Orientational kinetics of dipolar particles in a Maxwell fluid matrix: Inertialess limit for the rotary microrheology

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We study magnetic response of an assembly of ferroparticles suspended in a viscoelastic matrix which is modeled by a Maxwell fluid with a unique stress relaxation time. The problem refers to the magnetic microrheology approach where deformational properties of a complex fluid are tested with the aid of embedded nanoparticle probes set to motion by an external ac magnetic field. A possibility is considered to simplify the description of the orientational kinetics of the system at the expense of neglecting inertia effects in particle rotary motion. It is shown that in this aspect a Maxwell matrix differs essentially from the Newtonian one. In the latter the inertialess approximation for the particles of the size ~ 10 nm is valid practically unboundedly. For a viscoelastic matrix the inertialess approximation means an important restriction on the value of the stress relaxation time. Assuming weak nonequilibrium, the magneto-orientational relaxation times are found and low-frequency magnetic spectra of a viscoelastic suspension are determined in the presence of a constant (magnetizing) field.

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I. INTRODUCTION

Microrheology is a term which emphasizes that deformational properties of soft matter are probed with the aid of objects of very small size. Use of microprobes enables one to extend the traditional rheology methods (measuring of mechanical impedance) to formerly inaccessible realms of small linear scales and high frequencies. Indeed, a solid particle of diameter $a \sim 100$ nm suspended in a fluid is three-four orders of magnitude inferior in size than, for example, the sensor unit of a standard cone-plate rheometer. Moreover, the frequency of thermal rotary oscillations of the said particle ranges $\omega_T \sim \sqrt{k_B T/\rho a^5} \sim 10^6$ s^{-1} and at room temperature exceeds three orders of magnitude the maximal velocity gradient achievable in macroscopic experiments.

These circumstances become of vital importance in studies of complex fluids (polymer solutions and melts, biological substances, liquid crystals, etc.), where the spatial scale of supramolecular structures ranges tens and hundreds of nanometers. In such systems viscosity as well as other rheological parameters loses its scale and frequency invariancy: the result of the measurement with the aid of a mechanical probe depends on the size and oscillation frequency of the latter [1]. In turn, this means that microrheology can provide a good deal of valuable structural information on the medium under study. Let us mention two essential moments. First, use of nanoprobes allows one to identify "rheologically" even very small amounts of soft matter. Second, it has been already proven possible to introduce nanoparticles inside living cells [2]. Microrheology *in vivo* opens wide prospects for creation of new characterization tools in biology and biotechnology.

Diagnostics of the properties of a medium by its mechanical impedance implies that one registers displacements (response) of an embedded probe excited by some force. The immanent property of particles with the sizes of hundreds (even thousands) nanometers suspended in a fluid is their perpetual random walks due to the Brownian motion. Microrheology in its basic variant essentially uses this circumstance. So one measures the motion of a particle occurring in response to its thermal excitation [3–5]. The principal part of such an experiment is monitoring the spatial trajectory of a particle of a given size and measuring the magnitude and velocity of its displacements. Afterward this record is interpreted in the framework of some structural model thus evaluating rheological parameters of the medium. Usually, the process is recorded with the aid of some conventional optical tools. However, along with evident convenience, the optical observation technique has certain restrictions. Namely, the substance under study has to be transparent, the probing particle ought to possess enough contrast against the background and, last but not least, the minimal particle size cannot be much smaller than the wavelength of the light.

Involvement of magnetic micro- and nanograins as probes enables one to substantially modify the microrheology concept. We remark that we consider a dilute system where one may neglect all the interparticle interactions including the magnetic dipole-dipole ones. This is the limit which is most adequate for the microrheology framework since introduction of the probes should but minimally disturb the matrix under analysis. Given that, the particle responses are additive. Therefore, having notion of the signal level necessary for detection, one can determine the minimal particle concentration which would guarantee a trustworthy measurement.

Let each particle be a single-domain ferromagnetic crystal, i.e., a microscopic magnet with the size $a \gtrsim 10$ nm and the magnetic moment $\mu \sim I_s a^3$, where $I_s \sim 10^3$ G is the saturation magnetization of the material. Well below the Curie temperature the length of vector $\boldsymbol{\mu}$ may be set constant so that in a uniform magnetic field $\boldsymbol{H}_0$ the particle state is en-

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tirely characterized by the orientation of its magnetic moment. Note that vector $\boldsymbol{\mu}$ can rotate both inside the particle (internal rotary degrees of freedom) and together with the particle body (external rotary degrees of freedom).

If the external magnetic field is uniform and does not contain an alternating part, the particle motion reduces to the Brownian rotary diffusion in a given orientation-dependent potential. In principle, measuring the spectrum of the thermal magnetic noise and separating its components due to internal and external magneto-orientational processes, one can reconstruct the particle rheology at the spatial scale a and in the frequency ranges $\sim\omega_T$ and $\sim\tau_D\sim\zeta/T$; here ζ is the particle rotary resistance coefficient with τ_D being the Debye rotary diffusion time. Note that a modification of the standard (no field imposed) microrheology approach by switching from registration of the translational diffusion of the particles to measuring their rotary Brownian motion was proposed recently in Ref. [6].

With magnetic probes, application of an ac field $\boldsymbol{H}(t)$ allows one to excite—contactlessly and with controllable frequency and amplitude—magneto-orientational oscillations of particles. As the measurable quantity one may choose either the induced dynamic magnetization of the sample (phase-sensitive signal linear in H) or its spectral density (phase-insensitive signal quadratic in H). Under suitable conditions (large particles, transparent substances) the particle motion can also be registered by usual optical observations, see Ref. [2].

We end the description of the *magnetic microrheology* approach by summarizing its advantages over the basic variant of the method. First, mechanical oscillations of the probing particle are excited in a controllable and contactless way. Second, the response signal is the magnetization of the sample. It is measured with radiotechnical appliances and requires neither the particle-matrix optical contrast nor the transparency of the matrix itself. Third, the response amplitude is proportional to the net particle concentration and thus the minimal size of an individual particle might be reduced easily from hundreds of nanometers (the light wavelength) to few nanometers (loss of ferromagnetism as a cooperative effect). From the structural viewpoint, a sample prepared for a microrheology test should be a dilute ferrocolloid made on the base of the analyzed fluid. Methods of synthesis of such systems are well developed nowadays [7,8].

In the present paper we consider a microrheology model that is an assembly of non-interacting monodisperse magnetically hard spherical nanoparticles suspended in a bulk of a viscoelastic medium (Maxwell fluid). We write down the equations for the particle rotary motion with allowance for thermal fluctuations (Sec. II) and study the conditions under which the contributions to the rotary motion due to the particle inertia may be neglected (Sec. III). It turns out that, unlike the case of a Newtonian fluid, for a suspension based on a Maxwell fluid the particle smallness does not any longer suffice as itself to justify the inertialess approximation. In Sec. IV we detail the consequences of this fact. Then a Fokker-Plank equation for the orientational distribution function of the particles is derived and solved by means of the effective-field method. On this basis we obtain analytical formulas describing the change of the magneto-orientational relaxation times in a viscoelastic media (Sec. V) and evaluate the low-frequency magnetic spectra of a viscoelastic ferrocolloid (Sec. VI). General discussion of applicability of the inertialess approximation is given in Sec. VII.

II. STOCHASTIC EQUATIONS AND THE FULL KINETIC EQUATION

The work done hitherto on the orientational kinetics of ferrocolloids was predominantly focused on the cases where the carrier liquid is Newtonian, so that its rheology is solely characterized by its viscosity η [9,10]. For the problems of this type it is easy to make an estimation proving that if a particle is small enough ($\sim$10 nm), then its orientational motion in a rather wide frequency range $\omega\lesssim 1/\tau_I$ (definition and estimation for τ_I see below) may be described in a much simpler manner [9,10]. Namely, one may neglect inertia effects and pass to the so-called inertialess approximation, where the kinetic equation for the particle distribution function reduces to a diffusion equation in the orientational space. This approach is very convenient and is in wide use in statistical mechanics of disperse systems [11]. However, by no means does it allow for all the possible situations.

Below we consider a ferrocolloid with a viscoelastic matrix, which is embodied by a Maxwell fluid. We assume that this latter medium is characterized by just one stress relaxation time τ_M. The disperse phase of the colloid is assumed to consist of identical single-domain magnetically hard particles. As the particle magnetic moments have constant values and are rigidly fixed in the particle bodies, then the state of each particle is fully determined by orientation of the unit vector $\boldsymbol{e}=\boldsymbol{\mu}/\mu$. The set of equations describing under this condition the rotary dynamics of a magnetic Brownian particle has the form [12]

$$\mathcal{I}\frac{d}{dt}\boldsymbol{\Omega}=-\hat{\boldsymbol{J}}U+\boldsymbol{Q}(t),\quad \frac{d}{dt}\boldsymbol{e}=(\boldsymbol{\Omega}\times\boldsymbol{e}),\quad \hat{\boldsymbol{J}}=\left(\boldsymbol{e}\times\frac{\partial}{\partial\boldsymbol{e}}\right),$$

$$\tau_M\frac{d}{dt}\boldsymbol{Q}+\boldsymbol{Q}=-\zeta\boldsymbol{\Omega}+\boldsymbol{y}(t),\quad \langle y_i(t)y_j(t')\rangle=2\zeta T\delta_{ij}\delta(t-t'). \tag{1}$$

Here symbol $\times$ denotes vector product, $\hat{\boldsymbol{J}}$ is the infinitesimal rotation operator, and $\boldsymbol{y}(t)$ is a normalized white noise. In Eq. (1) the following notations are introduced: $\mathcal{I}$ is the particle moment of inertia, U is the interaction energy between the magnetic moment and the external field, $\boldsymbol{Q}$ is the friction torque due to the dissipative coupling of the particle to the carrier fluid. As mentioned, the time τ_M determines relaxation of elastic stresses in the medium. Together with the viscosity η it is a basic rheological parameter of the Maxwell model. Assuming that usual Stokes approximation holds, we take the particle rotary friction coefficient in the form $\zeta=6\eta V$, where V is the particle volume while T expresses temperature in energy units: $k_B=1$. Then the ratio $\eta V/\tau_M$ which relates the viscosity to the relaxation time has the dimensionality and the meaning of the per-particle portion of elastic energy induced in the matrix.

In the Newtonian fluid case ($\tau_M=0$) the set of equations (1) reduces to a single stochastic equation (Langevin equation)

$$\mathcal{I}\frac{d}{dt}\boldsymbol{\Omega}+\zeta\boldsymbol{\Omega}=-\hat{\boldsymbol{J}}U+\boldsymbol{y}(t), \tag{2}$$

with the same white noise as in Eq. (1). From Eq. (2) one sees clearly that the quantity $\tau_I=\mathcal{I}/\zeta$ is the reference "inertial" time which determines relaxation of the particle angular velocity. For a sphere of radius $a\sim 10$ nm in water ($\eta\sim 10^{-2}$ Ps) one gets estimation $\tau_I\sim 10^{-11}$ s. This shows that in the frequency range $\omega<1/\tau_I\sim 10^{11}$ s^{-1} the first term in the left-hand part of Eq. (2) may be neglected. This outlines the validity domain of the inertialess approximation in the Newtonian case.

Following the known rules, one can proceed from the set of Langevin equations (1) to the kinetic Fokker-Planck equation for the distribution function $W(\boldsymbol{e},\boldsymbol{\Omega},\boldsymbol{Q},t)$. The latter describes evolution of the statistical ensemble in the phase space comprising three vector variables: the orientation vector, the angular velocity and the friction torque. We derive this kinetic equation by means of Klimontovich method [13]. To commence the procedure, we rewrite the set of Langevin equations (1) in the form

$$\dot{x}_i=A_i(\boldsymbol{x},t)+y_i(t),\quad \langle y_i(t)y_j'(t)\rangle=2D_{ij}\delta(t-t'). \tag{3}$$

As the random process $\boldsymbol{y}(t)$ has zero mean value, then averaging of the stochastic equation (3) shows that $\boldsymbol{A}$ determines the drift (mean) velocity of change of the particle generalized coordinates $\boldsymbol{x}$. Coefficient D_{ij} here characterizes the intensity of thermal fluctuations and is called the diffusivity matrix.

Let us introduce the density of the Brownian particles in a s-dimensional phase space

$$\mathcal{N}(\boldsymbol{x},t)=\sum_{\alpha=1}^{N}\delta(\boldsymbol{x}-\boldsymbol{x}^{\alpha}(t)). \tag{4}$$

Here summation spans over all N particles constituting the statistical ensemble. In the stochastic process under study the particle number remains constant; due to that the phase density satisfies the normalizing condition

$$\int\mathcal{N}(\boldsymbol{x},t)d\boldsymbol{x}=N, \tag{5}$$

while time evolution of the phase density is governed by the continuity equation

$$\frac{\partial}{\partial t}\mathcal{N}(\boldsymbol{x},t)+\frac{\partial}{\partial\boldsymbol{x}}\{[\boldsymbol{A}+\boldsymbol{y}(t)]\mathcal{N}(\boldsymbol{x},t)\}=0. \tag{6}$$

By definition, the phase density averaged over the ensemble yields the particle distribution function

$$W(\boldsymbol{x},t)=N^{-1}\langle\mathcal{N}(\boldsymbol{x},t)\rangle. \tag{7}$$

In order to obtain the evolution equation for the distribution function, the continuity equation (6) is averaged over the ensemble rendering

$$\frac{\partial}{\partial t}\langle\mathcal{N}\rangle+\frac{\partial}{\partial\boldsymbol{x}}[\boldsymbol{A}\langle\mathcal{N}\rangle+\langle\boldsymbol{y}\,\delta\mathcal{N}\rangle]=0,\quad \delta\mathcal{N}=\mathcal{N}(\boldsymbol{x},t)-\langle\mathcal{N}(\boldsymbol{x},t)\rangle. \tag{8}$$

The result however does not have a closed form since it incorporates an unknown correlation function of the phase density fluctuations. Equation of motion for the latter one gets subtracting Eq. (8) from Eq. (6):

$$\frac{\partial}{\partial t}\delta\mathcal{N}+\frac{\partial}{\partial\boldsymbol{x}}(\boldsymbol{A}\,\delta\mathcal{N})+\frac{\partial}{\partial\boldsymbol{x}}(\boldsymbol{y}\langle\mathcal{N}\rangle+\boldsymbol{y}\,\delta\mathcal{N}-\langle\boldsymbol{y}\,\delta\mathcal{N}\rangle)=0. \tag{9}$$

As the random forces have zero correlation time, for evaluation of the quantity $\langle\boldsymbol{y}\,\delta\mathcal{N}\rangle$ it suffices to construct the solution of Eq. (9) for a time interval ε that is small in comparison with all the other reference times of the problem. Assuming also that the fluctuations are weak enough, i.e., $y_i\delta\mathcal{N}-\langle y_i\delta\mathcal{N}\rangle\ll y_i\langle\mathcal{N}\rangle$, we reduce Eq. (9) to

$$\frac{\partial}{\partial t}\delta\mathcal{N}+\frac{\partial}{\partial\boldsymbol{x}}(\boldsymbol{y}\langle\mathcal{N}\rangle)=0. \tag{10}$$

Integrating this over the above-mentioned interval ε and neglecting initial fluctuations, one finds

$$\delta\mathcal{N}(\boldsymbol{x},t)=-\frac{\partial}{\partial\boldsymbol{x}}\int_{t-\varepsilon}^{t}dt'\boldsymbol{y}(t')\langle\mathcal{N}(\boldsymbol{x},t')\rangle. \tag{11}$$

Substituting Eq. (11) in Eq. (9) with allowance for the random torque correlator (3), one gets the Fokker-Planck equation (FPE)

$$\frac{\partial}{\partial t}W(\boldsymbol{x},t)+\frac{\partial}{\partial x_i}[A_iW(\boldsymbol{x},t)]=\frac{\partial}{\partial x_ix_j}D_{ij}W(\boldsymbol{x},t). \tag{12}$$

Then from the general kinetic equation we proceed to its explicit form corresponding to the set of Langevin equations (1):

$$\begin{aligned}\frac{\partial}{\partial t}W(\boldsymbol{e},\boldsymbol{\Omega},\boldsymbol{Q},t)&+\left[\Omega_i\hat{J}_i-(\hat{J}_iU)\frac{\partial}{I\partial\Omega_i}\right]W\\&+\left(Q_i\frac{\partial}{I\partial\Omega_i}-\frac{\zeta}{\tau_M}\Omega_i\frac{\partial}{\partial Q_i}\right)W\\&=\frac{1}{\tau_M}\frac{\partial}{\partial Q_i}\left(Q_i+\frac{\zeta T}{\tau_M}\frac{\partial}{\partial Q_i}\right)W.\end{aligned} \tag{13}$$

We remark that the action of operator $\hat{\boldsymbol{J}}$ enclosed in parentheses is bounded by the latter, i.e., concerns only the potential function U. For a particular case of plane particle rotations (rigid rotator model) the corresponding equation was derived in Refs. [14,15]. A three-dimensional axially symmetrical Brownian particle was considered in Ref. 16. In the latter, however, only FPE for a particle in the absence of an external field ($U=0$) was obtained.

By direct substitution, it is easy to prove that the equilibrium solution of Eq. (13) is the extended Maxwell-Boltzmann distribution [14,15]:

$$W_0(\boldsymbol{e},\boldsymbol{\Omega},\boldsymbol{Q}) \propto \exp\left[-\frac{1}{2T}I\Omega^2 - \frac{1}{T}U(\boldsymbol{eH}) - \frac{\tau_M Q^2}{2\zeta T}\right]. \tag{14}$$

Integration of distribution (14) with respect to the variable Q transforms it in the conventional Maxwell-Boltzmann distribution $W_0(\boldsymbol{e},\boldsymbol{\Omega})$. This distribution is a direct consequence of the existence and availability of thermodynamic equilibrium between the particle ensemble and the thermal bath. As such $W_0(\boldsymbol{e},\boldsymbol{\Omega})$ is insensitive to the origin of the dissipative processes in the system. After integration with respect to the phase variable $\boldsymbol{\Omega}$, the function $W_0(\boldsymbol{e},\boldsymbol{\Omega})$ assumes the standard Boltzmann form

$$W_0(\boldsymbol{e}) \propto \exp\left[-\frac{1}{T}U(\boldsymbol{eH})\right], \tag{15}$$

which incorporates only the angular coordinates of the system.

III. EQUATIONS OF MOTION IN THE INERTIALESS LIMIT

To derive the inertialess approximation for the case where a magnetic particle is embedded in a Maxwell fluid, we first eliminate from the set (1) the viscous torque $\boldsymbol{Q}$. This results in a stochastic equation of the form

$$\mathcal{I}\left[\tau_M\frac{d^2}{dt^2} + \frac{d}{dt}\right]\Omega_i + [\zeta\delta_{ij} + \tau_M\hat{J}_i\hat{J}_jU(\boldsymbol{eH})]\Omega_j = -\hat{J}_iU(\boldsymbol{e}\tilde{\boldsymbol{H}}) + y_i(t); \tag{16}$$

here tilde denotes the magnetic field renormalized according to

$$\tilde{\boldsymbol{H}} \equiv \boldsymbol{H} + \tau_M\dot{\boldsymbol{H}} \equiv \boldsymbol{H} + \tau_M\frac{d\boldsymbol{H}}{dt}. \tag{17}$$

Formally, passing to the inertialess limit may be done by neglecting in the left-hand side of the equation the first bracket that stands alongside the particle moment of inertia $\mathcal{I}$. Then with the remaining stochastic equation one associates a Fokker-Planck equation, see Eqs. (3)–(12). A simple analysis shows, however, that for such a kinetic equation an equilibrium solution in the form of Boltzmann distribution (15) does not exist. Hereby, if based on Eq. (16) at $\mathcal{I}=0$, the theory falls in contradiction with the fundamental concept of statistical physics. Indeed, the absence of a Boltzmann-like solution refutes the very possibility of equilibrium between the particles and the suspending medium. As such it cannot be true.

The contradiction we have run into indicates that Eq. (16) at $\mathcal{I}=0$ is not an adequate Langevin equation for the inertialess limit. To resolve the situation, one has to modify the Langevin equation in such a way that it would yield a correct kinetic equation. A method realizing this principle and yielding amended stochastic equations (the so-called K-form) had been proposed by Klimontovich, see [17], for example. Following the main idea, we write the stochastic equation in the form

$$\Omega_i = -b_{ij}\hat{J}_jU(\boldsymbol{e}\tilde{\boldsymbol{H}}) + A_i + y_i(t) \tag{18}$$

with the notations

$$b_{ij} = \zeta_{ij}^{-1} = [\zeta\delta_{ij} + \tau_M\hat{J}_i\hat{J}_jU(\boldsymbol{eH})]^{-1},$$

$$\langle y_i(t)y_j(t')\rangle = 2D_{ij}(\boldsymbol{e})\delta(t-t'), \tag{19}$$

where $A_i(\boldsymbol{e})$ and $D_{ij}(\boldsymbol{e})$ are yet unknown vector and matrix, and b_{ij} is the orientational mobility tensor, a quantity that is inverse to the tensor friction coefficient ζ_{ij}. We remark essential differences between the stochastic equation (18) and the one obtained from (16) on setting $\mathcal{I}=0$. First, in the modified equation an additional drift term is included, and, second, the noise there is multiplicative. The latter follows from the fact that correlation function $\langle y_i(t)y_j(t')\rangle$ unlike the noise in Eq. (1) now depends on the dynamical variable $\boldsymbol{e}$. Proceeding in a standard way, we arrive at the Fokker-Planck equation corresponding to the Langevin equation (18):

$$\frac{\partial W(\boldsymbol{e},t)}{\partial t} = \hat{J}_i\{b_{ij}[\hat{J}_jU(\boldsymbol{e}\tilde{\boldsymbol{H}})] - A_i + \hat{J}_jD_{ij})\}W(\boldsymbol{e},t), \tag{20}$$

note that operator $\hat{\boldsymbol{J}}$ inside the square brackets acts only on function U. The kinetic equation (20), as well as the initial stochastic equation (18), needs to be closed since vector $\boldsymbol{A}$ and tensor D_{ij} are not yet determined. We base the closing procedure on the following considerations. As already noted, independently of the actual mechanism of dissipative interactions in the system, the equilibrium solution of the kinetic equation must have the form of Boltzmann distribution (15). Let us rewrite FPE (20) with the right-hand side that explicitly allows for this fact:

$$\frac{\partial}{\partial t}W = \hat{J}_ib_{ij}W\hat{J}_j[U(\boldsymbol{e}\tilde{\boldsymbol{H}}) + T\ln W]. \tag{21}$$

Indeed, the said solution readily turns up had one required that the inner bracket in Eq. (21) equals zero.

IV. ROTATIONAL MOBILITY OF A PARTICLE IN A VISCOELASTIC MATRIX

Comparing the right-hand sides of Eqs. (20) and (21), one finds the relation between the white noise intensity, orientational mobility and temperature. The expression for the thermofluctuational drift vector is obtained as well:

$$A_i = \hat{J}_jD_{ij}, \quad D_{ij} = Tb_{ij} = T[\zeta\delta_{ij} + \tau_M\hat{J}_i\hat{J}_jU(\boldsymbol{eH})]^{-1}. \tag{22}$$

As formulas (22) show, allowance for a finite memory time in the system results in a considerable change of the particle rotary diffusion process versus the case of a Newtonian fluid. The first of Eq. (22) renders the fluctuation-dissipation relationship for the problem under study. One sees that the angular mobility of a spherical particle becomes dependent on the type of the orientational potential and, hereby, anisotropic. Moreover, Eq. (22) shows that for the angles where $\hat{J}_i\hat{J}_jU>0$, the effective friction coefficient increases while in the regions where $\hat{J}_i\hat{J}_jU<0$ it diminishes.

Thus we have proven that, having been suspended in a medium with memory, a Brownian particle in the course of its rotations (both random and regular) lingers itself near favorable orientations (potential minima) and more fast leaves unfavorable directions (potential maxima). As one might have expected, at $\tau_M=0$ the Fokker-Planck equation (21) reduces to the well-studied equation describing particle rotary diffusion in an ordinary fluid, see [10], for example.

The first of relations (22) evidences that in a viscoelastic suspension in the presence of an external field there arises a specific interaction between the random and regular motions of the particle. This is how we interpret the appearance of the thermofluctuational drift $\boldsymbol{A}$ which is nonzero for any orientation-dependent function U. Tying up the random and regular processes, vector $\boldsymbol{A}$ has a dual origin. On the one hand, it is introduced by relation (18) as a regular (drift) torque acting on a particle. On the other hand, from formulas (22) it follows that the length of vector $\boldsymbol{A}$ is proportional to temperature that is typical for fluctuational terms and impossible for a regular one. We would like to stress that, however "anti-intuitive" does the thermofluctuational drift seem at first sight, its existence follows directly from the Boltzmann principle.

Apparently, the aforepresented considerations have more general relevance. For example, they equally could be applied to a nonconducting suspension of electrical dipoles, etc. To be specific, let us take a quick look on the effect of viscoelasticity of the carrier fluid on rotary dissipation in a suspension of single-domain particles. Consider a particle with a "frozen-in" magnetic moment $\mu=I_sV$. This particle is subjected to an external magnetic field $\boldsymbol{H}_0=\boldsymbol{H}_0\boldsymbol{h}$, so that its orientational potential is

$$U=-\boldsymbol{\mu}\boldsymbol{H}_0=-\mu H_0(\boldsymbol{eh}). \tag{23}$$

Substituting it in the Boltzmann distribution (15), one finds the equilibrium tensor friction coefficient ζ_{ij} of the particle, it is given by the first of formulas (19). After simple calculation one gets

$$\langle\zeta_{ij}\rangle_0=\zeta P_{ij}^{\parallel}+[\zeta+\mu H_0\tau_M\langle\boldsymbol{eh}\rangle_0]P_{ij}^{\perp},$$

$$P_{ij}^{\parallel}=h_ih_j,\quad \hat{P}_{ij}^{\perp}=\delta_{ij}-h_ih_j, \tag{24}$$

$$\langle\boldsymbol{eh}\rangle_0=L(\xi)\equiv 1/\tanh\,\xi-1/\xi,\quad \xi=\mu H_0/T. \tag{25}$$

Here we have introduced notations for the projecting tensors in the longitudinal and transverse (with respect to the field $\boldsymbol{H}_0$) directions. In more detail, the projecting technique is described below, see Eq. (37) and after. From expression (24) one sees that in the strongest way the magnetic field affects the transverse motion of the particle. The corresponding friction coefficient may be written as $\zeta_{\perp}^{\mathrm{eff}}=\zeta+\mu H\tau_ML(\xi)$. Presenting friction in this expression according to the Stokes formula $\zeta=6\eta V$, one gets an estimation for the effective field-dependent viscosity:

$$\eta_{\perp}^{\mathrm{eff}}=\eta+\frac{1}{6}\tau_MI_sHL(\xi). \tag{26}$$

To avoid any confusion we note that formula (26) does not result from a closed calculation of effective viscosity like the one done in Ref. [18] for the case of a usual magnetic fluid. The appropriate treatment of the actual problem is outlined in our presentation [19]; when accomplished, the work will make a subject of a separate publication.

Another important consequence of the presence of a finite stress relaxation time is renormalization of the field amplitude acting on the particle. This rescaling, see the argument of the potential function U in the kinetic equation (21), is expressed by relation (17). It is logical to call the result the *dynamic elasticity* as the modified field $\tilde{H}$ enters only the athermal part of the exerted torque and for the static regime ($dH/dt=0$) the renormalization is absent.

V. RELAXATION TIMES

The peculiarities of the rotary friction of a suspended particle reflect themselves in the relaxation of magnetization of a ferrocolloid. To characterize the effect, we do the following. First, on the basis of the above-derived kinetic equation (21), we obtain the chain-linked set for the moments of the distribution function. Then assuming weak deviations from equilibrium (small probing field), we uncouple the set in the lowest order. This results in a linear equation for the time derivative of the first moment whence the relaxation times are evaluated.

The evolution equation for the average value of any function of orientational state

$$\langle\Psi\rangle=\int d\boldsymbol{e}\Psi(\boldsymbol{e})W(\boldsymbol{e},t) \tag{27}$$

follows from the kinetic equation (21) after integrating it by parts and taking into account cyclic boundary conditions. Performing that, one gets

$$\frac{d}{dt}\langle\Psi\rangle=-\langle b_{ij}[\hat{J}_i\Psi][\hat{J}_jU(\boldsymbol{e}\tilde{\boldsymbol{H}})]\rangle+T\langle\hat{J}_jb_{ij}\hat{J}_i\Psi\rangle; \tag{28}$$

here, as in formula (20), action of operators $\hat{\boldsymbol{J}}$ is limited by square brackets.

As the orientational mobility tensor ought to be positive, from expression (19) it becomes clear that this is possible only if the field-induced friction is sufficiently small in comparison with the Stokes term. In what follows, we restrict ourselves by the linear in τ_M approximation. Given that, the expression for the orientational mobility may be written in the explicit form:

$$\begin{aligned} b_{ij}(\boldsymbol{eH})&=[\zeta\delta_{ij}+\tau_M\hat{J}_i\hat{J}_jU(\boldsymbol{eH})]^{-1}\\ &\approx\frac{1}{\zeta}\left(\delta_{ij}-\frac{\tau_M}{\zeta}\hat{J}_i\hat{J}_jU\right)\\ &=\frac{1}{\zeta}\{[1-m(\boldsymbol{eh})]\delta_{ij}+me_ih_j\},\quad m\equiv\frac{\tau_M}{\zeta}\mu H_0. \end{aligned} \tag{29}$$

Here we took into account that the potential energy (23) of a rigid dipole in an external magnetic field $\boldsymbol{H}$ contains the contributions from the constant component $\boldsymbol{H}_0=H_0\boldsymbol{h}^0$ and the probing signal $\boldsymbol{H}_1(t)=H_1(t)\boldsymbol{h}^1$. Under those conditions the vector of instantaneous orientation of the field in Eq. (29) and in those which will follow is given by

$$\boldsymbol{h}=[\boldsymbol{h}^0+\varepsilon(t)\boldsymbol{h}^1],\quad \varepsilon\equiv H_1/H_0,\quad \tilde{\varepsilon}\equiv 1+\tau_M\dot{\varepsilon}. \tag{30}$$

Substituting the orientational mobility (29) in the equation of motion (28), we get the evolution equation for the first moment

$$\frac{d}{dt}\langle e_i\rangle=-\frac{2T}{\zeta}\langle e_i\rangle+\frac{\mu H_0}{\zeta}(\tilde{h}_i-\langle e_ie_j\rangle\tilde{h}_j)-\frac{mT}{\zeta}(h_i-3\langle e_ie_j\rangle h_j)$$
$$-\frac{m\mu H_0}{\zeta}(\langle e_j\rangle\tilde{h}_ih_j-\langle e_ie_je_k\rangle\tilde{h}_jh_k), \tag{31}$$

where $\tilde{h}_i=h_i+\tau_M\dot{h}_i$ is vector $\boldsymbol{h}$ modified according to the scheme (17); note that after this transformation vectors $\boldsymbol{h}$ and $\tilde{\boldsymbol{h}}$ are not unit ones any longer. As seen from Eq. (31), viscoelasticity augments the order of coupling of the moment equation set in comparison with the Newtonian case, see [10]. Namely, now the equation for the first moment incorporates, along with the second one, the third moment as well. Equation (31) shows that in the case of an ordinary fluid ($m=0$) the rate of orientational relaxation is controlled by two parameters:

$$\tau_D=\zeta/2T,\quad \tau_H=\zeta/\mu H_0, \tag{32}$$

which describe, respectively, the reference time of rotary diffusion and the time of the particle orientation along the applied field. In the viscoelastic case in Eq. (31) one more parameter is present: $m=\tau_M/\tau_H$, which in the model studied here—the inertialess approximation—we have restricted by the condition $m<1$.

We close the equation for the first moment with the aid of the effective-field method [10]. It assumes that the nonequilibrium distribution function W entering Eq. (21) differs but slightly from the Boltzmann distribution (15) and admits the representation

$$W(\boldsymbol{e},t)=W_0(\boldsymbol{e},\boldsymbol{h}^0)\{1+a_i(t)[e_i-\langle e_i\rangle_0]\}, \tag{33}$$

$$W_0(\boldsymbol{e},\boldsymbol{h}^0)=\frac{\xi}{4\pi\mathrm{sh}\xi}\exp[\xi(\boldsymbol{e}\boldsymbol{h}^0)],\langle\cdots\rangle_0=\int\cdots W_0d\boldsymbol{e}. \tag{34}$$

Calculating the average value of the particle orientation vector with the distribution function (33) we get the relation between vector $\boldsymbol{a}$ and the observable macroscopic quantity—the non-equilibrium part of the first statistical moment—in the form of a linear equation set:

$$\langle e_i\rangle=\langle e_i\{1+a_j(t)[e_j-\langle e_j\rangle_0]\}\rangle_0=\langle e_i\rangle_0+a_j(t)N_{ij},$$

$$N_{ij}\equiv\langle e_ie_j\rangle_0-\langle e_i\rangle_0\langle e_j\rangle_0. \tag{35}$$

From here it follows that vector $\boldsymbol{a}$ is proportional to the nonequilibrium part of the net orientation and is given by formula

$$a_i(t)=(N_{ij})^{-1}[\langle e_j\rangle-\langle e_j\rangle_0]. \tag{36}$$

For calculation of the inverse matrix in Eq. (36) and in all further treatment of vector and tensor variables, it is convenient to use the projecting operator technique. In the system under study the macroscopic anisotropy is induced by the presence of a constant field $\boldsymbol{H}_0$ and thus is uniaxial. Under these conditions, any macroscopic characteristics that is a second-rank tensor can be expanded with respect to the set of the projecting tensors. For example,

$$N_{ij}=\langle e_ie_j\rangle_0-\langle e_i\rangle_0\langle e_j\rangle_0=N^{\parallel}P^{\parallel}_{ij}+N^{\perp}P^{\perp}_{ij}. \tag{37}$$

Basic tensors P_{ij} are constructed from the components of vector $\boldsymbol{h}^0$ according to

$$P^{\parallel}_{ij}=h^0_ih^0_j,\quad P^{\perp}_{ij}=\delta_{ij}-h^0_ih^0_j,\quad P^{\alpha}_{ij}P^{\beta}_{jk}=\delta_{\alpha\beta}P^{\alpha}_{ik},$$
$$\alpha,\beta=\parallel,\perp, \tag{38}$$

whence it is easy to see that the set is full and orthonormalized. In representation (38), derivation of the inverse matrix reduces to a simple scalar operation: inversion of the respective components. For tensor (37) one has

$$(N_{ij})^{-1}=\frac{1}{N_{\parallel}}P^{\parallel}_{ij}+\frac{1}{N_{\perp}}P^{\perp}_{ij}. \tag{39}$$

With allowance for Eqs. (37) and (39) the expression for the nonequilibrium correction to the distribution function W_0 takes the form

$$a_i(t)=\left[\frac{1}{N_{\parallel}}P^{\parallel}_{ij}+\frac{1}{N_{\perp}}P^{\perp}_{ij}\right][\langle e_j\rangle-\langle e_j\rangle_0],$$
$$N_{\parallel}=\langle\cos^2\vartheta\rangle_0-\langle\cos\vartheta\rangle_0^2,\quad N_{\perp}=\tfrac{1}{2}[1-\langle\cos^2\vartheta\rangle_0]; \tag{40}$$

here $\cos\vartheta=(\boldsymbol{e}\boldsymbol{h}^0)$. It is clear that with the aid of the distribution function in the form (33) one can find a linear (with respect to the variable $\boldsymbol{a}$) part of the moment of any order. Sequential usage of this procedure in Eq. (31) allows one to fully close the equation of motion for the first moment.

Linearization is done around the equilibrium state where the distribution function has the form (33) with $\boldsymbol{a}=0$. This means that all the equilibrium moments $\langle\cos^n\vartheta\rangle_0$ are known as well. Making use of the axial symmetry of the system and performing integration by parts, one obtains the recurrence relation

$$\langle\cos^{\ell}\vartheta\rangle_0\equiv C_{\ell}=\frac{e^{\xi}+(-1)^{\ell+1}e^{-\xi}}{2\sinh\xi}-\frac{\ell C_{\ell-1}}{\xi},\quad C_0=1. \tag{41}$$

As the expression for the equilibrium distribution may not depend on the actual mechanisms of dissipation, in the moment equation (31) the groups of terms standing alongside

the zero and first powers of the dissipative parameter m must turn to zero independently of one another. Writing down these conditions, one gets two relations

$$\frac{1}{\tau_H}[h_i^0 - \langle e_i e_j\rangle_0 h_j^0] = \frac{1}{\tau_D}\langle e_i\rangle_0,$$

$$\frac{1}{\tau_H}[h_i^0\langle e_j\rangle_0 - \langle e_i e_j e_k\rangle_0 h_k^0]h_j^0 = \frac{1}{2\tau_D}[3\langle e_i e_j\rangle_0 h_j^0 - h_i^0]. \quad (42)$$

In order to verify them, it suffices to take the projections on the direction of the constant magnetic field and use the recurrence relation (41).

First, we eliminate with the aid of equalities (42) those two terms in the right-hand side of Eq. (31), which depend solely on the constant external field. Then we linearize the resulting expression with respect to the Maxwell relaxation time τ_M and to the weak probing field ($\propto\varepsilon \ll 1$), see formula (30). After that the equation for the first moment takes the form

$$\begin{aligned}\frac{d}{dt}\langle e_i\rangle = &-\frac{1}{\tau_D}[\langle e_i\rangle - \langle e_i\rangle_0] - \frac{1}{\tau_H}[\langle e_i e_j\rangle - \langle e_i e_j\rangle_0]h_j^0 \\ &+ \frac{3m}{2\tau_D}[\langle e_i e_j\rangle - \langle e_i e_j\rangle_0]h_j^0 - \frac{m}{\tau_H}\{h_i^0 h_j^0[\langle e_j\rangle - \langle e_j\rangle_0] \\ &- [\langle e_i e_j e_k\rangle - \langle e_i e_j e_k\rangle_0]h_j^0 h_k^0\} + \frac{\tilde{\varepsilon}}{\tau_H}[\delta_{ij} - \langle e_i e_j\rangle_0]h_j^1 \\ &- \frac{m\varepsilon}{2\tau_D}[h_i^1 - 3\langle e_i e_j\rangle_0 h_j^1] - \frac{m\varepsilon}{\tau_H}[\delta_{ik}\langle e_j\rangle_0 - \langle e_i e_j e_k\rangle_0] \\ &\times(h_j^0 h_k^1 + h_j^1 h_k^0). \end{aligned} \quad (43)$$

Although looking cumbersome, this formula has a clear structure. All the terms which do not contain parameter ε, present the effect of the nonequilibrium parts of the first to third moments on the rate of change of the first moment. All the contributions proportional to ε stem from the direct cause of nonequilibrium: action of the external torque. In our treatment we assume that deviations of the moments are linear in the distribution function perturbations. This perturbation, in turn, may be expressed through the nonequilibrium part of the first moment $\langle \delta e_j\rangle = \langle e_j\rangle - \langle e_j\rangle_0$. This closes the moment equation. Presenting all second-rank tensors in the right-hand side of Eq. (43) in the form of expansions with respect to projecting operators (38), we transform the equation to

$$\frac{d}{dt}\langle \delta e_i\rangle = -\left[\frac{1}{\tau_\parallel}P_{ij}^\parallel + \frac{1}{\tau_\perp}P_{ij}^\perp\right]\langle \delta e_j\rangle + (f_\parallel P_{ij}^\parallel + f_\perp P_{ij}^\perp)h_j^1, \quad (44)$$

where the relaxation times $\tau_\parallel$ and $\tau_\perp$ are real and positive, and the coefficients $f_\parallel$ and $f_\perp$ are real functions.

Comparison of Eqs. (43) and (44) shows that to determine the times τ_α and force factors f_α it suffices to find explicit expressions for the nonequilibrium parts of the second and thirds moments. Performing obvious operations, one gets, for example,

$$[\langle e_i e_j\rangle - \langle e_i e_j\rangle_0] = [\langle e_i e_j e_k\rangle_0 - \langle e_i e_j\rangle_0\langle e_k\rangle_0]a_k. \quad (45)$$

Then, using representation (40) for vector $\boldsymbol{a}$ and expanding with respect to the projecting basis (38) the equilibrium second-rank tensor, which results from convolution of the third-rank tensor with the unit vector $\boldsymbol{h}^0$, one finds

$$[\langle e_i e_j\rangle - \langle e_i e_j\rangle_0]h_j^0 = \left[\frac{C_3 - C_2 C_1}{C_2 - C_1^2}P_{ij}^\parallel + \frac{C_1 - C_3}{1 - C_2}P_{ij}^\perp\right]\langle \delta e_j\rangle. \quad (46)$$

In a similar way we get expression for the dipolar part of the third moment perturbation:

$$[\langle e_i e_j e_k\rangle - \langle e_i e_j e_k\rangle_0]h_j^0 h_k^0 = \left[\frac{C_4 - C_3 C_1}{C_2 - C_1^2}P_{ij}^\parallel + \frac{C_2 - C_4}{1 - C_2}P_{ij}^\perp\right]\langle \delta e_j\rangle. \quad (47)$$

After substituting expansions (46) and (47) in Eq. (43) and simple transformations with the use of recurrence relations (41), we obtain the relaxation times of the first moment, that is, those of the system magnetization:

$$\tau_\parallel = 2\tau_D\frac{C_2 - C_1^2}{1 - C_2}\left[1 + q\frac{3C_2 - 1}{2(1 - C_2)}\right],$$

$$\tau_\perp = 2\tau_D\frac{1 - C_2}{1 + C_2}\left[1 + q\frac{\xi(C_1 + C_3)}{2(1 + C_2)}\right]; \quad (48)$$

here the viscoelasticity parameter may be written in several equivalent forms:

$$q \equiv \tau_M/\tau_D = 2\tau_M T/\zeta = 2\tau_M/(\xi\tau_H) = 2m/\xi, \quad (49)$$

see Eqs. (25), (29), and (32).

In the limit $q \to 0$ from Eq. (48) follow the well-known expressions for the field dependence of the orientation relaxation times of a magnetically hard Brownian particle suspended in a viscous (Newtonian) fluid [10]. As it should be, in the strong field limit ($\xi \to \infty$) the asymptotic values of the times satisfy the condition $\tau_\perp = 2\tau_\parallel$. In a viscoelastic fluid ($q \neq 0$) but at $H_0 = 0$ definition (41) yield $C_1 = C_3 = 0$ and $C_2 = 1/3$. Substituting these values in Eq. (48), one sees that the factors in front of q turn into zero identically. This yields $\tau_\parallel = \tau_\perp = \tau_D$ and again the situation coincides with that for a viscous fluid. Thus we see that in the absence of external field the viscoelasticity of the matrix does not affect the orientation relaxation times of a ferrocolloid. In terms of our model this follows from the fact that at $H_0 = 0$ the energy-scape of the magnetic moment turns into a plane [$U = \text{const}(\vartheta)$] with no extrema and, thus, without renormalization of the particle friction coefficient.

The effect of viscoelasticity on the magneto-orientational relaxation emerges as soon as the magnetizing field is nonzero. Then, as Eq. (48) shows, at any value of ξ both the longitudinal and transverse times exceed similar characteristics for the case of a Newtonian matrix. This agrees with the general conclusion made in the above, that in the presence of an external field the particle motion in the vicinity of potential minima slows down. The dependencies of the relaxation times on the magnetizing field at several values of the di-

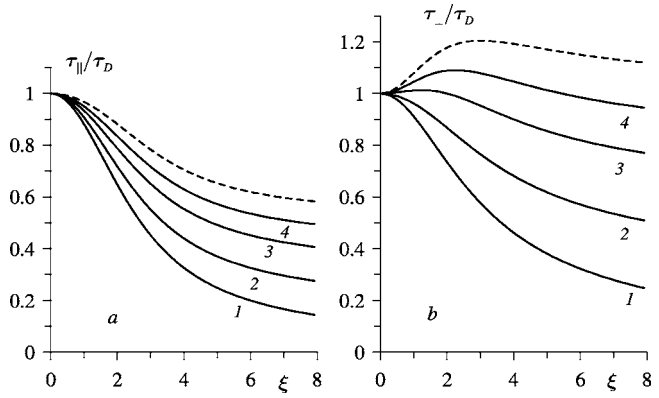

FIG. 1. Longitudinal (a) and transverse (b) times of magnetic relaxation as functions of the dimensionless applied field; at solid lines the viscoelasticity parameter is $q=0$ (1), 0.3 (2), 0.6 (3), 0.8 (4); the dashed lines correspond to $q=1$.

mensionless viscoelasticity parameter are shown in Fig. 1; the lowest curve at each graph corresponds to the case $q=0$, i.e., a linearly viscous matrix.

As seen from the graphs, in a non-Newtonian suspension the rotary diffusion of the particles affects considerably the magnetic relaxation. Indeed, the magnetization relaxation times (Fig. 1), being decreasing functions of ξ, are the greater the greater is τ_M. Moreover, in some cases the viscoelastic behavior is capable of changing the very character of the dependence $\tau_\perp(\xi)$. Let us write down expansions of functions $\tau_{\perp,\parallel}$ at weak fields

$$\frac{\tau_\parallel}{\tau_D} \approx 1 + \frac{1}{10}\left(q - \frac{4}{3}\right)\xi^2, \quad \frac{\tau_\perp}{\tau_D} \approx 1 + \frac{1}{5}\left(q - \frac{1}{2}\right)\xi^2. \quad (50)$$

From here one sees that derivatives $d\tau_\alpha/d\xi$ can change sign. For $\tau_\parallel$ it becomes positive at $q>4/3$ while for $\tau_\perp$ the initial growth takes place yet at $q>1/2$. This means that at sufficient viscoelasticity the time of orientational relaxation first grows with the field and only then begins to decrease tending to the asymptotic law $\tau_\alpha \propto 1/\xi$. In result, a maximum of τ occurs at $\xi \sim 1$. However, it turns out that one may be sure only in the maximum of the $\tau_\perp(\xi)$ dependence. As is shown below, the inertialess approximation incorporates as a necessary assumption the condition $q<1$. Due to this restriction, Eq. (48) at $q>4/3$ might become incorrect. Because of that, the maximal value of the viscoelasticity parameter used to make plots in Fig. 1 is $q=1$ (dashed lines).

Consider the transverse relaxation time in the parameter interval $1/2<q<1$. In this region the inertialess approximation is valid and, according to Eq. (50), function $\tau_\perp(\xi)$ grows in the weak-field domain. Therefore, the occurrence of a maximum is completely justified. Let us give an example. Numeric evaluation with Eq. (48) at the viscoelasticity level $q=0.8$ yields a "hump" of $\tau_\perp$ at $\xi_{\max} \approx 2.21$. Testing this value on the validity of the condition $m<1$, we write the latter in the form $\xi<2/q$ whence at $q=0.8$ we get $\xi<2.5$. So we see that the obtained value of $\xi_{\max}$ lies below this boundary.

At strong fields the expressions in square brackets in Eq. (48) tend to the common limit $(1+m)$, where the parameter $m=\tau_M/\tau_H$ is defined by Eqs. (29) and (32). Therefore, the asymptotic (at $H_0 \to \infty$) relation $\tau_\perp = 2\tau_\parallel$, which connects the times of magneto-orientational relaxation in the case of a rigid dipole in a viscous fluid, holds in the viscoelastic case as well.

VI. DYNAMIC MAGNETIC SUSCEPTIBILITY

Linear susceptibility $\chi(\omega)$ with respect to an external ac field is a very important characteristics of any system. Magnetization of a dilute colloid containing per its unit volume n identical particles, each of which possesses the magnetic moment μ, is

$$\boldsymbol{M} = n\mu\langle \boldsymbol{e} \rangle; \quad (51)$$

with the statistical averaging described by Eq. (27). We present the linear response of magnetization to the harmonic probing field $\boldsymbol{H}_1(t) = H_1 \cos \omega t \boldsymbol{h}^1$ in a standard form

$$\delta M_i = n\mu\langle \delta e \rangle = \tfrac{1}{2}[\chi_{ik}(-\omega) + \chi^*_{ik}(\omega)]H_1 h^1_k. \quad (52)$$

Thus defined dynamic susceptibility is a macroscopic second-rank tensor and may be expanded with respect to the projecting basis (46) as $\chi_{ik} = \chi_\parallel P^\parallel_{ik} + \chi_\perp P^\perp_{ik}$. Substituting a solution in the form (52) in Eq. (44), one finds

$$\chi_\alpha(\omega) = \frac{n\mu}{1/\tau_\alpha - i\omega}\frac{f_\alpha(\omega)}{H_1}, \quad \alpha = \parallel, \perp, \quad (53)$$

thus getting a general description for the components of susceptibility for the case where the probing field is directed either along $(\boldsymbol{h}^0\boldsymbol{h}^1 = \pm 1)$ or across $(\boldsymbol{h}^0\boldsymbol{h}^1 = 0)$ the magnetizing field $\boldsymbol{H}_0$.

The expressions for the components of the force f_α obtained by projecting the corresponding terms of Eq. (43) are

$$\frac{f_\parallel(\omega)}{H_1} = \frac{\mu}{\zeta}\left[(1-C_2)(1-i\omega\tau_M) - 2m(C_1 - C_3) + \frac{m}{\xi}(3C_2 - 1)\right],$$

$$\frac{f_\perp(\omega)}{H_1} = \frac{\mu}{2\zeta}\left[(1+C_2)(1-i\omega\tau_M) - 2mC_3 + \frac{m}{\xi}(1-3C_2)\right], \quad (54)$$

which after using recurrence relations (41) yields

$$\frac{f_\parallel}{H_1} = \frac{\mu}{\zeta}(1-C_2)\left[1 - i\omega\tau_M - q\frac{3C_2 - 1}{2(1-C_2)}\right],$$

$$\frac{f_\perp}{H_1} = \frac{\mu}{2\zeta}(1+C_2)\left[1 - i\omega\tau_M - q\frac{\xi(C_1 + C_3)}{2(1+C_2)}\right]. \quad (55)$$

Substituting this in the general formula (53) and taking into account the explicit form (48) of the relaxation times, one arrives finally at the expressions for the dynamic susceptibility components

$$\chi_{\parallel}=3\chi_0(C_2-C_1^2)\frac{1-i\omega\tau_M}{1-i\omega\tau_{\parallel}},\quad \chi_{\perp}=\frac{3}{2}\chi_0(1-C_2)\frac{1-i\omega\tau_M}{1-i\omega\tau_{\perp}},$$

$$\chi_0=\frac{n\mu^2}{3T}, \tag{56}$$

where χ_0 is the static susceptibility. For a Newtonian carrier fluid ($m=0$) from Eq. (56) there follow well-known formulas for the dynamic susceptibility of a dilute assembly of rigid dipoles [10]. It is noteworthy that when calculating with Eq. (53) the additional terms in the force (55), they depend on frequency and are linear in τ_M, are balanced exactly by the corresponding corrections to the relaxation times (48). This means that in the linear in τ_M approximation the said effects "work" independently of each other. Namely, the dynamic renormalization of the acting field renders an additional term $\propto i\omega\tau_M$ in the numerators of formulas (56) while enhancement of the particle residence time in the vicinity of the equilibrium states causes increase in the relaxation times $\tau_{\parallel}$ and $\tau_{\perp}$.

Separating in Eq. (56) the real and imaginary parts, one has

$$\frac{\chi_{\parallel}'}{\chi_0}=3(C_2-C_1^2)\frac{1+\omega^2\tau_D^2q\psi_{\parallel}}{1+\omega^2\tau_D^2\psi_{\parallel}^2},\quad \frac{\chi_{\parallel}''}{\chi_0}=3(C_2-C_1^2)\frac{\omega\tau_D(\psi_{\parallel}-q)}{1+\omega^2\tau_D^2\psi_{\parallel}^2}; \tag{57}$$

$$\frac{\chi_{\perp}'}{\chi_0}=\frac{3}{2}(1-C_2)\frac{1+\omega^2\tau_D^2q\psi_{\perp}}{1+\omega^2\tau_D^2\psi_{\perp}^2},$$

$$\frac{\chi_{\perp}''}{\chi_0}=\frac{3}{2}(1-C_2)\frac{\omega\tau_D(\psi_{\perp}-q)}{1+\omega^2\tau_D^2\psi_{\perp}^2}; \tag{58}$$

here $\psi_{\alpha}=\tau_{\alpha}/\tau_D$ are the normalized relaxation times for the magnetization components.

From Eqs. (57) and (58) the effect of viscoelasticity on the real parts of the susceptibility components is readily seen. Indeed, in the limit $\omega\tau_D\to\infty$ functions $\chi_{\parallel}'$ and $\chi_{\perp}'$ instead of turning to zero, as it happens in the Newtonian case ($q=0$), are finite and turn, respectively, into

$$\frac{\chi_{\parallel}'}{\chi_0}\approx\frac{3q}{\psi_{\parallel}}(C_2-C_1^2)\to\begin{cases}q & \text{at } \xi\ll 1,\\ 6/\xi^2 & \text{at } \xi\gg 1;\end{cases}$$

$$\frac{\chi_{\perp}'}{\chi_0}\approx\frac{3q}{2\psi_{\perp}}(1-C_2)\to\begin{cases}q & \text{at } \xi\ll 1,\\ 3/\xi & \text{at } \xi\gg 1.\end{cases} \tag{59}$$

The asymptotic frequency behavior $\chi_{\alpha}'/\chi_0=q$ in zero magnetizing field, where the susceptibility is isotropic, was found yet in Refs. [12,16]. As Eq. (59) shows, in a finite magnetizing field the susceptibility components differ from one another due to both the static and the relaxation factors in formulas (56).

A fundamental property of the linear susceptibility is the positiveness of the imaginary part that is a consequence of the immanent presence of friction. This means that along with the conditions imposed on the parameters ξ and q in above, there are two additional ones:

$$2\frac{C_2-C_1^2}{1-C_2}\left[1+q\frac{3C_2-1}{2(1-C_2)}\right]-q>0,$$

$$2\frac{1-C_2}{1+C_2}\left[1+q\frac{\xi(C_1+C_3)}{2(1+C_2)}\right]-q>0. \tag{60}$$

Linearizing these relations for $\xi<1$ and using expressions (50), one finds that in the weak field limit the conditions of positiveness of the imaginary parts of different susceptibility components coincide and hold only at

$$q<1. \tag{61}$$

In other words, Eq. (61) should be added to the set of necessary validity conditions of the inertialess approximation; note that above we have already mentioned the condition $q<1$ in this capacity. Analyzing inequalities (60) in the strong field case ($\xi\gg 1$) does not yield any new restrictions: for the longitudinal case condition $\xi<2/q$ is recovered, while the second of inequalities (60) holds identically.

Evidently, a simple asymptotic analysis cannot justify inequalities (60) at arbitrary variations of the Langevin argument ξ. At finite values ($\xi\sim 1$), due to transcedentness of conditions (60) a check on their validity must be done numerically. For that, the second of inequalities (60) is turned into equation yielding $\psi_{\parallel}-q=0$. Its solution shows that for $0<q<0.8$ the evaluated root ξ_* is very close to the hyperbola $2/q$. At higher viscoelasticity, ξ_* drastically turns to zero. This means that at $q\to 1$ the width of the interval of ξ, within which the inertialess approximation is valid, reduces in a fast way. On the basis of a numeric check, it is more practical to replace the restriction $q<1$ by $q<0.8$.

Sample plots of the components of the dynamic susceptibilities are given in Figs. 2 and 3. At each of these graphs the uppermost pane corresponds to the case of a Newtonian matrix, comparison against the plots lying right below helps to understand the effect of viscoelasticity on $\chi(\omega,\xi)$. We begin consideration with the frequency dependencies of the longitudinal and transverse susceptibilities, Fig. 2. Both families have much in common. First, with growth of q, in the real part of the spectrum (not shown here) intercrossings of the lines $\chi_{\perp}'$ disappear. Besides that, the lines themselves become much more flat and well separated. As to the reduction of the imaginary parts (energy absorption) with the ξ growth, it is quite expectable since the enhancement of the magnetizing field "freezes" the orientational motion of the particles; this tendency holds for any q. The overall analysis of the curves χ'' shows that in the presence of viscoelasticity the absorption spectrum possess the following peculiarities. The direction of the peak shift in the spectra $\chi_{\alpha}''(\omega)$ depends on q. At small q, under magnetization the peaks shift rightward, while at $q\lesssim 1$ the "humps" of χ'' move leftward, i.e., to lower frequencies. Another feature of the absorption spectra, which is due to the viscoelasticity of the matrix, is a certain narrowing of the lines $\chi_{\alpha}''(\omega)$ with q.

The above described specificity of the frequency behavior of the dynamic susceptibility are easy to interpret recalling the effect of viscoelasticity on the respective relaxation times, see Eq. (48). Indeed, the growth of $\tau_{\parallel}$ and $\tau_{\perp}$ with the

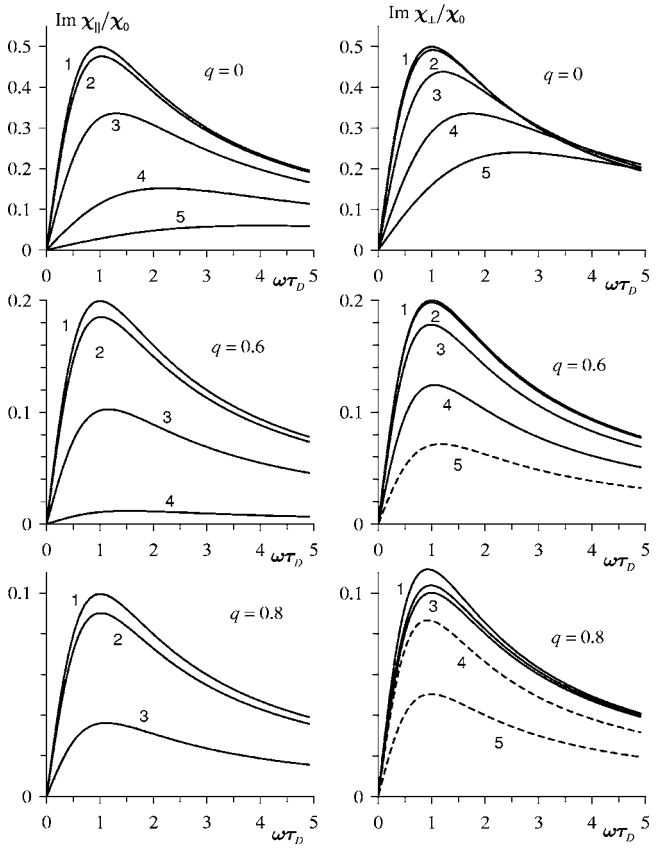

FIG. 2. Imaginary parts of the dynamic magnetic susceptibilities as functions of frequency at the magnetizing field ξ=0.1 (1), 0.5 (2), 1.5 (3), 3 (4), 5 (5).

parameter q means slowing down of the relaxation. Accordingly, the Debye-type spectral lines narrow in comparison to the Newtonian case and shift to lower frequencies. At small q this effect is counteracted and dominated by the opposite tendency caused by the ordinary diminution of τ_α with ξ and does not resolve. This viscoelasticity effect, as one may see in the second and third rows of plots in Fig. 2, overtakes at q closer to unity.

Another consequence of the viscoelasticity is the decrease of $\chi''_\alpha(\omega,\xi)$ (clearly visible at the peaks) with q, see the vertical scales in Figs. 2 and 3 top to bottom. This strong change is again a direct consequence of viscoelasticity. To prove that, let us recall a conventional viscoelastic Maxwell element which is a chain-link of a spring and damper. Unlike a sole damper (viscous fluid) the response of such an element is partially instant (the spring) and partially retarded (the damper). Moreover, the partition of the responses in favor of the instant one is proportional to $\omega\tau_M$ that is often referred to as dynamic elasticity, see after (26). As the instant part of the response is frequency independent, it contributes only to the real part of the susceptibility and, accordingly, "disappears" from the imaginary component. In our description this effect manifests itself as the renormalization given by Eq. (17). For a harmonic probing field one has

$$H_1+\tau_M(dH_1/dt)=H_1(1-i\omega\tau_M)=H_1(1-iq\omega\tau_D); \tag{62}$$

the emerging dispersion factor explicitly enters the numerators of formulas (56). From there it splits between the real and imaginary parts in Eqs. (57) and (58). In consequence, the asymptotic equation (59) at small ξ yields augmented $\chi'_\alpha\sim q$ instead of zero. To explain the graph heights in Figs. 2 and 3, we consider the imaginary parts of Eqs. (57) and (58) in the same limit and estimate them at the peak values which for $\xi\ll 1$ are all located at $\omega\tau_D\sim 1$. This gives

$$\chi''_\alpha|_{\max}\sim\tfrac{1}{2}(1-q). \tag{63}$$

Figures 2 and 3 confirm that the heights of the peaks found numerically decrease with q in close agreement with this simple prediction.

Consider now the field dependencies of the susceptibilities. The real parts of $\chi_\parallel(\xi)$ and $\chi_\perp(\xi)$, we do not plot them here, look similar. Comparison shows that viscoelasticity suppresses a weak maximum at frequency $\omega\tau_D\sim 1$ inherent to the Newtonian case. Under developed viscoelasticity ($q\sim 1$) the curves $\chi'(\xi)$ for both orientations become monotonic, acquire alike shapes and get closer by their absolute values.

The part of the dynamic susceptibility that is most sensitive to viscoelasticity is its imaginary component. In Fig. 3 at the graphs of χ'' for q=0.6 and 0.8 we have put vertical lines whose coordinates equal to the values ξ_m, at which the numerator in expression (57) changes its sign from positive to negative. To the right of these points the inertialess approximation, strictly speaking, loses its validity. If to compare the imaginary parts of $\chi_\parallel(\xi)$ and $\chi_\perp(\xi)$, one notes disappearance of a weak maximum of $\chi''_\parallel$, which in the Newtonian case exists for $\omega\tau_D\gtrsim 1$. Another important effect of viscoelasticity is a considerable narrowing of the lines with the q growth. Finally, at developed viscoelasticity ($q\sim 1$) the maxima at the dependencies $\chi''_\perp(\xi)$ appear anew, but this time they are much more distinctive and narrow than in the Newtonian case, see the curves for q=0.8. Moreover, the maxima exist for arbitrary ξ, seemingly getting stronger at $\omega\tau_D\sim 1$. Note also that the maxima of $\chi''_\perp(\xi)$ are located in the range of ξ where the inertialess approximation is valid. This gives a serious argument in favor of real existence of this specific behavior.

VII. DISCUSSION

Studies of Brownian motion in a viscoelastic (Maxwell) fluid were commenced by Volkov and Leonov, see Refs. [16,20,21]. The considered here rotary variant of the microrheology problem was discussed in Ref. [16]. There a set of chain-linked moment equations describing inertialess motion of a Brownian particle in a Maxwell fluid was presented. However the derivation procedure applied in Ref. [16] was not entirely consistent, its only adequate feature being the renormalization of the instant acting field ($\boldsymbol{H}\rightarrow\boldsymbol{H}+\tau_M d\boldsymbol{H}/dt$). As to the effective friction coefficient, the authors of Ref. [16] simplified it by replacing a generally an-

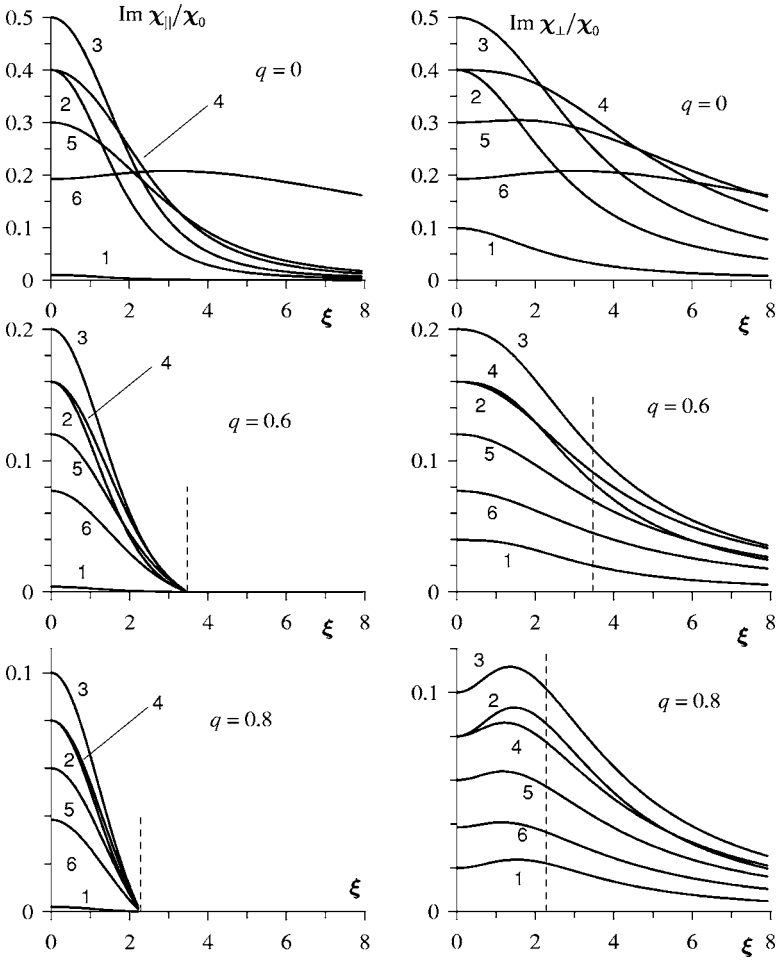

FIG. 3. Imaginary parts of the dynamic magnetic susceptibilities as functions of the magnetizing field at the frequency parameter $\omega\tau_D$ =0.01 (1), 0.5 (2), 1 (3), 2 (4), 3 (5), 5 (6); the dashed vertical line shows the right-hand border of the interval of applicability for the inertialess approximation.

isotropic relation (29) by the isotropic mean value:

$$\zeta\delta_{ij} - \tau_M\mu H_0\hat{J}_i\hat{J}_j(\boldsymbol{eh}) \to [\zeta + \tau_M(\mu H_0)\langle \boldsymbol{e}\rangle\boldsymbol{h}]\delta_{ij}. \quad (64)$$

This step entailed a serious drawback: the resulting first-moment equation has the same order of linking (the closest neighbor moments) as that for the case of a linearly viscous (Newtonian) fluid. In result, the obtained chain of equations turned out to be just a minor modification of that characteristic of the well-known case of a Newtonian matrix. Meanwhile, as our Eq. (31) clearly indicates, for the case of a Brownian particle in a Maxwell fluid the type of linking in the set of the moment equations is different: coupled are the closest and next-to-closest terms. We also remark that concerning the particle magnetic moment relaxation times and its dynamic susceptibilities the scope of Ref. [16] was restricted solely to the case of zero external field.

Admitting that experimental data on the subject are insofar quite few, a more available check is to correlate the above-obtained kinetic coefficients and characteristics with the results of the preceding work on viscoelastic ferrocolloids. In Ref. [12], not employing the inertialess approximation, the dynamic susceptibility of an isotropic (nonmagnetized, H_0=0) assembly of plane rotators was studied. The formula obtained there for the dynamic susceptibility at weak viscoelasticity in the low-frequency range $\omega \ll \sqrt{\zeta/\mathcal{I}\tau_M}$ has the form

$$\chi(\omega) = \chi_0\frac{1-i\omega\tau_M}{1-i\omega\tau_D}. \quad (65)$$

This is exactly the limit to which tend our relationships (56) under zero field. The requirement of positiveness of the imaginary part of susceptibility following from Eq. (65) coincides with condition (61). Exactly the same formula was obtained in Ref. [16] for the 3D case. Thus one infers that the particle rotary kinetics for 2D and 3D cases are very similar.

Orientational Brownian motion of a plane rotator in a harmonic potential with allowance for inertial effects was studied in Ref. [22]. This work enables one to verify formulas (56) in another limiting case. Namely, consider a strongly oriented ("magnetized through") system where deviations of the particle axes from the axis of the texture are small. Obtained in Ref. [22], low-frequency component of the imaginary part of the transverse susceptibility has the form:

$$\chi_{\perp}(\omega) = \frac{n\mu^2}{K}\frac{1-i\omega\tau_M}{1-i\omega\tau_r}, \quad \tau_r \equiv \frac{\zeta}{K} + \tau_M. \quad (66)$$

Here K is the rigidity constant of the harmonic potential $U = \frac{1}{2}K\vartheta^2$. To compare with the model under study, one has to make a replacement $K \Rightarrow \mu H_0$. Then taking into account the asymptotics $C_2 \approx 1-2/\xi$ one finds that the second of formulas (56) turns into Eq. (66).

Finally, we summarize the conditions of applicability for the inertialess approximation. This simplified description results from dropping out some part of the terms in the complete stochastic equation (16). Performing estimations in (16), one finds that to neglect the inertial part of the equation in comparison with its viscous part is possible if the condition

$$\mathcal{I}\tau_M\omega^2 + \mathcal{I}\omega \ll \zeta + \tau_M \frac{\partial^2 U}{\partial \vartheta^2}, \tag{67}$$

holds; here ω is the reference frequency. In the absence of external field inequality (67) splits into two:

$$\omega \ll \omega_M \equiv \frac{1}{\sqrt{\tau_I \tau_M}}, \quad \omega \ll \frac{1}{\tau_I}, \tag{68}$$

by the order of magnitude the quantity ω_M is the resonance frequency of orientational oscillations of particles in a viscoelastic matrix, see [12]. In nanodisperse suspensions the time τ_I is a sufficiently small quantity: $\lesssim 10^{-11}$ s. It is primarily because of that that the inertialess approximation, where one sets $\tau_I = 0$, is so practical. Asserting from this viewpoint inequalities (68), we infer that a viscoelastic suspension might be considered to contain inertialess particles only if $\tau_M > \tau_I$. This, in turn, means that conditions (68) are exhausted by the first of the above-written relations. The latter, due to relative smallness of the inertial time τ_I, does not make too strong a restriction. Moreover, as stated above, the case of zero field is trivial as here the viscoelasticity of the matrix does not manifest itself in magnetic spectra.

Consider now the case of nonzero magnetizing field $\boldsymbol{H}_0$. For the potential (23), condition (67) evidently breaks for the angle interval where $\zeta + \tau_M \mu H_0 \cos\vartheta \leqslant 0$. Therefore, an additional restriction turns up: τ_M must be smaller than the Debye time $\tau_D = \zeta/2\mathrm{T}$ of thermal orientational diffusion. The same condition is recovered if one requires that the imaginary part of the susceptibility (65) obtained in Ref. [12] is non-negative, i.e., the system absorbs energy. In above, see Sec. VI, considering the expressions for the dynamic susceptibility, we have mentioned that for its practical use this restriction must be yet more rigid: $q = \tau_M/\tau_D \lesssim 0.8$. In usual (linearly viscous) magnetic fluids at low concentrations of the magnetic phase the time τ_D by the order of magnitude ranges from 5×10^{-6} (a matrix with the viscosity of water) to 5×10^{-3} (a matrix with the viscosity of glycerol). These low values of the Debye time imply that the inertialess approximation might be used only at relatively weak viscoelasticity. This makes an essential difference with a Newtonian magnetic fluid. Indeed, if in Newtonian media the inertialess limit is virtually universal, in a viscoelastic nanosuspension a correct description of orientational kinetics at arbitrary stress relaxation time is achieved only when the extended kinetic equation is used. The basics for such an approach are given in Ref. [12].

VIII. CONCLUSIONS

A suspension of solid dipolar nanoparticles in a viscoelastic (Maxwell) fluid characterized by a unique stress relaxation time τ_M is considered. All the particles are identical, the dipolar property of each particle is specified as a hard (frozen-in) magnetic moment. We build up the inertialess approximation for the orientational kinetics of such a system and analyze the validity range of the latter. The corresponding condition takes the form $\tau_M < \tau_D$, where τ_D is the Brownian rotary diffusion time of an individual particle of a suspension.

In the framework of the inertialess approximation the relaxation times of magnetization are evaluated for a situation where an arbitrary constant magnetizing field is imposed on the suspension. This provides a model for magnetic microrheological diagnostics of a complex fluid, i.e., for testing the rheology of the matrix of a suspension by exciting mechanical motion of the embedded nanoparticles. One finds that in comparison with the Newtonian case the relaxation times in a magnetized suspension increase considerably. At developed viscoelasticity ($\tau_M < 0.8\tau_D$) the dependence of the transverse relaxation time on the magnetizing field intensity becomes nonmonotonic. The occurring maximum of $\tau_\perp(\xi)$ is located in the range where the Langevin argument ξ of an individual particle is of the order of unity.

For zero and small magnetizing fields ($\xi \ll 1$) in the limit $\omega\tau_M > 1$ the dynamic susceptibilities have a simple frequency asymptotics yielding $\chi' \propto q$ and $\chi'' \propto (1-q)$, where the viscoelasticity parameter is $q = \tau_M/\tau_D$, see Eqs. (59)–(63).

At nonzero magnetizing (constant) field the viscoelasticity of the matrix contributes to shapes of the low-frequency magnetic spectra. The corresponding susceptibilities have specific quasi-Debye forms which evidence the basically relaxational type of the probing field induced (forced) oscillations. Simple analytical formulas for the principal components of the dynamic susceptibility tensor of a viscoelastic ferrocolloid are derived and discussed. These expressions extend the formerly existing description to the case of magnetizing fields of arbitrary strength.

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[1] F. Brochard Wyart and P. G. de Gennes, Eur. Phys. J. E **1**, 93 (2000).
[2] C. Wilhelm, J. Browaeys, A. Ponton, and J. C. Bacri, Phys. Rev. E **67**, 011504 (2003).
[3] T. G. Mason, K. Ganesan, J. H. van Zanten, D. Wirtz, and S. C. Kuo, Phys. Rev. Lett. **79**, 3282 (1997).
[4] F. Gittes, B. Schnurr, P. D. Olmsted, F. C. MacKintosh, and C. F. Schmidt, Phys. Rev. Lett. **79**, 3286 (1997).
[5] A. J. Levine and T. C. Lubensky, Phys. Rev. Lett. **85**, 1774 (2000).
[6] Z. Cheng and T. G. Mason, Phys. Rev. Lett. **90**, 018304 (2003).
[7] F. Cousin, V. Cabuil, and P. Levitz, Langmuir **18**, 1466 (2002).
[8] J. A. Galicia, O. Sandre, F. Cousin, D. Guemghar, C. Ménager, and V. Cabuil, J. Phys.: Condens. Matter **15**, S1379 (2003).
[9] M. I. Shliomis, Sov. Phys. Usp. **112**, 153 (1974).
[10] Yu. L. Raikher and M. I. Shliomis, Adv. Chem. Phys. **87**, 595 (1994).
[11] V. N. Pokrovsky, *Statistical Mechanics of Dilute Suspensions* (Nauka, Moscow, 1973) (in Russian).
[12] Yu. L. Raikher and V. V. Rusakov, Phys. Rev. E **54**, 3846 (1996).
[13] Yu. L. Klimontovitch, *Statistical Physics* (Nauka, Moscow, 1982) (in Russian).
[14] Yu. L. Raikher and V. V. Rusakov, J. Mol. Liq. **71**, 81 (1997).
[15] J. L. Déjardin, Phys. Rev. E **58**, 2808 (1998).
[16] V. S. Volkov and A. I. Leonov, Phys. Rev. E **64**, 051113 (2001).
[17] Yu. L. Klimontovich, *Statistical Theory of Open Systems, Vol. 1* (Yanus, Moscow, 1995) (in Russian).
[18] M. I. Shliomis, Sov. Phys. JETP **34**, 1291 (1972).
[19] Yu. L. Raikher and V. V. Rusakov, *Proceedings of the 11th International Plyos Conference on Magnetic Fluids* (Ivanovo, Russia, 2004), p. 171 (in Russian).
[20] V. S. Volkov, Zh. Eksp. Teor. Fiz. **98**, 168 (1990) [Sov. Phys. JETP **71**, 93 (1990)].
[21] V. S. Volkov and A. I. Leonov, J. Chem. Phys. **104**, 5922 (1996).
[22] Yu. L. Raikher, V. V. Rusakov, W. T. Coffey, and Yu. P. Kalmykov, Phys. Rev. E **63**, 031402 (2001).