Dynamic susceptibility of viscoelastic magnetic liquids

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We study the kinetics of orientational processes in an ensemble of Brownian dipole particles in a viscoelastic medium (a Maxwellian liquid). Such a medium constitutes a simple model of a polymer solution; its main feature is the allowance for a time lag in mechanical stresses. We construct the frequency dependence of the magnetic susceptibility of the system. Finally, we show that the absorption spectra have a complicated rake-like structure whose parameters are determined by viscosity and the stress relaxation rate in the suspension matrix. © *1996 American Institute of Physics.* [S1063-7761(96)01711-8]

1. INTRODUCTION

Let us describe a simple scheme for classifying the dispersions of magnetic nanoparticles in liquid matrices that reveals the essential features of the liquid carrier. We divide suspensions into three categories:

- suspensions in Newtonian liquids, which are commonly known as magnetic liquids or ferroliquids;
- suspensions in liquid crystals, also known as ferroliquid crystals; and
- suspensions in non-Newtonian liquids (complex magnetic liquids).

Of these three classes of nanocomposite media, ferroliquids have been intensively studied in the last 30 years (see, e.g., Refs. 1 and 2 and the related bibliographies[3]). Ferroliquid crystals, whose possible existence was suggested in 1970 in Refs. 4 and 5, have been thoroughly studied both theoretically and experimentally.[6,7] As for the last item in the above list, the study of complex magnetic liquids is only beginning, with the field of activity being extremely broad. One can easily imagine how diverse the properties of such suspensions can be, depending on the properties of the carriers (polymer solutions, liquid biological systems, etc.). The magnetic response of such media is largely determined by the mechanical mobility of the particles and hence by the hydrodynamic properties of the suspension matrix.

In the present paper we study the dynamic susceptibility of an ensemble of Brownian particles in a Maxwellian liquid. The latter can be interpreted as the simplest model of a polymer solution. Of course, in view of its simplicity the theory does not take into account a number of details that are important for real polymers, but it allows for what we believe to be the main viscoelastic effect: the effect of the time lag in mechanical stresses on the frequency dependence of the magnetic response. The approach we develop is a direct outgrowth of the studies in the statistical mechanics of suspensions based on complex liquids, started by Refs. 8 and 9.

In Sec. 2 we describe the model and derive the equations of orientational motion of a single-domain Brownian ferroparticle in a viscoelastic liquid. In Sec. 3 we calculate the correlation function of the moments of random forces and on was it to derive a system of Langevin equations that provides a complete statistical description of the problem. In Sec. 4 we obtain a general expression for the linear dynamic susceptibility and classify the possible types of viscoelastic magnetic suspensions. Finally, in Sec. 5 we present and analyze the results of calculations of the susceptibility within a broad range of values of the material parameters of the ferromagnetic suspensions.

2. A DIPOLE PARTICLE IN A VISCOELASTIC LIQUID

Let us examine the rotational motion of a particle with a rigid dipole moment in a viscoelastic (Maxwellian) liquid. The choice of a two-dimensional model is determined by the simplicity of such a model. In similar problems the three-dimensional variant of the theory, which leads to considerable mathematical complications, yields results that differ from the two-dimensional case only by factors of order unity.[10]

The particle in this model is a rigid disk of radius a positioned in the plane of the external magnetic field $\mathbf{H}$, whose direction fixes the polar axis of the system of coordinates. The particle's dipole moment $\boldsymbol{\mu}$ has a constant absolute value and a direction that is fixed in the disk's plane. The orientation of the vector $\boldsymbol{\mu}$ in relation to the polar axis is specified by the angle ϑ.

The equation of orientational motion of a particle in a liquid matrix is

$$I\ddot{\vartheta}+Q(t)+\mu H\sin\vartheta=y(t), \tag{1}$$

where the dots stand for time derivatives, I is the particle's moment of inertia, $Q(t)$ is the frictional torque, and $y(t)$ is the random torque (which allows for thermal motion in the liquid).

In the model of a viscoelastic Maxwellian liquid the frictional torque, with which the carrier liquid acts on the rotating particle, is determined by the following equation:

$$\dot{Q}=-\frac{1}{\tau_M}(Q-Q_0),\quad Q_0=\zeta\dot{\vartheta}, \tag{2}$$

where ζ is the friction coefficient, and τ_M is the characteristic time of relaxation of elastic stresses. Here ζ is proportional to the viscosity η of the liquid and depends on the particle size and shape. In low-concentration suspensions the time τ_M and the viscosity are characteristics of the liquid proper and are insensitive to the particle's presence.

In order to clarify the meaning of the relaxation equation (2) we plug the harmonic angle–time dependence, $\vartheta=\vartheta^{(0)}\exp(-i\omega t)$, into it. For the amplitude of the frictional torque $Q=\text{Re }Q-i\text{Im }Q$ we obtain

$$\text{Re }Q^{(0)}=\frac{\zeta\omega^2\tau_M}{1+\omega^2\tau_M^2}\vartheta^{(0)},\quad \text{Im }Q^{(0)}=\frac{\zeta\omega}{1+\omega^2\tau_M^2}\vartheta^{(0)}.$$

Clearly, at low frequencies ($\omega\tau_M\ll 1$) only the imaginary part of the resistance is important. Indeed, $Q\approx -i\text{ Im }Q\propto\dot{\vartheta}$ implies that in this limiting case the frictional torque is determined primarily by the liquid's viscosity. According to (2), for a Newtonian liquid, which corresponds to $\tau_M\rightarrow 0$, we have $Q=Q_0$. At high frequencies $Q\approx\text{Re}Q\propto\vartheta$ with a high accuracy, so that the medium resembles a rigid body with an elastic modulus η/τ_M. In this limit the reaction of the system to an external perturbation is of a reversible, nondissipative, nature. Thus, in the intermediate frequency range the Maxwellian medium is characterized by a combination of viscous (liquid) and elastic (rigid-body) responses.

3. THE LANGEVIN EQUATIONS

We examine the statistical properties of the random torque $y(t)$ in Eq. (1). While $\langle y(t)\rangle=0$ can be assumed to be given *a priori*, the correlations function $\langle y(t)y(0)\rangle$ requires a definition. The calculation can be conveniently done according to the well-known scheme (see, e.g., Ref. 11, Chap. 11).

We start by noting that the statistics of $y(t)$ is determined solely by thermal motion, i.e., by the orientational diffusion of the particles in the liquid matrix. This means that we can put $H=0$ in Eq. (1). Denoting the angular velocity of a particle by $\Omega=\dot{\vartheta}$ and applying a Fourier transformation to the systems of equations (1) and (2), we arrive at the following relationship between the spectral amplitudes of the random moment and the angular velocity:

$$y_\omega=\left(-iI\omega+\frac{\zeta}{1-i\omega\tau_M}\right)\Omega_\omega\equiv K(\omega)\Omega_\omega. \tag{3}$$

According to the Wiener–Khinchin theory, for any stationary random process $f(t)$ the correlation function of the Fourier components can be written as

$$\begin{gathered}\langle f_\omega f_{\omega'}\rangle=2\pi(f^2)_\omega\delta(\omega+\omega'),\\ (f^2)_\omega\equiv\int_{-\infty}^{\infty}dt\;e^{i\omega t}\langle f(t)f(0)\rangle,\end{gathered} \tag{4}$$

where the last relationship is definition of the spectral density. Combining Eqs. (3) and (4), we arrive at a relationship between the spectral densities of the fluctuations y and Ω:

$$(y^2)_\omega=K(\omega)K(-\omega)(\Omega^2)_\omega. \tag{5}$$

To obtain the function $(\Gamma^2)_\omega$ we use the Onsager principle (see, e.g., Ref. 11, Chap. 13). This principle makes it possible, starting at Eqs. (1) and (12), to write a system of equations determining the time evolution of the respective correlation functions:

$$\begin{gathered}I\frac{d}{dt}\langle\Omega(t)\Omega(0)\rangle=-\langle Q(t)\Omega(0)\rangle,\\ \left(1+\tau_M\frac{d}{dt}\right)\langle Q(t)\Omega(0)\rangle=\zeta\langle\Omega(t)\Omega(0)\rangle.\end{gathered} \tag{6}$$

For the initial conditions for such a system it is natural to take $\langle\Omega^2(t)\rangle=\langle\Omega^2(0)\rangle=T/I$, which represent a corollary of the equipartition theorem. (Note that here and in what follows the temperature T is expressed in energy units, i.e., $k_B=1$.) Applying to (6) a one-sided Fourier transformation according to

$$(\Omega^2)_\omega^+=\int_0^\infty dt\;e^{i\omega t}\langle\Omega(t)\Omega(0)\rangle,$$

we find $(\Omega^2)_\omega^+=K^{-1}(\omega)T$, where the impedance $K(\Omega)$ is defined by Eq. (3). The spectral density of Ω is related to $(\Omega^2)_\omega^+$ as follows:

$$(\Omega^2)_\omega=(\Omega^2)_\omega^++(\Omega^2)_{-\omega}^+=2\text{ Re}(\Omega^2)_\omega^+, \tag{7}$$

which follows directly from the definition of $(\Omega^2)_\omega$. Substituting (7) in (5) yields

$$(y^2)_\omega=2T\text{ Re}[K(\omega)]=\frac{2\zeta T}{1+\omega^2\tau_M^2}, \tag{8}$$

which shows that the spectral density of the random torque is frequency-dependent and is reduced to white noise only in the $\tau_M\rightarrow 0$ limit, i.e., in the case of a Newtonian liquid. If we perform the inverse Fourier transformation, from Eq. (8) we obtain the correlation function

$$\langle y(t)y(0)\rangle=2\zeta T\exp\left(-\frac{|t|}{\tau_M}\right),$$

which shows that the random torque with which the Maxwellian liquid acts on the particle has a correlation time τ_M.

The simple form of the frequency dependence of $(y^2)_\omega$, which is specified by (8), makes it possible to introduce an auxiliary stochastic equation,

$$\hat{R}y\equiv\left(1+\tau_M\frac{d}{dt}\right)y=f(t),\quad\langle f(t)f(0)\rangle=2\zeta T\delta(t), \tag{9}$$

and to consider y a dynamic variable on which the white thermal noise $f(t)$ acts. Note that the linear lag operator $\hat{R}$ on the left-hand side of Eq. (9) coincides with the operator in Eq. (2) for Q. In other words, the fluctuation and frictional torques have the same frequency dispersion. Applying the operator $\hat{R}$ to Eq. (1) and employing Eqs. (2) and (9), we arrive at the stochastic equation

$$\ddot{\Omega}+\frac{1}{\tau_M}\dot{\Omega}+\frac{1}{I}\left(\frac{\zeta}{\tau_M}+\mu H\cos\vartheta\right)\Omega$$

$$=-\frac{\mu}{I\tau_M}\sin\vartheta\hat{R}H+\frac{1}{I\tau_M}f(t), \tag{10}$$

which together with the white-noise correlator in (9) and the kinematic relationships

$$\frac{d\vartheta}{dt}=\Omega,\quad \frac{d\Omega}{dt}=\dot{\Omega}, \tag{11}$$

form a closed system of Langevin equations. We can use it to develop any convenient statistical description, say, derive the corresponding Fokker–Planck equation. Some results pertaining to the derivation and solution of the kinetic equation can be found in Refs. 12 and 13. This route proves universal but is extremely formidable.

Below we use Eqs. (10) and (11) to calculate the dipole correlation function determining the initial dynamic susceptibility. Note that in the $\tau_M \to 0$ limit the model describes the orientational Brownian motion of dipole particle in an ordinary (Newtonian) liquid. Here the set of dynamic variables is reduced to ϑ and Ω. If viscoelasticity is taken into account, the set broadens and includes the additional quantity $\dot{\Omega}$.

4. DYNAMIC SUSCEPTIBILITY

Setting the goal of studying the initial susceptibility, we employ the linear-response approximation. According to the Kubo–Tomita theory (see, e.g., Ref. 14), the dynamic susceptibility is expressed in terms of the equilibrium of the correlation function of an observed quantity. For this quantity we take the projection of the magnetization of the system on the direction of the applied linearly polarized field **H**:

$$M(t)=c\mu p(t),\quad p(t)=p[\vartheta(t)]\equiv\cos\vartheta(t), \tag{12}$$

where c is particle number density. Here the basic formula becomes

$$\frac{\chi(\omega)}{\chi_0}=-\int_0^\infty dt\, e^{i\omega t}\frac{d}{dt}\frac{\langle p(t)p(0)\rangle}{\langle p^2\rangle}, \tag{13}$$

where $\chi_0=c\mu^2/2T$ is the static susceptibility of the ensemble of independent magnetic dipoles, and the angular brackets stand for statistical averaging over the equilibrium state with $\mathbf{H}=0$.

We transform the second relationship in (12) according to standard trigonometric formulas, we obtain

$$\langle p(t)p(0)\rangle=\frac{1}{2}\langle p[\vartheta(t)-\vartheta(0)]$$

$$+p[\vartheta(t)+\vartheta(0)]\rangle=\frac{1}{2}p(\Delta\vartheta), \tag{14}$$

where $\Delta\vartheta=\vartheta(t)-\vartheta(0)$, and in a stationary random process the function of p of the sum of angles vanishes. To calculate the equilibrium correlation function (14) we must know the statistical properties of the ensemble. Obviously, the angle ϑ is a Gaussian random quantity: according to (10), in an equilibrium system with $H=0$ this angle is described by a linear equation whose right-hand side contains the white noise f. Then averaging in (14) yields

$$\langle p(\Delta\vartheta)\rangle=\exp\left[-\frac{1}{2}\langle(\Delta\vartheta)^2\rangle\right]. \tag{15}$$

To calculate the mean-square angular fluctuations we write Eq. (10) with $H=0$ in the following form:

$$\Omega(t)=\frac{\Omega(0)}{\Delta\lambda}(\lambda_+e^{\lambda_-t}-\lambda_-e^{\lambda_+t})+\frac{\dot{\Omega}(0)}{\Delta\lambda}(e^{\lambda_+t}-e^{\lambda_-t})$$

$$+\frac{1}{I\tau_M\Delta\lambda}\int_0^t dt' f(t')[e^{\lambda_+(t-t')}-e^{\lambda_-(t-t')}], \tag{16}$$

where $\Omega(0)$ and $\dot{\Omega}(0)$ are the initial values of the angular velocity and acceleration, and the decay constants $\lambda_\pm$ can be found by solving the characteristic equation

$$\lambda^2+\frac{\lambda}{\tau_M}+\frac{1}{\tau_M\tau_I}=0. \tag{17}$$

Here we have introduced the inertial time

$$\tau_I=\frac{I}{\zeta}, \tag{18}$$

which describes the rate of relaxation of the angular momentum of the particle with a moment of inertia I and a friction coefficient ζ. Solving Eq. (17), we find that the phase decay constants are

$$\lambda_\pm=-\frac{1}{2\tau_M}\pm i\sqrt{\frac{1}{\tau_I\tau_M}-\frac{1}{4\tau_M^2}},\quad \Delta\lambda=\lambda_+-\lambda_-. \tag{19}$$

This implies that when $\tau_M \gg \tau_I$, the system experiences natural oscillations whose frequency is determined by the inertia of the particle and the elastic response of the liquid surrounding the particle. Multiplying Eq. (15) by $\Omega(0)$ and averaging over the ensemble of realizations of the random force f, we find that

$$\langle\Omega(t)\Omega(0)\rangle=\langle\Omega^2(0)\rangle\frac{\lambda_+e^{\lambda_-t}-\lambda_-e^{\lambda_+t}}{\Delta\lambda}. \tag{20}$$

In deriving this equation we allowed for the fact that $\langle\Omega(0)\dot{\Omega}(0)\rangle=0$, while for the average value of the square of the angular velocity we have the equipartition theorem

$$\langle\Omega^2(0)\rangle=\frac{T}{I}.$$

By definition, the phase and angular velocity are related as follows:

$$\Delta\vartheta(t)=\int_0^t dt'\Omega(t'),$$

which for the square of the equilibrium fluctuation of the phase yields

$$\langle(\Delta\vartheta)^2\rangle=2\int_0^t dt'\int_0^{t'} dt''\langle\Omega(0)\Omega(t'-t'')\rangle. \tag{21}$$

Plugging (20) into (21) and doing elementary integration, we arrive at the expression

$$\langle(\Delta\vartheta)^2\rangle=\frac{2T}{I\Delta\lambda}\left[\frac{\lambda_-^2-\lambda_+^2}{\lambda_+\lambda_-}t+\frac{\lambda_-^3-\lambda_+^3}{\lambda_+^2\lambda_-^2}\right.$$
$$\left.+\frac{\lambda_+}{\lambda_-^2}e^{\lambda_-t}-\frac{\lambda_-}{\lambda_+^2}e^{\lambda_+t}\right],$$

which after simple algebraic transformations is reduced to

$$\langle(\Delta\vartheta)^2\rangle=\frac{2}{\tau_D}\left[t+\tau_M-\tau_I+\frac{\tau_M}{\sqrt{1-1/4M}}\right.$$
$$\left.\times\exp\left(-\frac{t}{2\tau_M}\right)\cos(\omega_M t-\psi)\right], \tag{22}$$

where

$$\omega_M=\frac{1}{2\tau_M}\sqrt{4M-1},\quad \tan\psi=\frac{1-3M}{(1-M)\sqrt{4M-1}}, \tag{23}$$

with the dimensionless ratio $M=\tau_M/\tau_I$.

As is characteristic of a thermalized system, Eq. (22) acquires a Debye relaxation time

$$\tau_D=\frac{\zeta}{T}, \tag{24}$$

which determines the rate of the differential diffusion of the particle. The ratio $D=\tau_D/\tau_I$ is one more dimensionless parameter of the problem. For extremely short times ($\lambda t\ll 1$) Eq. (22) leads to the following dynamic result:

$$\langle(\Delta\vartheta)^2\rangle=\frac{T}{I}t^2=\langle\Omega^2\rangle t^2,$$

while in the Newtonian-liquid limit ($\tau_M\to 0$) Eq. (22) yields the well-known asymptotic behavior (see, e.g., Ref. 15):

$$\langle(\Delta\vartheta)^2\rangle=\frac{2}{\tau_D}[t-\tau_I(1-e^{-t/\tau_I})].$$

Plugging (22) into (15), allowing for (14), and using the Kubo formula (13), we arrive at an expression for the dynamic susceptibility of a viscoelastic magnetic suspension in the form

$$\frac{\chi(\omega)}{\chi_0}=1+i\omega\int_0^\infty dt\, e^{i\omega t}G(t), \tag{25}$$

$$G(t)=\exp\left\{\frac{1-M}{D}\left[1-e^{-t/2\tau_M}\frac{\cos(\omega_M t-\psi)}{\cos\psi}\right]\right\}e^{-t/\tau_D}. \tag{26}$$

Note that the dipole correlation function (26) is nonlinear in the phase fluctuations. The fact that the transition (14) from the correlator of a dynamic variable (the angle ϑ) to the correlator of an observable ($p=\cos\vartheta$) is nonlinear suggests that resonant singularities in the susceptibility spectrum (16) may occur not only near the natural frequency ω_M but also at multiple harmonics.

Even an approximate analysis of the above expression is complicated. The reason is primarily the large number of characteristic times that enter into Eq. (16). Indeed, in addition to the three parameters τ_I, τ_M, and τ_D this equation contains another time scale, the natural frequency $\omega_M=\sqrt{\tau_I\tau_M}$ of the rotational oscillations of the particle. To simplify our discussion, we select the inertial tine τ_I as the unit of measurement. Note that even for large granules ($a\sim 10^3$nm) and such nonviscous liquids or water ($\eta\sim 10^{-2}$P) this scale is extremely small ($\tau_I\sim a^2/10\eta\sim 10^{-6}$s). Next, since we are interested in the effects caused by viscoelasticity, we put

$$\tau_I\ll\sqrt{\tau_M\tau_I}\ll\tau_M. \tag{27}$$

In these conditions the specific form of the frequency dependence of the susceptibility is determined by the relative position of the Debye time τ_D on the time scale (27), which suggests the following classification of suspensions by the degree of the viscoelasticity of the matrix:

$$\begin{aligned}&(1)\ \text{weak, i.e.,}\ \tau_I\ll\sqrt{\tau_M\tau_I}\ll\tau_M\ll\tau_D,\\ &(2)\ \text{developed, i.e.,}\ \tau_I\ll\sqrt{\tau_M\tau_I}\ll\tau_D<\tau_M,\\ &(3)\ \text{strong, i.e.,}\ \tau_I\ll\tau_D<\sqrt{\tau_M\tau_I}\ll\tau_M.\end{aligned} \tag{28}$$

Below we show that the susceptibility spectra differ dramatically from case to case.

5. ABSORPTION SPECTRA

The integral in (25) is fairly complicated and cannot be evaluated analytically, but its form is suitable for approximate integration. We have developed a computation algorithm that operates satisfactorily in all three ranges of the above classification (28). The families of curves describing the imaginary part of the dynamic susceptibility (absorption) are depicted in Figs. 1 and 2. But before discussing the results of numerical calculations let us analyze the asymptotic behavior. To this end we expand the dipole correlation function (16) in a a power series in τ_M/τ_D and restrict our discussion to the case important from the practical viewpoint: $M,\ D\gg 1$. As a result we obtain

$$G(t)=e^{-q}\sum_{k=0}^{\infty}\frac{q^k}{k!(\cos\psi)^k}\exp(-\gamma_k t)\cos^k(\omega_M t-\psi), \tag{29}$$

where

$$q=\frac{\tau_M}{\tau_D},\quad \gamma_k=\frac{1}{\tau_D}+\frac{k}{2\tau_M},\quad \tan\psi=\frac{3}{2\sqrt{M}}.$$

Using the complex-valued expression for the cosine, we arrive at the following formula:

$$G(t)=e^{-q}\sum_{k=0}^{\infty}\frac{(\tilde{q}/2)^k}{k!}e^{-\gamma_k t}\sum_{l=0}^{k}C_l^k e^{i(k-2l)\alpha}, \tag{30}$$

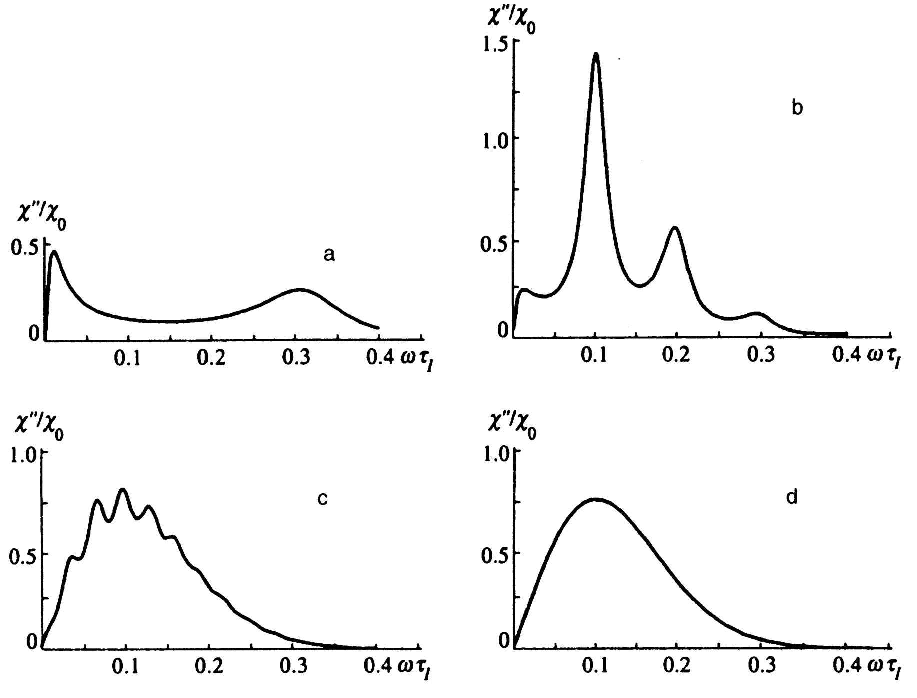

FIG. 1. Absorption lines for $D=10^2$ at $M=10$ (a), 10^2 (b), 10^3 (c), and 10^4 (d).

where $\tilde{q}=q/\cos\psi$, $\alpha=\omega_M t-\psi$, and $C_l^k=k!/(k-l)!l!$ is a binomial coefficient. We transform the double sum in (30) to order the exponentials according to the multiplicity of the natural frequency ω_M. Introducing the notation

$$\Phi_k(t)=\left(\frac{\tilde{q}}{2}\right)^k\frac{e^{-\gamma_k t}}{k!},$$

we can write (30) in the form

$$G(t)=e^{-q}\sum_{k=0}^{\infty}\Phi_k(t)(e^{i\alpha}+e^{-i\alpha})^k=e^{-q}[\Phi_0(t)+\Phi_1(t)\times(e^{i\alpha}+e^{-i\alpha})+\Phi_2(t)(e^{i\alpha}+e^{-i\alpha})^2+\cdots].\quad(31)$$

Grouping the terms in this series by the powers of the exponential $e^{i\alpha}$, we get

$$G(t)=e^{-q}\sum_{n=0,\pm1,\pm2,\ldots}A_n(t)e^{i\alpha n},$$

$$A_n(t)=\sum_{l=0}^{\infty}\Phi_{|n|+2l}(t)C_l^{|n|+2l}=\sum_{l=0}^{\infty}\frac{(\tilde{q}/2)^{|n|+2l}}{l!(|n|+l)!}e^{-\gamma_{|n|+2l}t}.\quad(32)$$

Equation (31) clearly shows that the expansion amplitudes are even functions of the index n, a fact taken into account in (32). For the dipole correlation function we have

$$G(t)=e^{-q}\sum_{n=0,\pm1,\pm2,\ldots}e^{i\alpha n}\sum_{l=0}^{\infty}\frac{(\tilde{q}/2)^{|n|+2l}}{l!(|n|+l)!}e^{-\gamma_{|n|+2l}t}.\quad(33)$$

The same result can be obtained directly from the expansion (30) if we put $n=k-2l$ and change the summation limits appropriately.

We plug the correlator (33) into the Kubo formula (25) and integrate with respect to time, which is now an elemen-

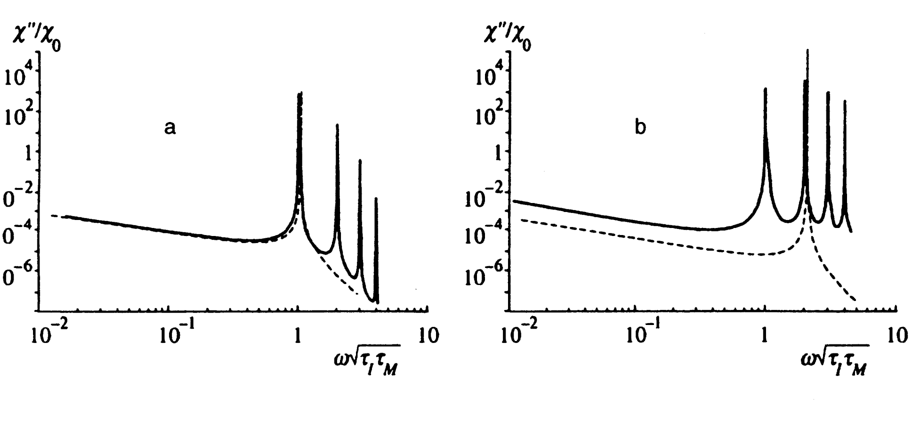

FIG. 2. Absorption spectra for (a) $D=10^9$ and $M=10^8$, and (b) $D=3\times10^8$ and $M=10^9$. The dashed curves represent the results of calculations by formula (35).

tary operation. After summing the terms with equal (absolute) values of the index n we arrive at a formula for the susceptibility:

$$\frac{\chi(\omega)}{\chi_0}=1+i\omega e^{-q}\times\sum_{l=0}^{\infty}\frac{(\tilde{q}/2)^{2l}}{l!}\left\{\frac{1}{(\gamma_{2l}-i\omega)l!}+2\times\sum_{n=1}^{\infty}\frac{(\tilde{q}/2)^n}{(n+l)!}\frac{(\gamma_{n+2l}-i\omega)\cos(n\psi)+n\omega_M\sin(n\psi)}{(n\omega_M)^2+\gamma_{n+2l}^2-\omega^2-2i\omega\gamma_{n+2l}}\right\}. \tag{34}$$

This expression is convenient for qualitative analysis. We start with weak viscoelasticity ($\tau_M\ll\tau_D$; see (28)). Equation (34) then implies that to within second−order terms,

$$\frac{\chi(\omega)}{\chi_0}=\frac{1-q}{1-i\omega\tau_D}+\frac{q\omega_M}{2(\omega_M-\omega)-i/\tau_M}. \tag{35}$$

This result coincides with the one obtained in Ref. 9 by directly solving the Langevin equation (4) by Coffey's method.[15] The first term on the right-hand side of Eq. (35) is the ordinary Debye susceptibility with a small correction due to the viscoelasticity of the matrix. The second term reflects the vibrational nature of the relaxation of the ensemble of magnetic particles in a medium with dynamic elasticity. Equation (35) implies that the height of the peak (the resonance) of the imaginary part of the susceptibility is of order $\tau_M\sqrt{M}\tau_D$, which means that the peak becomes indistinguishable only when $\tau_M\sqrt{M}\ll\tau_D$, so that the latter relationship may be considered the condition for observing weak viscoelasticity in a magnetic suspension.

Equation (34) suggests that as the parameter q, or viscoelasticity, increases the peaks at multiple frequencies, $2\omega_M$, $3\omega_M$, etc., begin to be resolved. In the vicinity of each resonance the expression (23) simplifies considerably, so that the susceptibility can be represented by a combination of Lorentzians:

$$\frac{\chi(\omega)}{\chi_0}\simeq1+e^{-q}\sum_{n=1}^{\infty}\Omega_n\sum_{l=0}^{\infty}\frac{(q/2)^{n+2l}}{(n+l)!l!}\frac{(\Omega_n-\omega)+i\gamma_{n+2l}}{(\Omega_n-\omega)^2+\gamma_{n+2l}^2}, \tag{36}$$

with $|\Omega_n-\omega|\ll\omega_M$, where $\Omega_n=\sqrt{(n\omega_M)^2+\gamma_k^2}\simeq n\omega_M$. The imaginary part of the susceptibility determined by Eq. (36) consists of a sequence of equidistant peaks. The envelope of the spectrum monotonically decreases for $q<2$ and has a maximum at the thermal frequency $\omega_T=\sqrt{T/I}$ for $q>2$; note that ω_T does not depend on the rheological characteristics of the liquid. The shape of an individual peak also changes as viscoelasticity increases. While for $q<2$ each peak can be considered, with high accuracy, a homogeneously broadened Lorentzian, for $q>2$ each resonance is a packet of closely located Lorentzian lines with comparable amplitudes, which means that inhomogeneous broadening is predominant.

As the viscoelasticity grows still further, the number N of distinguishable peaks grows without limit ($N\sim\sqrt{q}$) and their width remains practically constant, $\Delta\omega_n\simeq1/\tau_D(1+n/q)$, where n is the number of the peak. At the same time, the distance between the peaks decreases like $\omega_M=\omega_T\sqrt{q}$. This is concluded by the transition to the limiting shape of a line: the peaks merge into a smooth contour (see Fig. 1d) with a maximum at ω_T. It is quite natural that the condition for merging of peaks ($\omega_M\sim1/\tau_D$) coincides with item (3) in (28).

The condition for merging of resonance peaks means that period of natural oscillations of the particles exceeds the orientational (Debye) relaxation time. In other words, these oscillations do not noticeably contribute to the susceptibility. In this limit the above expansion in parameter q proves to be inconvenient. But if we go back to the expression (26) for the dipole correlation function, we can easily show that in this limit it is reduced to

$$G(t)=\exp\left(-\frac{\omega_T t^2}{2}\right),\quad \omega_M<\frac{1}{\tau_D}. \tag{37}$$

This expression reflects the fact that with strong viscoelasticity only the dynamic section of the phase fluctuations noticeably contribute to susceptibility. In such short time intervals each particle can assume to be rotating freely, and the spread of angular velocities in the ensemble is determined by the equilibrium distribution function, so that $\langle\Delta\vartheta^2\rangle=\langle\Omega^2\rangle t^2=(T/I)t^2$. By plugging the correlation function (37) into the Kubo formula (25) we arrive at the following simple result:

$$\frac{\chi(\omega)}{\chi_0}=1+i\omega\int_0^{\infty}dt\,\exp\left(i\omega t-\frac{T}{2I}t^2\right)=1-2x\,e^{-x^2}\int_0^x dt\,e^{t^2}+i\sqrt{\pi}xe^{-x^2}, \tag{38}$$

with $x=\omega\sqrt{2}\omega_T$. Thus, in the limit of strong viscoelasticity the spectrum of the dipole susceptibility of the suspension is transformed into the well-known dependence for a system of independent rotators (see, e.g., Ref. 16). Note that as the elasticity of the liquid grows ($\tau_M\to\infty$ at $\eta=\text{const}$), viscous damping becomes negligible. However, the χ'' vs ω curve remains nonsingular and positive. To understand the nature of absorption in this case we note that in a thermalized system at any external frequency ω there is always a fraction of particles whose angular velocities are close to ω. It is this subsystem that interacts with the fields most strongly. Here the particles whose angular velocities are smaller than the external frequency accelerate (absorb energy), while the particles with angular velocities exceeding ω slow down (release energy). Since in an equilibrium ensemble the energy distribution $f(E)$ is a decreasing function of E, absorption always exceeds emission, and χ'' remains positive. Such absorption is known as Landau damping. In relation to molecular spectra theory, where the situation resembles the one studied here, the mechanism of Landau damping was examined in Ref. 16.

6. DISCUSSION

The study done in Secs. 2–5 was based on a consistent use of kinetic theory. For a better estimate of the range of applicability of the results it would be interesting to compare them with the predictions of another model. However, we known of no publications of this type, and so suggest a simple alternative, the more so that a phenomenological approach seems at first glance fully feasible. We examine a model that can be called the dispersive viscosity approximation.

As is well known (see, e.g., Ref. 17), the equation of motion of macroscopic magnetization in a suspension of rigid dipoles can be written as follows:

$$\tau_D \frac{dm}{dt}+m=\chi_0 H, \tag{39}$$

with τ_D defined in (24). When the inertial term is introduced, Eq. (39) becomes

$$\frac{I}{T}\frac{d^2m}{dt^2}+\tau_D\frac{dm}{dt}+m=\chi_0 H. \tag{40}$$

Now, allowing for the fact that the resistance ζ and hence τ_D are proportional to the viscosity of the matrix, we introduce dispersion into the viscosity. To this end in (40) we replace the torque with its instantaneous value:

$$\frac{I}{T}\frac{d^2m}{dt^2}+\tilde{Q}+m=\chi_0 H, \tag{41}$$

assuming that the stationary state is attained in a characteristic time interval τ_M. The simplest equation for finding $\tilde{Q}$ has the form

$$\tau_M\frac{d\tilde{Q}}{dt}=-\tilde{Q}+\tau_D\frac{dm}{dt}. \tag{42}$$

Equations (41) and (42) form a closed system, from which $\tilde{Q}$ can be excluded by differentiation. As a result we arrive at the equation

$$\tau_I\tau_M\tau_D\frac{d^3m}{dt^3}+\tau_I\tau_D\frac{d^2m}{dt^2}+(\tau_D+\tau_M)\frac{dm}{dt}+m$$
$$=\chi_0\left(H+\tau_M\frac{dH}{dt}\right). \tag{43}$$

Note that according to the principle of a phenomenological approach, Eq. (43), in contrast to (10), can be assumed to be a final, or macroscopic, equation.

Equation (43) leads to the following expression for the dynamic susceptibility:

$$\frac{\chi}{\chi_0}=\frac{1-i\omega\tau_M}{(1-i\omega\tau_M)(1-\omega^2\tau_I\tau_D)-i\omega\tau_D}, \tag{44}$$

which coincides with our results in Ref. 9 for χ obtained by applying Coffey's method and by solving the appropriate Fokker–Planck equation to lowest order in q. Clearly, Eq. (44) always predicts only one peak in χ'' and does not contain a rake-like spectrum similar to the one in Figs. 1b and c, i.e., agrees with the definition of weak viscoelasticity (item (1) in (28)).

Thus, the assumption about simple dispersion of viscosity in the macroscopic equation of motion encompasses only the case of weak viscoelasticity in (28) and cannot be applied to other regions. On the other hand, although the results of the kinetic treatment do seem unconventional, under further analysis they appear to be quite logical.

The semimicroscopic approach closely resembling the one developed in Secs. 2–5 has been recently employed in the theory of dielectric spectroscopy of molecular liquids. Coffey *et al.*[18] studied the so-called wandering oscillator approximation.[19] In this model a molecule and its immediate surroundings constitute a system of two coaxial classical rotators suspended in an effectively viscous medium. The inner disk of the wandering oscillator carries a constant dipole moment, and its rotation is restricted only by the elastic bond with the nonpolar "rim." It is the rim that sustains viscous drag and Brownian jolts brought about by the surrounding liquid. The calculations of Coffey *et al.*[18] suggested that at least in principle such a rake-like structure of the dielectric absorption spectrum as the one in Fig. 1c is possible. But the estimates done in Ref. 18 showed that for molecular solutions the range of material parameters within which well developed and strong viscoelasticities are possible (see (28)) lands into the nonphysical region, and hence there is no way in which a rake-like structure can be observed in the spectrum.

At first glance the above result is completely refuted by the results of measurements of the spectra of dielectric absorption of HCl molecules in liquid inert gases.[20,21] The experimental curves clearly resemble those in Fig. 1c, i.e., viscoelasticity is fairly well-developed. The set of equidistant peaks and the respective envelope centered at ω_T are also clearly visible. But the contradiction is illusory. The point is that the fine structure of low-temperature HCl spectra is of a purely quantum nature and is caused by transitions between the rotational levels of the molecule. The fact that the spectrum is equidistant (just as it is in the classical effect describe above) is accidental. The difference becomes clear if one recalls that the observed molecular peaks are multiples of $\omega\sim\hbar/I$, while the model of a viscoelastic suspension predicts their multiplicity to be $\omega_M=\sqrt{I\tau_M/\zeta}$. The fact that the line profiles coincide in the high-temperature limit must be considered trivial since any rotation of molecules is of course semiclassical.

We see that the absorption spectra corresponding to developed and strong viscoelasticities (see (28)) cannot be encountered in molecular systems. Let us show that the situation is much more favorable for magnetic suspensions. For estimates we take a solid spherical particle of radius $a\sim0.1\ \mu$m in a Maxwellian liquid with a viscosity $\eta\sim1$ P and a stress relaxation time $\tau_M\sim0.1$s. This yields

$$\tau_I\sim\frac{a^2}{\eta}\sim10^{-10}\text{s},\quad \tau_D\sim\frac{a^3\eta}{k_BT}\sim3\times10^{-2}\text{s}, \tag{45}$$

which corresponds to dimensionless numbers $M=10^9$ and $D=3\times10^8$, and in dimensional form to a characteristic natural frequency $\omega_M\sim3\times10^5\ \text{rad}^{-1}$ and a linewidth

$\Delta\omega_m \sim 10-100\,\mathrm{rad}^{-1}$. These values are not only accessible but are quite common in measurements of magnetic susceptibility.

Examples of absorption spectra found numerically for suspensions with parameters used in the estimates (45) are depicted in Fig. 2. There is clearly a difference between spectra with $M<D$ and $M>D$. In the first case (Fig. 2a) the initial peak is the highest, and the height of each subsequent peak decreases by a factor of almost ten in comparison to the height of the preceding peak (note that the log scale is used on the vertical axis, too). In the opposite case (Fig. 2b) the peaks first become taller, so that a certain inner peak (in our case the second) from the sequence of peaks is the tallest. Note that the peak heights decrease much more slowly than those in Fig. 2a. The dashed curves in Figs. 2a and b depict the frequency dependence of absorption predicted by the alternative model of dispersive viscosity discussed above. Clearly, as the elasticity of the liquid grows, the difference between the kinetic and phenomenological models become greater.

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Note added in proof (August 28, 1996). When this article was in press, we discovered a phenomenological model similar to the dispersive viscosity approximation discussed in Sec. 5 and suggested by L. A. Dávalos-Orojco and L. F. del Castillo in J. Colloid and Interface Sci. **178**, 69 (1996), who examined the rotational viscosity of suspensions of solid spherical particles in non-Newtonian liquids.

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