cases as in Fig. 1.

In so doing, an additional dynamic variable, the Markov random torque, was introduced, which is considered as the solution of an additional stochastic equation with a delta-correlated random torque. Thus the problem of rotational Brownian motion in a Maxwell fluid was reduced to the statistical description of an extended dynamic system (15) and (17). Directly from this dynamic system, the kinetic equation (24) was derived for the joint probability distribution of orientation, angular velocity, and acceleration of a Brownian particle in a Maxwell fluid. This kinetic equation gives the complete statistical description of the non-Markov process.

In Sec. IV, the Brownian orientation dynamics was formulated for axisymmetric particle moving in a Maxwell fluid. In this case, the orientation equation of a particle in the presence of the time-dependent external field was established in the form of Eq. (30) which contains inertial and viscoelastic effects. In noninertial approximation, the problem was reduced to Eq. (31) or its approximate analog, Eq. (32). These are nonlinear stochastic equations for the unit vector of particle orientation. With the use of this equation, the set of nonlinear relaxation equations for the moments (34)–(37) was obtained in Appendix B. Asymptotic solutions (39) and (40) for small and large values of parameters characterizing the strength of the field as compared to the thermal effects, were found for one-time moments in the stationary (equilibrium) case. It should be noted that the nonlinear stochastic equations (31) allow an exact solution, which will be described elsewhere.

The present paper studied a particle with a permanent dipole moment along its axis of symmetry. An external (electric or magnetic) field affects the orientation of such a particle. A simple linearized equation for the mean dipole moment (41) was derived by direct averaging of the Eq. (34) characterizing the evolution of the one-time first moment of particle orientation. Using this equation, the linear noninertial response was calculated for the time-dependent external field. For the oscillating external field with the constant amplitude, the expression (47) for dynamic susceptibility was obtained. It was found that there exists a nonzero high-frequency limiting susceptibility, which increases with increasing the relaxation time of the fluid. In the Debye theory this high-frequency limiting susceptibility is equal to zero.

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APPENDIX A: ROTATIONAL MOBILITY OF AXISYMMETRIC PARTICLES IN LINEAR VISCOELASTIC FLUID

Consider a rigid axisymmetric particle immersed in an isotropic, viscoelastic incompressible quiescent fluid defined by the linear constitutive equations

$$\sigma_{ij} = -p\,\delta_{ij} + 2\int_0^\infty G(s)\,\gamma_{ij}(t-s)\,ds, \tag{A1}$$

$$G(t) = \int_0^\infty H(\tau)e^{-t/\tau}d\ln\tau.$$

Here σ_{ij} is the stress tensor, p is the pressure, $G(t)$ is the relaxation modulus, γ_{ij} is the strain rate, a symmetric part of the velocity gradient, and $H(\tau)$ is the distribution function of relaxation times. The simplest possible viscoelastic fluid is described by the Maxwell model with just one relaxation time τ_0. In this case,

$$H(\tau) = 2\,\eta\,\delta(t-\tau_0), \quad G(t) = (\eta/\tau_0)e^{-t/\tau_0}, \tag{A2}$$

where η is the viscosity of fluid. The Maxwell fluid is an appropriate particular case to begin studying the Brownian motion in viscoelastic fluids. In general, the complex viscosity of a viscoelastic fluid is defined as

$$\eta[\omega] = \int_0^\infty G(t)e^{i\omega t}dt. \tag{A3}$$

In the case of the discrete relaxation spectrum,

$$H(\tau) = 2\sum_{\alpha=1}^{N} \eta_\alpha\,\delta(\tau-\tau_\alpha),$$

the complex viscosity has the form

$$\eta[\omega] = \sum_{\alpha=1}^{N} \frac{\eta_\alpha}{1-i\omega\tau_\alpha}. \tag{A4}$$

Here τ_α are the relaxation times, and η_α are the relaxation viscosities.

When a torque $\mathbf{M}(t)$ acts on a particle, the particle rotates with the angular velocity $\mathbf{\Omega}(t)$. For small value of $\mathbf{M}$ the angular velocity $\mathbf{\Omega}(t)$ is a linear functional of $\mathbf{M}$. For a viscous fluid, hydrodynamic torque acting on the axisymmetric particle is defined by [16]:

$$M_i = -\zeta^r_{ij}\Omega_j, \quad \zeta^r_{ij} = \eta B_{ij}. \tag{A5}$$

Here ζ^r_{ij} is the rotation friction tensor, and B_{ij} is an intrinsic tensor depending only on the size and shape of a particle. It should be noted that there is no coupling between translation and rotational motions for axisymmetric particles.

Taking the Fourier transform of Eq. (A5), and using the well-known principle of correspondence between viscous and viscoelastic linear problems, yields

$$M_i(\omega) = -\eta[\omega]B_{ij}\Omega_j(\omega). \tag{A6}$$

Here $M_i(\omega)$ and $\Omega_i(\omega)$ are the Fourier components of the torque and angular velocity, and the extension of the viscous case to the viscoelastic one was made by substituting the Newtonian viscosity η by the frequency-dependent viscosity $\eta[\omega]$ from Eq. (A4). Hereafter the following notations for the two-sided and one-sided Fourier transforms are used:

$$x(\omega)=\int_{-\infty}^{\infty}x(t)e^{i\omega t}dt,\ \ x[\omega]=\int_{0}^{\infty}x(t)e^{i\omega t}dt.$$

Thus in the viscoelastic case, the torque $\mathbf{M}(t,\mathbf{e})$ is easily obtained from Eq. (A6) in the form of a linear memory functional:

$$M_i(t)=-B_{ij}\int_0^{\infty}G(s)\Omega_j(t-s)\,ds. \tag{A7}$$

Equation (A7) motivates the use of the memory function form in the rotational Langevin equation. It is seen that Eq. (A5) for the viscous fluid is the special case of Eq. (A7) when $\eta(t)=2\eta\delta(t)$. For a Maxwell fluid with a single exponential relaxation function (A2), Eq. (A7) can be rewritten in the form of the differential equation,

$$\tau\frac{dM_i}{dt}+M_i=-\zeta_{ij}^r\Omega_j, \tag{A8}$$

describing the relaxation of torque. For an axisymmetric particle, the rotational friction tensor may be decomposed into the components parallel and orthogonal to the particle symmetry axis:

$$\zeta_{ij}^r=\zeta_{\parallel}^r e_j e_j+\zeta_{\perp}^r(\delta_{ij}-e_ie_j). \tag{A9}$$

Here e_i is the unit vector directed along the symmetry axis of a particle, and $\zeta_{\parallel}^r$ and $\zeta_{\perp}^r$ are the longitudinal and transverse coefficients of rotational friction.

A simple example of an anisotropic axisymmetric particle is infinitesimally thin circular disk, for which the tensor of rotation friction counted off relative to the disk center is [16]

$$\zeta_{ij}^r=\frac{32}{3}\eta b^3\delta_{ij}. \tag{A10}$$

Here b is the disk radius. The flat disk is isotropic for rotational motion. The torque acting on the disk for the rotation about its diameter is the same as for the rotation about its symmetry axis. The most interesting are the ellipsoidal particles. The disklike particles, such as red blood cells and mica flakes, could be approximated by oblate spheroids. The thin circular disk is a degenerated case of a spheroid. The rodlike particles, such as glass fibers, viruses, proteins, and stiff polymer molecules, can be approximated by the prolated spheroids. The rotational Stokes problem is completely solved for the ellipsoid [16]. For long thin prolate spheroids, the rotational friction coefficient $\zeta_{\perp}^r$ has the simple form

$$\zeta_{\perp}^r=\frac{16\pi\eta a^3}{3[2\ln(2s)-1]},\ \ s=1/b\gg 1, \tag{A11}$$

where a and b are, respective, polar and equatorial radii. This expression correlates well with the approximate result [17] for the thin rods.

APPENDIX B: EVOLUTION EQUATIONS FOR ONE-TIME MOMENTS OF ORIENTATION VECTOR

The direct averaging Eq. (32) results in the evolution equation for the average of the first moment $\langle e_i(t)\rangle$

$$\nu(t)\frac{d\langle e_i\rangle}{dt}=\lambda(h_i-\langle e_ie_k\rangle h_k)+\frac{1}{\zeta_{\perp}^r}\varepsilon_{ijk}\langle\xi_j^e e_k\rangle$$

$$(\lambda=\mu/\zeta_{\perp}^r). \tag{B1}$$

The unknown correlator $\langle\xi_i^e e_k\rangle$ in Eq. (A1) is calculated using the Furutsu-Novikov formula,

$$\langle\xi_i^e(t)e_k(t)\rangle=\int_0^t\langle\xi_i^e(t)\xi_n^e(s)\rangle\left\langle\frac{\delta e_k(t)}{\delta\xi_n^e(s)}\right\rangle ds. \tag{B2}$$

Calculating the functional derivative due to Eq. (32),

$$\frac{\delta e_i(t)}{\delta\xi_j^e(t)}=\frac{1}{\zeta_r}\varepsilon_{ijk}e_k \tag{B3}$$

and employing the fluctuation-dissipation relation (33), yields

$$\langle\xi_i^e(t)e_k(t)\rangle=-T\varepsilon_{ikj}\langle e_j\rangle. \tag{B4}$$

Substituting Eq (B4) into Eq. (B1) and using well-known formulas (e.g., see [18]),

$$\begin{gathered}\varepsilon_{pqs}\varepsilon_{snr}=\delta_{pn}\delta_{qr}-\delta_{pr}\delta_{qn},\\ \varepsilon_{pqs}\varepsilon_{sqr}=\delta_{qn}\varepsilon_{pqs}\varepsilon_{snr}=-2\delta_{pr},\end{gathered} \tag{B5}$$

results in the kinetic equation (34) for the mean orientation, which contains the second-order one-time moment.

The evolution equation for the second-order moment $\langle e_ie_k\rangle$ follows from Eq. (32) as

$$\nu(t)\frac{d\langle e_ie_k\rangle}{dt}=\lambda[\langle e_i\rangle h_k+\langle e_k\rangle h_i-2\langle e_ie_ke_j\rangle h_j]$$

$$+\frac{1}{\zeta_{\perp}^r}[\varepsilon_{ijn}\langle\xi_j^e e_ne_k\rangle+\varepsilon_{kjn}\langle\xi_j^e e_ne_i\rangle]. \tag{B6}$$

Using the Furutsu-Novikov formula, results in

$$\langle\xi_i^e(t)e_n(t)e_k(t)\rangle=\int_0^t\langle\xi_i^e(t)\xi_m^e(s)\rangle\left[\left\langle e_n(t)\frac{\delta e_k(t)}{\delta\xi_m^e(s)}\right\rangle\right.$$

$$\left.+\left\langle e_k(t)\frac{\delta e_n(t)}{\delta\xi_m^e(s)}\right\rangle\right]ds. \tag{B7}$$

Equation (B7), when combined with Eqs. (33) and (B5), yields

$$\langle\xi_i^e e_ne_k\rangle=-T[\varepsilon_{ins}\langle e_se_k\rangle+\varepsilon_{iks}\langle e_se_n\rangle]. \tag{B8}$$

Substituting Eq. (B8) into Eq. (B6) and using Eq. (B5) yields Eq. (35) describing the evolution of the second one-time moment.

The equation for the third moment $\langle e_i e_k e_j \rangle$ has the form

$$\nu(t)\frac{d\langle e_i e_k e_j\rangle}{dt} = \lambda[\langle e_i e_k\rangle h_j + \langle e_i e_j\rangle h_k + \langle e_k e_j\rangle h_i - 3\langle e_i e_k e_j e_n\rangle h_n] + \frac{1}{\xi_\perp^r}[\varepsilon_{ins}\langle \xi_n^e e_s e_k e_j\rangle + \varepsilon_{kns}\langle \xi_n^e e_s e_i e_j\rangle + \varepsilon_{jns}\langle \xi_n^e e_s e_i e_k\rangle]. \quad \text{(B9)}$$

The Furutsu-Novikov formula leads to the relation

$$\langle \xi_i^e e_j e_k e_e\rangle = -T\lfloor \varepsilon_{ijs}\langle e_s e_k e_e\rangle + \varepsilon_{iks}\langle e_s e_j e_e\rangle + \varepsilon_{ies}\langle e_s e_j e_k\rangle\rfloor. \quad \text{(B10)}$$

Substituting Eq. (B10) into Eq. (B9) with the use of Eq. (B5) yields Eq. (36) which describes the evolution of the third one-time moment.

Equation (37) for the fourth moment $\langle e_i e_k e_j e_l\rangle$ is derived using Eqs. (33) and (B5), along with the relation

$$\langle \xi_m^e e_s e_j e_k e_l\rangle = -T\lfloor \varepsilon_{msp}\langle e_p e_j e_k e_l\rangle + \varepsilon_{mjp}\langle e_p e_s e_k e_l\rangle + \varepsilon_{mkp}\langle e_p e_s e_j e_l\rangle + \varepsilon_{mlp}\langle e_p e_s e_j e_k\rangle\rfloor \quad \text{(B11)}$$

that follows from the Furutsu-Novikov formula.

[1] P. Debye, *Polar Molecules* (Dover, New York, 1929).
[2] K. A. Valiev and E. N. Ivanov, Sov. Phys. Usp. **16**, 1 (1973).
[3] W. T. Coffey, Adv. Mol. Relax. Interact. Processes **17**, 169 (1980).
[4] G. Wyllie, Phys. Rep. **61**, 327 (1980).
[5] J. McConnel, *Rotational Brownian Motion and Dielectric Theory* (Academic, London, 1980).
[6] V. S. Volkov and G. V. Vinogradov, J. Non-Newtonian Fluid Mech. **15**, 29 (1984).
[7] R. F. Rodriguez and E. Salinas-Rodriguez, J. Phys. A **21**, 2121 (1988).
[8] V. S. Volkov, Sov. Phys. JETP **71**, 93 (1990).
[9] V. S. Volkov and A. I. Leonov, J. Chem. Phys. **104**, 5922 (1996).
[10] Yu. L. Raikher and V. Rusakov, Phys. Rev. E **54**, 3846 (1996).
[11] J.-L. Dejardin, Phys. Rev. E **58**, 2808 (1998).
[12] J. H. van Zanten and K. P. Rufener, Phys. Rev. E **62**, 5389 (2000).
[13] M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).
[14] V. I. Klyatskin and V. I. Tatarskii, Sov. Phys. Usp. **16**, 494 (1973).
[15] K. Furutsu, J. Res. Natl. Bur. Stand., Sect. D **667**, 303 (1963); E. A. Novikov, Sov. Phys. JETP **20**, 1290 (1965).
[16] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1965).
[17] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University, Oxford, 1986).
[18] G. E. Mase, *Theory and Problems of Continuum Mechanics* (McGraw-Hill, New York, 1970).