Contribution of particle inertial effects to resonance in ferrofluids

P. C. Fannin and W. T. Coffey*
Department of Electronic & Electrical Engineering, Trinity College, Dublin 2, Ireland
(Received 21 June 1995)

The effect of the moment of inertia of single domain ferromagnetic particles on the frequency-dependent complex susceptibility $\chi(\omega)=\chi'(\omega)-i\chi''(\omega)$ of ferrofluids is reported. It is demonstrated that particle inertial effects that arise from rotational Brownian motion can give rise to a resonant behavior, which is indicated by the real component $\chi'(\omega)$ becoming negative at a frequency substantially lower than the Larmor frequency. This provides a possible explanation for previously published data that display such an effect in the 10 to 100 MHz region. The Langevin treatment of Brownian motion is used to incorporate thermal agitation into a model which represents, for the purpose of analysis, a typical ferroparticle, P, as a composite particle comprising a magnetic particle, P_m (assumed to be spherical), which may rotate inside and in contact with a concentric rigid sphere, P_s, representing the surfactant, so that P_m and P_s may have different angular velocities about a common center. This leads to a three-dimensional form of the itinerant oscillator model in the small oscillation approximation. The model predicts inertia corrected Debye relaxation in the form of the Rocard equation that arises for P_m and P_s rotating as a unit, and resonance behavior arising from the relative motion of P_m and P_s.

PACS number(s): 47.90.+a, 75.50.Mm, 75.60.Jp, 76.90.+d

I. INTRODUCTION

Previously reported measurements of the complex susceptibility of ferrofluids [1,2] have shown an apparent resonance, indicated by the real component $\chi'(\omega)$ becoming negative at a frequency lower than that predicted by the existing theory of ferromagnetic resonance in fine particles. A typical example of such experimental data, measured over the approximate frequency range 0.2 kHz to 300 MHz, is given in Sec. VIII for a colloidal suspension of cobalt ferrite in isopar-*m*. The $\chi'(\omega)$ component of these data exhibits an apparent resonance at a frequency of approximately 50 MHz. Here we demonstrate that this effect can be attributed to inertial effects arising from the magnetic particle and its surfactant.

The particles commonly used in magnetic fluids have radii ranging from 2 to 10 nm. As these particles are in the single domain region, they can be considered to be in a state of uniform magnetization with magnetic moment μ given by

$$\mu=M_s v_m \ , \tag{1}$$

where M_s (Wb/m^2) denotes the saturation magnetization and v_m is the volume of the particle. The magnetic moments have preferred orientation(s) (easy axes) relative to the particles due to the magnetic anisotropy K, which generally arises from a combination of shape and magnetocrystalline anisotropy.

Consider a system of such spherical particles immersed in a liquid carrier, with each particle possessing a magnetic moment; these particles undergo Brownian rotation due to thermal agitation of the carrier liquid. The Brownian motion is random with no preferential direction, and the time associated with the rotational diffusion is the Brownian relaxation time τ_D [3], where

$$\tau_D=2v\eta/kT \ , \tag{2}$$

v is the hydrodynamic volume of the particle in m^3, and η is the dynamic viscosity of the carrier liquid in N s/m^2.

The magnetic moment may also reverse direction *within the particle* by overcoming an energy barrier, which for uniaxial anisotropy is given by Kv_m. The probability of such a transition is approximately equal to $\exp\sigma$, where σ is the ratio of anisotropy energy to thermal energy (Kv_m/kT). The time of the magnetic moment reversal, or switching time, is referred to [2] as the Néel relaxation time τ. Néel, by assuming discrete orientations of the magnetic moments, estimated the relaxation time τ to be

$$\tau=\tau_0 \exp\sigma \ , \tag{3}$$

with τ_0 having an often quoted approximate value of 10^{-9} *s* [4].

Brown [4] improved on Néel's work, providing for a continuous distribution of orientations by constructing the Fokker-Planck equation for the density of magnetic moment orientations on a sphere of radius M_s, and arrived at his asymptotic expressions for high and low barrier heights, which for the simplest uniaxial potential of the crystalline anisotropy may be described [4] approximately as

$$\tau_N=\begin{cases}\tau_0\sigma^{-1/2}\exp\sigma, & \sigma\geq 2\\ \tau_0\sigma, & \sigma\ll 1 \ .\end{cases} \tag{4}$$

*Corresponding author.

1063-651X/95/52(6)/6129(12)/$06.00

A ferrofluid has a distribution of particle sizes, and this implies the existence of a distribution of relaxation times; in general, both Brownian and Néel relaxation mechanisms will contribute to the magnetization with an effective relaxation time τ_{eff}, where

$$\tau_{\text{eff}}=\tau_N\tau_D/(\tau_N+\tau_D) \ . \tag{4'}$$

The dominant mechanism of a particle will be that with the shortest relaxation time. Thus if $\tau_N \gg \tau_D$, then from (4') $\tau_{\text{eff}}=\tau_D$, whereas if $\tau_N \ll \tau_D$, $\tau_{\text{eff}}=\tau_N$.

The theory of orientational relaxation developed by Debye [3] is used to determine the frequency-dependent complex susceptibility $\chi(\omega)$, where $\chi(\omega)-\chi'(\omega) -i\chi''(\omega)$, of ferrofluids. This theory holds for spherical particles when the magnetic dipole-dipole interaction energy is small compared to the thermal energy kT.

According to the Debye theory, $\chi(\omega)$ has a frequency dependence given by the equation

$$\chi(\omega)-\chi_\infty=(\chi_0-\chi_\infty)/(1+i\omega\tau_{\text{eff}}) \ , \tag{5}$$

where

$$\tau_{\text{eff}}=1/\omega_m=1/2\pi f_m \ , \tag{6}$$

where f_m is the frequency at which $\chi''(\omega)$ is a maximum and χ_0 and χ_∞ denote susceptibility values at $\omega=0$ and at very high frequencies.

For simplicity, Eq. (5) is often approximated to [3]

$$\chi(\omega)=\chi_0/(1+i\omega\tau_{\text{eff}}) \ . \tag{7}$$

Furthermore, $\chi(\omega)$ may also be expressed in terms of its longitudinal, $\chi_\parallel(\omega)$, and transverse, $\chi_\perp(\omega)$, components, with

$$\chi(\omega)=(\chi_\parallel(\omega)+2\chi_\perp(\omega))/3 \ . \tag{8}$$

The Debye theory can be described physically in terms of the magnetization aftereffect function $b(t)$ [5] and its corresponding correlation function $\rho(t)$ [6]. The function $b(t)$ is the response to a small steady field $\mathbf{H}$, which has been applied to a system of single domain ferromagnetic particles at time $t=-\infty$ and which is suddenly switched off at $t=0$. This results in a decay transient of the magnetization $\mathbf{M}_r(t)$, of the form [5]

$$\mathbf{M}_r(t)-\mathbf{M}_0=(\chi_0-\chi_\infty)\mathbf{H}b(t) \ , \tag{9}$$

where $\mathbf{M}_0$ is the equilibrium magnetization. The corresponding autocorrelation function $\rho(t)$, which is an average measure of the decaying magnetization, is related to $b(t)$ by the equation [5]

$$\rho(t)=3kTb(t) \ . \tag{10}$$

The theory we have described, however, does not take account of inertial effects arising from the finite mass of the particles. To investigate the effect of the inertia of the ferroparticles on the complex susceptibility of ferrofluids, Fannin, Charles, and Relihan [7] used the treatment of Langevin [6,8] to incorporate thermal agitation into the analysis. In the dynamical model chosen, both the magnetic particle and its surfactant were conceived of as a rigid body having a moment of inertia I, constrained to rotate about an axis normal to itself, that is, a space-fixed axis rotator, so that the magnetic moment is assumed to make an angle θ with a fixed direction in space.

The equation of motion of a typical rotator following removal of the previously steady external field $\mathbf{H}$ is

$$I\ddot{\theta}+\zeta\dot{\theta}=\lambda(t) \ , \tag{11}$$

where I denotes the moment of inertia of the particle about a diameter, ζ is the damping coefficient, and $\lambda(t)$ is the random white noise driving torque, which arises from the Brownian motion of the surroundings.

The results of Fannin, Charles, and Relihan [7], when analyzed using this model, showed that a condition of the real component $\chi'(\omega)$ going negative, albeit of a minuscule level, could arise in the frequency range concerned. However, this was merely an inertial and not a resonance effect, as Eq. (11) by its very nature cannot exhibit resonant behavior.

The deficiency in the above approach lay in the fact that a ferroparticle, which consists of a magnetic particle and its surfactant, was treated as a single rigid body. Here it is demonstrated that a scheme that can qualitatively explain the experimental results is to postulate a relative motion of the magnetic particle and surfactant. Thus the ferroparticle P is represented as a composite rigid body comprising a rigid magnetic particle P_m (assumed to be spherical), which may rotate inside and in contact with a concentric rigid hollow sphere P_s, representing the surfactant, so that P_m and P_s may have different angular velocities, as illustrated in Figs. 1 and 2. This is a three-dimensional form of the itinerant oscillator model [9] if considered in the small oscillation ap-

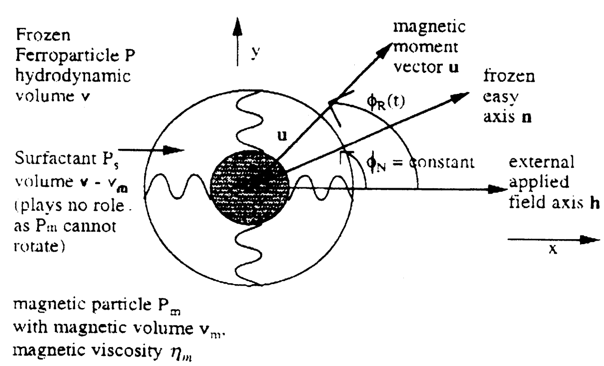

FIG. 1. Geometry for ferrofluid particle P with frozen carrier liquid matrix; P is immobile so that the easy axis $\mathbf{n}$ is frozen at (in general) a constant angle ϕ_N in space relative to the reference direction $\mathbf{h}$, taken as that of the external applied field. The surfactant P_s and the inertia of P play no role because there are no hydrodynamic torques due to the carrier. The diagram is drawn for rotation in the X-Y plane for simplicity; $\mathbf{u}$ rotates about the z axis in the medium of magnetic viscosity η_m inside the frozen magnetic particle P with angular velocity $\omega_R=\dot{\phi}_R(t)\mathbf{k}$. I_R = moment of inertia of surfactant; I_N = moment of inertia of magnetic particle.

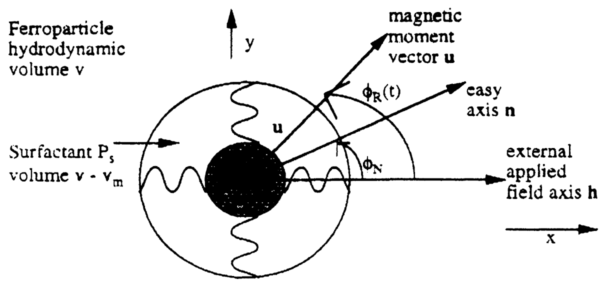

FIG. 2. Model for ferroparticle P in carrier liquid matrix (shown for rotation in X-Y plane); P rotates because of the torques imposed by the surrounding fluid; P_m rotates relative to P_s. P_m is treated as a rigid disk of moment of inertia I_N (carrying a magnetic moment vector **u**, which can swivel about the origin O) subjected to torques $Kv_m \sin 2(\phi_N-\phi_R)$, $6\eta_m v_m(\dot{\phi}_N-\dot{\phi}_R)$, and $\lambda^{(n)}(t)$ arising from the interaction energy U and the relative motion of **u** and **n**, with P_m rotating (and so also the easy axis) about the point O with angular velocity $\omega_N=\dot{\phi}_N\mathbf{k}$;**u** rotates about O with angular velocity $\omega_R=\dot{\phi}_R(t)\mathbf{k}$ and makes an angle $\phi_R(t)$ with **h**, which is used to specify the orientation of P and thus a point on the outer rim of a rigid annulus P_s of moment of inertia I_R representing the surfactant. P_s is subject to reaction damping torques, $-6\eta_m v_m(\dot{\phi}_N-\dot{\phi}_R)_1-\lambda^{(n)}(t)$ and $-Kv_m \sin[2(\phi_N-\phi_R)]$; a torque $M_s v_m H \sin\phi_R(t)$, arising from the applied external field **H**; and the stochastic torques $6\eta_F v(\dot{\phi}_R-\omega_F),\lambda^{(u)}(t)$, arising from the carrier fluid. To simplify the model it is subsequently assumed that P_m and P_s are coupled through the magnetic torque only.

proximation. It leads to inertia corrected Debye relaxation in the form of the Rocard equation, which arises for P_m and P_s rotating as a unit, and resonance behavior arising from the relative motion of P_m and P_s. We shall now describe the Néel and Debye relaxation mechanisms separately and subsequently explain how they may be combined in the itinerant oscillator model just mentioned.

II. RELAXATION IN A FROZEN LIQUID MATRIX

The analysis that has been invariably used hitherto assumes for the purpose of the discussion the Néel relaxation of a ferrofluid, a *frozen carrier liquid matrix,* i.e., a *frozen easy axis* **n**, so that only the magnetic moment axis **u** can rotate. The ferroparticle has therefore *no mechanical degrees of freedom* and so the inertia plays no role, the solid state Néel process of rotation of **u** inside the particle being the only mechanism of reorientation. On the other hand, for the purpose of the discussion of the Debye (Brownian relaxation), it is assumed that the magnetic moment is *frozen along the easy axis* so that **u**‖**n**, but the ferroparticle now *has mechanical degrees of freedom,* and so the magnetic moment may rotate *in unison* with the ferroparticle under the influence of the mechanical torques arising from the surrounding carrier fluid. Here the inertia of the ferroparticle will come into play, and the behavior is exactly like that of a rigid polar molecule in the inertia corrected Debye theory of dielectric relaxation, the rotation of **u** in the carrier liquid being the only mechanism of reorientation because it is clamped rigidly to the easy axis.

In order to proceed, let us, following [10], consider the equation governing the average of the magnetization of a ferroparticle of linear dimensions <150 Å (so that it is a single domain particle) when **n** is frozen. The magnetic volume of the particle is v_m, so that, as before, the magnitude of the magnetic moment is

$$\mu = M_s v_m \ , \tag{12}$$

where M_s is the saturation magnetization. The magnetic moment vector then satisfies [4] the Landau-Lifshitz equation, so that the equation governing the time evolution of the average of the magnetization **M** is

$$\dot{\mathbf{M}} = \gamma(\mathbf{M}\times\mathbf{H}_{ef}) + \frac{\alpha\gamma}{M_s}(\mathbf{M}\times\mathbf{H}_{ef})\times\mathbf{M} \ . \tag{13}$$

We denote the total field acting on the ferroparticle, i.e., the anisotropy field plus the external field by $\mathbf{H}_{ef}$. The corresponding value of the diffusion time is

$$\tau_N \cong \frac{M_s v_m}{2\alpha\gamma kT} \ .$$

Now

$$\frac{\dot{\mathbf{M}} v_m}{M_s v_m} = \dot{\mathbf{u}} \tag{14}$$

and

$$\mathbf{H}_{ef} = -\frac{\partial V}{\partial \mathbf{M}} = -\frac{\partial U}{\partial \mu} \ , \tag{15}$$

where U is the Gibbs free energy, which for uniaxial anisotropy is

$$U = v_m V = -\mathbf{H}\mu(\mathbf{u}\cdot\mathbf{h}) - Kv_m(\mathbf{u}\cdot\mathbf{n})^2 \ , \tag{16}$$

$$\mathbf{H}_{ef} = -\frac{\partial U}{\partial \mu} = H\mathbf{h} + \frac{2K}{M_s}(\mathbf{u}\cdot\mathbf{n})\mathbf{n} \ , \tag{17}$$

V being the Gibbs free energy density and **h** denoting a unit vector in the direction of the applied field **H**. In general **h** will not be parallel to **n**. Equation (13) now becomes

$$\dot{\mathbf{u}} = \gamma(\mathbf{u}\times\mathbf{H}_{ef}) + \alpha\gamma(\mathbf{u}\times\mathbf{H}_{ef})\times\mathbf{u} \ , \tag{18}$$

which has the form of the kinematic relation

$$\dot{\mathbf{u}} = \boldsymbol{\omega}_u \times \mathbf{u} \ , \tag{19}$$

where the angular velocity of the magnetic moment vector **u** is

$$\begin{aligned}\boldsymbol{\omega}_u &= -\gamma\mathbf{H}_{ef} + \alpha\gamma\mathbf{u}\times\mathbf{H}_{ef} \\ &= \boldsymbol{\omega}_L + \boldsymbol{\omega}_R \ .\end{aligned} \tag{20}$$

Now

$$\boldsymbol{\omega}_L = -\gamma\mathbf{H}_{ef}$$

is the velocity of free (Larmor) precession about the direction of the effective field $\mathbf{H}_{ef}$, while $\boldsymbol{\omega}_R$ is the component of the angular velocity proportional to the damping constant α. The damping extinguishes the precession of the magnetic moment after a time $(\alpha\omega_L)^{-1}$, so that $\mathbf{u}\|\mathbf{h}$. The vector ω_R obeys the equation

$$\frac{\boldsymbol{\omega}_R}{\alpha\gamma}=\mathbf{u}\times\mathbf{H}_{ef}$$

or

$$\frac{\boldsymbol{\omega}_R v_m M_s}{\alpha\gamma}+\mathbf{u}\times\frac{\partial U}{\partial \mathbf{u}}=\mathbf{0}\ . \tag{21}$$

We write

$$\tau_N=\frac{M_s v_m}{2\alpha\gamma kT}=\frac{3\eta_m v_m}{kT}\ ,$$

where

$$\eta_m=\frac{M_s}{6\alpha\gamma} \tag{22}$$

is called the *magnetic viscosity.* Equation (22) follows by analogy with the Debye formula

$$\tau_D=4\pi\eta a^3(kT)^{-1}\ .$$

Thus, eliminating $\alpha\gamma$, we have the average torque equation when $\mathbf{n}$ is *frozen:*

$$6\eta_m v_m\boldsymbol{\omega}_R+\left\{\mathbf{u}\times\frac{\partial U}{\partial \mathbf{u}}\right\}=\mathbf{0}\ . \tag{23}$$

Hence the magnetic moment behaves as a rigid rotator of volume v_m with zero inertia (because no *physical rotation* of the ferroparticle occurs) in a potential well U embedded in a "liquid" of viscosity η_m (Fig. 1). Equation (23) refers to the average behavior of $\boldsymbol{\omega}_R$. If we wish to discuss *not the average* but the *particular* behavior of $\boldsymbol{\omega}_R$, we must consider the instantaneous equation of motion incorporating the stochastic torques due to thermal agitation of the surroundings. This is

$$6\eta_m v_m\boldsymbol{\omega}_R+\left\{\mathbf{u}\times\frac{\partial U}{\partial \mathbf{u}}\right\}=\boldsymbol{\lambda}^{(u)}(t)\ , \tag{24}$$

where the correlation functions of the components of the white noise torque $\boldsymbol{\lambda}^{(u)}$, which is *purely magnetic* in origin, satisfy

$$\overline{\lambda_i^{(u)}(t)\lambda_j^{(u)}(t')}=\frac{2kT\alpha}{\gamma M_s v}\delta_{ij}\delta(t-t')\ , \tag{25}$$

i and j referring to different cartesian axes, $i,j=1,2,3$.

In order to determine the frequency dependence of the longitudinal component $\chi_{\|}(\omega)$ of the susceptibility of the system governed by Eq. (24), it is supposed that the external field $\mathbf{H}$ is applied parallel to $\mathbf{n}$ and is suddenly switched off at a time $t=0$, with the condition that $\xi=v_m HM_s kT\ll 1$ being imposed in order to ensure linearity of the response. The alternating current response may then be obtained by linear response theory. Since $\mathbf{h}$ is assumed parallel to $\mathbf{n}$, the gyromagnetic terms play no role in the determination of the longitudinal susceptibility as they automatically drop out of the Fokker-Planck equation [11]. The limitations of the assumption that $\mathbf{h}\|\mathbf{n}$ have been discussed by Dormann [12].

III. RELAXATION WITH MAGNETIC MOMENT FROZEN ALONG THE EASY AXIS

Equations (13) and (24) refer purely to magnetic relaxation, since the ferroparticle P is embedded in a *frozen carrier liquid matrix.* If the carrier matrix melts, the easy axis $\mathbf{n}$ of the ferroparticle can now physically rotate because of hydrodynamic torques imposed by the carrier liquid. Hence if we assume that $\mathbf{u}$ is frozen parallel to $\mathbf{n}$ so that the Néel mechanism of orientation described above is inoperative, then the ferroparticle P behaves as a rigid rotator of moment of inertia I rotating in the carrier fluid, and the equation of motion of P before $\mathbf{H}$ is switched off is

$$I\dot{\boldsymbol{\omega}}_R(t)+6\eta_F v(\boldsymbol{\omega}_R-\boldsymbol{\omega}_F)+v_m M_s\mathbf{u}\times\mathbf{H}=\boldsymbol{\lambda}^{(u)}(t)\ . \tag{26}$$

Here the torques are *purely hydrodynamic* in origin so that

$$\overline{\lambda_i^{(u)}(t)\lambda_j^{(u)}(t')}=12kT\eta_F v\delta_{ij}\delta(t-t')\ ,\qquad \zeta=6\eta_F v \tag{27}$$

and v is the hydrodynamic volume of the particle; the orientation of P in the liquid is specified by the magnetic moment vector $\mathbf{u}$.

In two dimensions the angle between $\mathbf{u}$ and $\mathbf{H}=H\mathbf{h}$ is $\phi_R(t)$. As usual we suppose that $\mathbf{H}$ is switched off at a time $t=0$ in order to obtain the after-effect solution. If inertial effects are small, i.e., the inertial parameter

$$\gamma=\frac{kTI}{\zeta^2}\le 0.05\ , \tag{28}$$

and if the local angular velocity of the fluid $\boldsymbol{\omega}_F=\mathbf{0}$, then Eq. (26) leads to the Rocard equation for inertia-corrected Debye relaxation. Resonant behavior is not possible, although $\chi'(\omega)$ has the desirable feature of becoming negative at a certain critical frequency, as observed experimentally [1,2].

IV. COMBINED EFFECT OF NÉEL AND DEBYE RELAXATION

The analysis we have just given cannot describe the joint effects of the Debye and Néel relaxation, as it is obvious that both mechanisms are treated *independently.* In order to combine the two effects, we suppose that the ferroparticle P rotating in the liquid carrier is made up of two composite particles P_m and P_s, which may swivel relative to each other about the same common point O, as illustrated in Fig. 2. P_m is treated as a rigid sphere of volume v_m and moment of inertia I_N, representing the magnetic particle; while P_s is a hollow rigid sphere of volume $v-v_m$ and moment of inertia I_R representing the surfactant; v is the hydrodynamic volume of P, which is assumed spherical; and both P_m and P rotate about the common center O. P_m is subjected to a torque arising from the magnetic interaction energy U [Eq. (16)] and white noise and damping torques arising from the *relative* motion of $\mathbf{u}$ and $\mathbf{n}$ (Fig. 2).

Hence the equation of motion of P_m is

$$I_N\dot{\omega}_N+6\eta_m v_m(\omega_N-\omega_R)+\left[\mathbf{n}\times\frac{\partial U}{\partial \mathbf{n}}\right]=\boldsymbol{\lambda}^{(n)}(t) . \tag{29}$$

The equation of motion of the surfactant P_s the orientation of the ferroparticle P and thus P_s in the liquid, being specified by the direction of the magnetic moment vector $\mathbf{u}$, just as in Eq. (26)—is

$$I_R\dot{\omega}_R+6\eta_m v_m(\omega_R-\omega_N)+6\eta_F v(\omega_R-\omega_F)+\left[\mathbf{u}\times\frac{\partial U}{\partial \mathbf{u}}\right]=-\boldsymbol{\lambda}^{(n)}(t)+\boldsymbol{\lambda}^{(u)}(t) . \tag{30}$$

In Eq. (30), $I_R\dot{\omega}_R$ is the inertial torque due to the motion of P_s, the second and fifth terms are the stochastic reaction (braking) torques arising from the relative motion of P_m and P_s, the fourth term is the magnetic interaction torque, and the third and sixth terms are the stochastic braking torques imposed on P by the carrier liquid, where ω_F is the local angular velocity of the liquid. In addition, by Newton's third law, we have, if the applied field $\mathbf{H}$ is switched off at a time $t=0$,

$$\left[\mathbf{u}\times\frac{\partial U}{\partial \mathbf{u}}\right]+\left[\mathbf{n}\times\frac{\partial U}{\partial \mathbf{n}}\right]=\mathbf{0} , \tag{31}$$

since in the absence of $\mathbf{H}$,

$$U=U(\mathbf{\Omega}_R-\mathbf{\Omega}_F) , \tag{32}$$

where $\mathbf{\Omega}_R$ and $\mathbf{\Omega}_F$ denote the sets of Eulerian angles specifying the orientations of $\mathbf{u}$ and $\mathbf{n}$, respectively, relative to the applied field axis $\mathbf{h}$. This is taken as the reference axis, thus emphasizing that one may never assume that $\mathbf{h}$ and $\mathbf{n}$ are collinear. The viscous drag coefficient of P_s is calculated from the hydrodynamic radius a of the ferroparticle P and again follows from the Debye formula

$$\tau_D=\frac{4\pi\eta_F a^3}{kT}=\zeta/2kT ,$$

so that

$$\zeta=8\pi\eta_F a^3=6\eta_F v ,$$

whence $\overline{\lambda_i^{(u)}(t)\lambda_j^{(u)}(t')}$ is given by Eq. (27), since the damping on P_m is purely magnetic in origin.

We note that the equation of motion of the complete ferroparticle P consisting of P_m and P_s is

$$I_R\dot{\omega}_R+I_N\dot{\omega}_N+6\eta_F v(\omega_R-\omega_F)+\mu v_m(\mathbf{u}\times\mathbf{H})=\boldsymbol{\lambda}^{(u)}(t) , \tag{33}$$

which reduces to Eq. (26) if $\omega_R=\omega_N$, that is, P_m rotates in unison with P_s, or the magnetic moment is frozen along the easy axis. We shall also suppose that $\lambda_i^{(u)}(t)$ and $\lambda_i^{(n)}(t)$ are statistically independent, that is, their cross-correlation functions vanish. Equations (29) and (30) represent a three-dimensional form of the itinerant oscillator model [9,13]. They may be simplified and ultimately decoupled into sum and difference angular variables as in the zero damping and noise limit (see the Appendix). This may be accomplished if we suppose in Eq. (30) that the magnetic interaction torque is the most significant factor in the coupling of the motion of P_m and P_s and that the mutual coupling through the damping and white noise torques is very small in comparison to this. We shall again suppose that the local angular velocity of the fluid is zero.

Equations (29) and (30) now become

$$I_N\dot{\omega}_N+6\eta_m v_m\omega_N+\left[\mathbf{n}\times\frac{\partial U}{\partial \mathbf{n}}\right]=\boldsymbol{\lambda}^{(n)}(t) , \tag{34}$$

$$I_R\dot{\omega}_R+6\eta_F v\omega_R+\left[\mathbf{u}\times\frac{\partial U}{\partial \mathbf{u}}\right]=\boldsymbol{\lambda}^{(u)}(t) , \tag{35}$$

which is a simplified three-dimensional form of the itinerant oscillator model [13,14]. The *combined* motion of P_m and P_s gives rise to inertia corrected Debye absorption. The fast *relative* (libration) motion $\mathbf{\Omega}_R-\mathbf{\Omega}_N$ giving rise to resonance absorption as is shown briefly below.

V. RESONANT BEHAVIOR

The model may qualitatively explain the experimental results by demonstrating that a resonance, that is magnetomechanical in origin can arise in $\chi_{\parallel}(\omega)$ for a ferrofluid if P_m is allowed to rotate relative to P_s. This is in addition to the high-frequency ferromagnetic resonance [8] of the transverse component $\chi_{\perp}(\omega)$ of the susceptibility arising from the precession of $\mathbf{u}$ about the axis of the effective field; cf. Eq. (20). The inclusion of the inertial terms in Eqs. (27) and (30) and the fact that $\mathbf{h}$ and $\mathbf{n}$ are not collinear will induce a coupling between the transverse and longitudinal relaxation, thus affecting the ferromagnetic resonance. We suppose, however, that this may be ignored in a first approximation. An estimate of the resonant frequency may be made by restricting the motion to rotation in a plane, so that having switched $\mathbf{H}$ off at a time $t=0$,

$$I_N\dot{\omega}_N+6\eta_m v_m\omega_N-U'(\phi_R-\phi_N)=\lambda^{(n)}(t), \quad t>0 , \tag{36}$$

$$I_R\dot{\omega}_R+6\eta_F v\omega_R+U'(\phi_R-\phi_N)=\lambda^{(u)}(t) \tag{37}$$

with

$$U(\phi_R-\phi_N)=-Kv_m\cos^2(\phi_R-\phi_N) , \tag{38}$$

where

$$\omega_R=\dot{\phi}_R, \quad \omega_N=\dot{\phi}_N . \tag{39}$$

If we write

$$\Phi=\frac{I_R\phi_R+I_N\phi_N}{I_R+I_N}, \quad \psi=\frac{\phi_R-\phi_N}{2} \tag{40}$$

and further impose the condition

$$\frac{6\eta_m v_m}{I_N}=\frac{6\eta_F v}{I_R}=\beta=\frac{\zeta_N}{I_N}=\frac{\zeta_R}{I_R}\ , \tag{41}$$

that is,

$$\frac{\zeta_N}{\zeta_R}=\frac{I_N}{I_R}\ , \tag{42}$$

so that with $I_R \ll I_N$ (as we expect since the mass of the surfactant is much less than that of the magnetic particle), the condition $\zeta_R \ll \zeta_N$ is automatically satisfied; thus P_m, the magnetic particle, is heavily damped; Eqs. (36) and (37) decouple into [14]

$$(I_R+I_N)\ddot{\Phi}+(I_R+I_N)\beta\dot{\Phi}=\lambda^{(n)}(t)+\lambda^{(u)}(t)\ , \tag{43}$$

$$\ddot{\psi}+\beta\dot{\psi}+\frac{Kv_m}{2}\left[\frac{1}{I_R}+\frac{1}{I_N}\right]\sin 4\psi=\frac{1}{2}\left[\frac{\lambda^{(n)}}{I_N}-\frac{\lambda^{(u)}}{I_R}\right]. \tag{44}$$

Here

$$U(\phi_R-\phi_N)=-Kv_m\cos^2(\phi_R-\phi_N)\ , \tag{45}$$

so that

$$U'(\phi_R-\phi_N)=Kv_m\sin[2(\phi_R-\phi_N)]\ . \tag{46}$$

Equation (43) represents *inertia-corrected Debye relaxation,* both particle P_m and surfactant P_s rotating as a unit in the fluid. Equation (44), on the other hand, describes the *relative motion of the magnetic particle and surfactant,* with the angular frequency of small oscillation Ω being

$$\Omega=\left[2Kv_m\left[\frac{1}{I_R}+\frac{1}{I_N}\right]\right]^{1/2}\approx\left[\frac{2Kv_m}{I_R}\right]^{1/2}, \tag{47}$$

so that resonance may occur at this frequency. A brief account of the calculation of $\chi_{\parallel}(\omega)$ from Eqs. (43) and (44) is given in the Appendix.

We note that the restriction to small oscillations of the ψ motion allows one [14] to calculate from Eqs. (43) and (44) the decay function

$$b(t)=(\mu^2/3kT)\langle\cos\phi_R(0)\cos\phi_R(t)\rangle_0$$

of the magnetic moment in closed form. The subscript zero on the angular braces denotes that the average is to be evaluated in the absence of **H**. Such a restriction requires, however, that $2\psi=\phi_R-\phi_N$ (which is also, as we have defined it, the angle between the magnetic moment direction **u** and the easy axis direction **n**) be small $\leq 30°$. This means that the slow Néel relaxation process (in a strict sense we can no longer speak of a pure Debye or pure Néel process since the solid state and hydrodynamic processes are irrevocably mixed in the model), which [15,16] demands escape over the hills of the potential U, is disregarded. Thus, in order to include the Néel process, the $\cos^2 2\psi$ potential of Eq. (45) must be used in order to calculate $b(t)$. The contribution to $b(t)$ of the Φ motion (P_m and P_s rotating as a unit) is the same as in the small oscillation approximation; however, the exact contribution of the ψ motion, which now describes both the *fast* process of oscillations in the wells of U and the relatively *slow* Néel (activation) process of escape over the hills of U, must be evaluated numerically in the manner described in Ref. [16]. The Néel process should then manifest itself as an additional Debye type of absorption (with characteristic angular frequency of maximum absorption the inverse of the Néel time), lying in the frequency range between the inertia-corrected Debye absorption due to the Φ motion and the resonance absorption due to the rapid oscillations of **u**.

VI. MAGNETIC MOMENT AUTOCORRELATION FUNCTION

Equations (43) and (44) may be solved exactly in the small oscillation approximation, as described in the context of the far infrared dielectric absorption of polar fluids [14]. We have (see the Appendix) for the normalized magnetic moment autocorrelation function $C_\mu(t)$ in the underdamped case

$$\begin{aligned}C_\mu(t)&=\frac{\langle\cos\phi_R(0)\cos\phi_R(t)\rangle_0}{\langle\cos^2\phi_R(0)\rangle_0}=\frac{\langle\cos\Phi(0)\cos\Phi(t)\rangle_0}{\langle\cos^2\Phi\rangle}\mathrm{Re}\langle\exp ia\Delta\psi\rangle_0\\&=\frac{\langle\cos\Phi(0)\cos\Phi(t)\rangle_0}{\langle\cos^2\Phi\rangle_0}\exp\left[-a^2\frac{\langle\Delta\psi\rangle_0^2}{2}\right]\\&=\exp\left[\frac{-kT}{(I_R+I_N)\beta^2}(\beta t-1+e^{-\beta t})\right]\exp\left\{\frac{-kT}{(I_R+I_N)\Omega^2}[1-x(t)]\right\},\end{aligned} \tag{48}$$

where

$$x(t)=\exp(-\beta t/2)[\cos\Omega_1 t+(\beta/2\Omega_1)\sin\Omega_1 t] \tag{49}$$

and

$$\Omega_1^2=\Omega^2-\beta^2/4\ , \tag{50}$$

where $a=2I_N/(I_R+I_N)$.

The first term in Eq. (48) represents inertia-corrected

Debye relaxation, where we expect that $I_R \ll I_N$, so that **u** may oscillate rapidly. The leading term is the contribution to the relaxation due to P_m and P_s rotating as a unit. The behavior is like that of a *solid* ferroparticle of moment of inertia I_R+I_N. The second term represents relaxation due to the *relative* motion of P_m and P_s. It appears, owing to the oscillatory nature of the argument of the second exponential, that resonant behavior will be exhibited in the frequency domain. This is the exact solution for $C_\mu(t)$ in the small oscillation approximation for the system governed by Eqs. (36) and (37). In order to calculate $\chi_\parallel(\omega)$, the longitudinal component of the complex susceptibility, it is again necessary to use linear response theory. The calculation of the Fourier transform of Eq. (48) is cumbersome, however, because of the transcendental functions occurring in the arguments of the exponentials. Nevertheless, the calculation can be carried out exactly [14], leading to an expression for $\chi_\parallel(\omega)$ as a triple sum, showing that, *theoretically*, the longitudinal susceptibility comprises an infinite set of damped resonances. In practice, however, only the fundamental mode should be of significance since $kT[(1+I_r^{-1})\Omega^2 I_N]^{-1} \ll 1$. Hence, it is possible to write a simple analytical formula for $\chi_\parallel(\omega)$, as will be presently demonstrated. Before doing this, however, it is useful to express the solution in terms of the following four parameters, namely,

(i) the inertial parameter γ, where

$$\gamma = kT((I_N+I_R)\beta^2)^{-1} ; \tag{51}$$

(ii) the Debye relaxation time τ_D, where

$$\tau_D=(I_N+I_R)\beta/kT ; \tag{52}$$

(iii) the natural frequency of oscillation Ω as defined in Eq. (47);

(iv) the inertia ratio I_r, where

$$I_r=\frac{I_N}{I_R} . \tag{53}$$

The friction parameter β is then

$$\beta=1/\gamma\tau_D . \tag{54}$$

Hence,

$$C_\mu(t)=\exp\left\{-\left[t/\tau_D-\gamma+\gamma\exp\left[-\frac{t}{\gamma\tau_D}\right]\right]\right\} \times\exp\left\{\frac{-[1-x(t)]}{\gamma\tau_D^2\Omega^2(1+I_r^{-1})}\right\} , \tag{55}$$

where,

$$x(t)=\exp(-t/2\gamma\tau_D)[\cos\Omega_1 t+(2\Omega_1\gamma\tau_D)^{-1}\sin\Omega_1 t] \tag{56}$$

and

$$\Omega_1^2=\Omega^2-\frac{1}{4\gamma^2\tau_D^2} . \tag{57}$$

In any particular situation the measured parameters Ω and τ_D will be regarded as fixed, and the parameters I_r and γ are adjusted to obtain a fit to the experimental results. We remark that it is also possible to calculate $C_\mu(t)$ exactly for rotation in a plane in the small oscillation approximation by using the exact equations, Eqs. (29) and (30), respectively, which include coupling between $\dot\phi_N$ and $\dot\phi_R$ in the damping torques. However, the characteristic equation of the system, which is a cubic in s, as in the present discussion, no longer factorizes; hence it is impossible to neatly separate the motion into Φ and ψ variables, and thus the methods described in Ref. [15] must be adapted in this case.

VII. THE COMPLEX SUSCEPTIBILITY

Referring to our discussion above, if we use the exact expression for $C_\mu(t)$ to calculate $\chi_\parallel(\omega)$, it is generally easiest to use the fast Fourier transform (FFT) algorithm. However, we remarked that in general one would expect that $kT[(1+I_r^{-1})\Omega^2 I_N]^{-1} \ll 1$, in order that the harmonic approximation to the potential be justified. If this is so we may use the result (see the Appendix), namely, that with $s=i\omega$,

$$\chi_\parallel(s)/\chi_\parallel'(0)=1-\int_0^\infty C_\mu(t)\exp(-st)dt \tag{58}$$

is accurately represented by

$$\frac{kT}{I_R+I_N}\frac{1}{(s+1/\tau_D)}\times\left[\frac{1}{s+\beta}+\frac{I_N}{I_R}\frac{s}{s^2+\beta s+\Omega^2}\right] =\frac{1}{(s\tau_D+1)(s\gamma\tau_D+1)} +\frac{I_r}{\Omega^2}\frac{(\gamma\tau_D)^{-1}s}{(s\tau_D+1)\left[\frac{s^2}{\Omega^2}+\frac{s}{\Omega^2\gamma\tau_D}+1\right]} . \tag{59}$$

This equation is the Rocard equation [5,6] describing inertia corrected Debye relaxation, added to which is the response of a damped harmonic oscillator filtered by a Debye process. The Rocard equation represents the *low-frequency response* arising from the combined motion of P_m and P_s, while the harmonic oscillator portion is the *high-frequency response* originating from the relative motion, which exhibits resonant behavior at a frequency $\omega=\Omega$. One may in turn separate this equation into its real and imaginary parts, so that

$$\frac{\chi_\parallel'(\omega)}{\chi_\parallel'(0)}=\frac{1-\omega^2\gamma\tau_D^2}{(1+\omega^2\tau_D^2)(1+\omega^2\gamma^2\tau_D^2)} +\frac{\frac{I_r\omega}{\gamma\tau_D\Omega^2}\left[\frac{\omega}{\gamma\tau_D}\Omega^2+\omega\tau_D\left[1-\frac{\omega^2}{\Omega^2}\right]\right]}{(1+\omega^2\tau_D^2)\left[\left[1-\frac{\omega^2}{\Omega^2}\right]^2+\frac{\omega^2}{\Omega^4\gamma^2\tau_D^2}\right]} , \tag{60}$$

$$\frac{\chi_{\parallel}''(\omega)}{\chi_{\parallel}'(0)}=\frac{\omega(1+\gamma)\tau_D}{(1+\omega^2\tau_D^2)(1+\omega^2\gamma^2\tau_D^2)}-\frac{I_r\omega}{\gamma\tau_D\Omega^2}\times\frac{\left[\left[1-\frac{\omega^2}{\Omega^2}\right]-\frac{\omega^2}{\gamma\tau_D\Omega^2}\right]}{(1+\omega^2\tau_D^2)\left[\left[1-\frac{\omega^2}{\Omega^2}\right]^2+\frac{\omega^2}{\Omega^4\gamma^2\tau_D^2}\right]} . \quad (61)$$

The sharpness of the resonance absorption peak will be determined by the Q factor, which is

$$Q=\Omega/\beta=\gamma\tau_D\Omega . \quad (62)$$

VIII. RESULTS AND SIMULATIONS

Initially, it was necessary to determine the dependence of the model equations, Eqs. (60) and (61), representing the normalized components of $\chi'(\omega)$ and $\chi''(\omega)$ on the variable fitting parameters γ and I_r respectively, τ_D and Ω being fixed at values of 10 μs and 3.14×10^8 rad/s. Figure 3(a) shows a plot of $\chi'(\omega)$ and $\chi''(\omega)$ normalized against log[f (Hz)] with $\gamma=2\times10^{-4}$ and I_r varying from 180 to 1140 in five steps of 240, while Fig. 3(b) simply highlights the high-frequency region of the data. Figure 4(a) shows a similar plot, but in this case I_r is fixed at 180 and γ has values of (1) 2 10^{-4}, (2) 0.8 10^{-4}, (3) 0.45 10^{-4}, and (4) 0.31 10^{-4}, respectively; for this case, Fig. 4(b) illustrates the high-frequency region of the data. From these plots the following relevant points, pertaining to the model fitting, emerge:

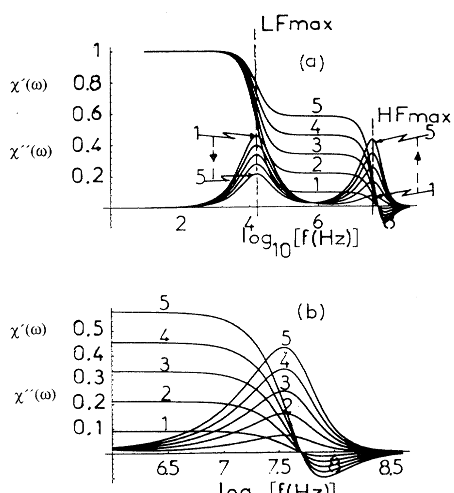

FIG. 3. (a) Plot of $\chi'(\omega)$ and $\chi''(\omega)$ against $\log_{10}$ [(f Hz)] with $\gamma=2\times10^{-4}$ and I_r having values of (1) 180, (2) 420, (3) 660, (4) 900, and (5) 1140, respectively. Both plots are normalized by $\chi'(0)$. (b) Highlights of the high-frequency region of the data of (a).

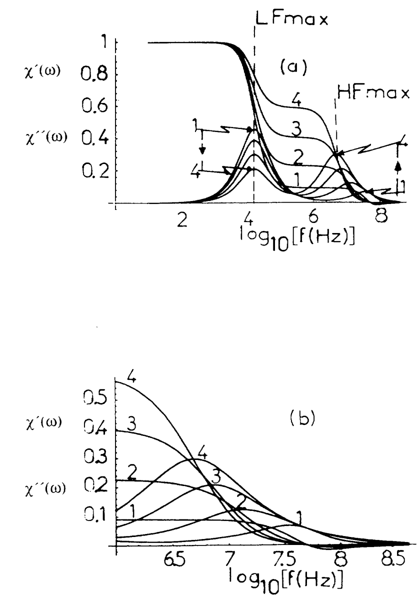

FIG. 4. (a) Plot of $\chi'(\omega)$ and $\chi''(\omega)$ against $\log_{10}$ (f Hz) with I_r fixed at 180 and γ having values of (1) 2 10^{-4}, (2) 0.8 10^{-4}, (3) 0.45 10^{-4}, and (4) 0.31 10^{-4}, respectively; again both plots are normalized by $\chi'(0)$. (b) Highlights of the high-frequency region of the data of (a).

(i) *Increasing I_r while τ_D, Ω, and γ remain fixed results in* (a) an increase in the high-frequency plateau of $\chi'(\omega)$, (b) an increase in the high-frequency negative component of $\chi'(\omega)$, (c) an increase in the high-frequency absorption peak of $\chi''(\omega)_{\text{HF max}}$, (d) a reduction in the low-frequency absorption peak of $\chi''(\omega)_{\text{LF max}}$, and (e) no change in the frequencies at which $\chi''(\omega)_{\text{HF max}}$, and $\chi''(\omega)_{\text{LF max}}$ occur.

(ii) *Decreasing γ while τ_D, Ω, and I_r remain fixed results in* (a) an increase in the high-frequency plateau of $\chi'(\omega)$, (b) a reduction in the high-frequency negative component of $\chi'(\omega)$, (c) a shift to a lower-frequency absorption peak of $\chi''(\omega)_{\text{HF max}}$, (d) an increase in the high-frequency absorption peak of $\chi''(\omega)_{\text{HF max}}$, and (e) a reduction in the low-frequency absorption peak of $\chi''(\omega)_{\text{LF max}}$.

Having become familiar with the theoretical model, one may apply it to experimentally derived data; thus the frequency-dependent complex susceptibility of a ferrofluid sample of cobalt ferrite in isopar-m, with an approximate median particle diameter of 9.5 nm, was determined over the frequency range 0.1 kHz to 400 MHz. A plot of this data against log[f(Hz)] is shown in Fig. 5(a), with the $\chi'(\omega)$ component becoming negative at a frequency of 50 MHz and the $\chi''(\omega)$ component revealing the presence of two absorption peaks at approximate frequencies of 16 kHz [$\chi''(\omega)_{\text{LF max}}$] and 40 MHz [$\chi''(\omega)_{\text{HF max}}$], respectively; this lower frequency corresponds to a Brownian relaxation time, τ_D, of 10 μs. The corresponding fit obtained from Eqs. (60) and (61), using parameter values of $\tau_D=10$ μs, $\Omega=2\pi\times50\times10^6$ rad s^{-1},

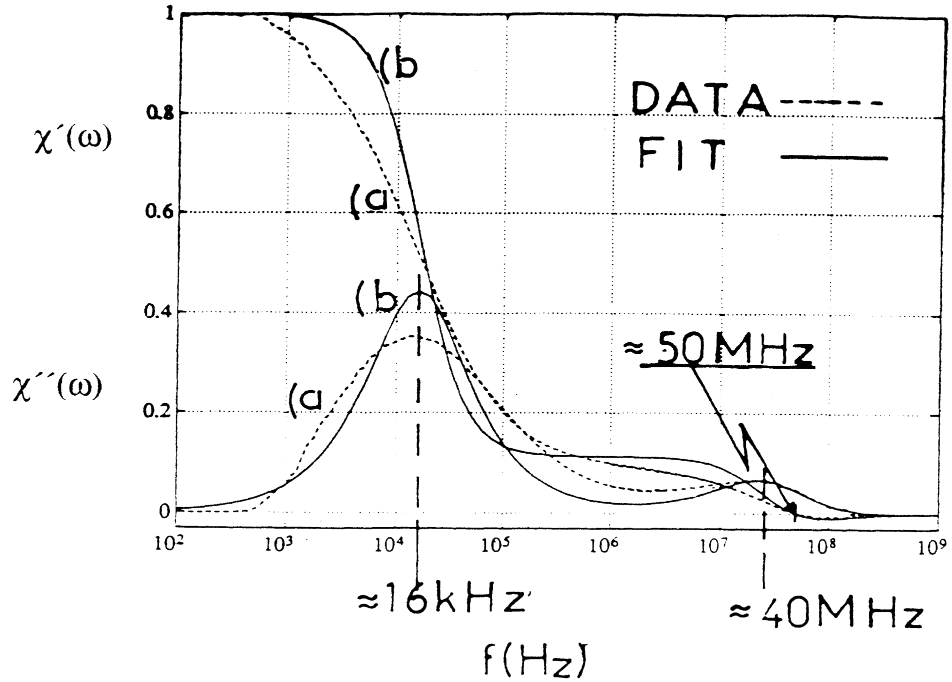

FIG. 5. (a) Plot of $\chi'(\omega)$ and $\chi''(\omega)$ against $\log_{10}f$ (Hz) of experimental data, with

$\chi''(\omega)_{\mathrm{LFmax}}=16$ K Hz,

$\chi''(\omega)_{\mathrm{HF\ max}}=40$ MHz,

and the $\chi'(\omega)$ component going negative at a frequency of approximately 50 MHz. (b) Fit obtained to the experimental data by use of Eqs. (60) and (61), using parameter values of $\tau_D=10$ μs, $\Omega=2\pi\ 50.10^6$ rad s^{-1}, $\gamma=2\ 10^{-4}$, and $I_r=180$. All plots are normalized by $\chi'(0)$.

$\gamma=2\times10^{-4}$, and $I_r=180$, is shown in Fig. 5(b). This is a very satisfactory fit, and the discrepancies in the experimental and theoretical profiles can in part be attributed to the fact that a ferrofluid consists of a distribution of particle sizes, a factor that the model, in its present form, fails to take into account.

IX. CONCLUSION

The effect of the moment of inertia of single domain ferromagnetic particles on the frequency-dependent complex susceptibility, $\chi(\omega)=\chi'(\omega)-i\chi''(\omega)$, of ferrofluids is reported. It is demonstrated that particle inertial effects, arising from rotational Brownian motion and the finite mass of the particles, can give rise to a condition whereby the real component, $\chi'(\omega)$, takes on a negative value at a frequency substantially lower than the Larmor frequency, thus providing a possible explanation for present and previously published data [1,2] that display such an effect in the 10 to 100 MHz region.

A model of the dynamical behavior of a ferroparticle, in which the Langevin treatment of Brownian motion is used to incorporate thermal agitation, is presented. It is shown that this model, which takes into account the relative motion of the magnetic moment and easy axis, can qualitatively explain the experimental results obtained for a ferrofluid sample of cobalt ferrite in isopar-m over the frequency range 0.2 KHz to 300 MHz. The model takes into account the relative motion of the axes by representing the ferroparticle P as a composite rigid body comprising a rigid magnetic particle P_m (assumed to be spherical), which may rotate inside and in contact with a concentric rigid sphere P_s, representing the surfactant, so that P_m and P_s may have different angular velocities about a common center. It constitutes, in the small oscillation approximation, a three-dimensional form of the itinerant oscillator model. The model accordingly predicts, for the longitudinal component of the complex susceptibility, inertia-corrected Debye relaxation in the form of the Rocard equation, which arises for P_m and P_s rotating as a unit and resonance behavior arising from the relative motion of P_m and P_s, thus providing a quantative explanation of the experimental results.

ACKNOWLEDGMENT

We thank S. W. Charles of the Department of Chemistry, University College of North Wales for useful discussions and for the provision of ferrofluid samples.

APPENDIX: SUMMARY OF THE SIMPLIFIED ITINERANT OSCILLATOR MODEL

We shall first calculate the angular-velocity autocorrelation function for the simplified itinerant oscillator model governed by Eqs. (36), (37), and (41),

$$r(t)=\langle \dot\phi_R(0)\dot\phi_R(t)\rangle_0 ,$$

as it is useful in the calculation of the orientational correlation function $C_\mu(t)$. Again the "0" subscript on the averaging brackets indicates the equilibrium ensemble average. In terms of our Φ and ψ variables, $r(t)$ becomes

$$\langle[\dot\Phi(0)+a\dot\psi(0)][\dot\Phi(t)+a\dot\psi(t)]\rangle_0$$
$$=\langle\dot\Phi(0)\dot\Phi(0)\rangle_0+a\langle\dot\psi(0)\dot\Phi(t)\rangle_0+a\langle\dot\Phi(0)\dot\psi(t)\rangle_0$$
$$+a^2\langle\dot\psi(0)\dot\psi(t)\rangle_0 .$$

Now Φ and ψ are *independent* random variables, whence

$$\langle \dot{\Phi}(0)\dot{\psi}(t)\rangle_0 = \langle \dot{\Phi}(0)\rangle_0 \langle \dot{\psi}(t)\rangle_0 = 0 ,$$
$$r(t) = \langle \dot{\Phi}(0)\dot{\Phi}(t)\rangle_0 + a^2 \langle \dot{\psi}(0)\dot{\psi}(t)\rangle_0 . \quad \text{(A1)}$$

The foregoing result is perfectly general and holds no matter what the form of U, the only restrictive condition being Eq. (41). The ψ correlation function may be written immediately from the known results for free rotation about a space-fixed axis [5,6]. The Φ angular-velocity correlation function is then (where t means $|t|$ from now on)

$$\langle \dot{\Phi}(0)\dot{\Phi}(t)\rangle_0 = \langle \dot{\Phi}^2\rangle_0 e^{-\beta t} .$$

The average $\langle \dot{\Phi}^2\rangle_0$ is found by inspection of the Hamiltonian

$$\tfrac{1}{2}I_N\dot{\phi}_N^2 + \tfrac{1}{2}I_R\dot{\phi}^2 + U(\phi_R - \phi_N) = \tfrac{1}{2}(I_R + I_N)\dot{\Phi}^2 + \frac{2I_R I_N}{I_R + I_N}\dot{\psi}^2 + U(2\psi) .$$

We have by the equipartition theorem

$$\tfrac{1}{2}(I_R + I_N)\langle \dot{\Phi}^2\rangle_0 = \tfrac{1}{2}kT .$$

Thus

$$\langle \dot{\Phi}(0)\dot{\Phi}(t)\rangle_0 = [kT/(I_R + I_N)]e^{-\beta t} . \quad \text{(A2)}$$

The ψ velocity correlation function, on the other hand, can only be had in closed form in the small oscillation approximation. This may be written immediately from the results of [17] for the harmonic oscillator in the underdamped case, so that

$$\langle \dot{\psi}(0)\dot{\psi}(t)\rangle_0 = \langle \dot{\psi}(0)^2\rangle_0 \exp(-\tfrac{1}{2}\beta t)[\cos\Omega_1 t - (\tfrac{1}{2}\beta/\Omega_1)\sin\Omega_1 t] .$$

In order to determine $\langle \dot{\psi}^2\rangle_0$ we refer again to the Hamiltonian. Since Φ and ψ are independent, we again have

$$\tfrac{1}{2}[4I_R I_N/(I_R + I_N)]\langle \dot{\psi}^2\rangle_0 = \tfrac{1}{2}kT .$$

Thus

$$\langle \dot{\psi}^2\rangle_0 = kT(I_R + I_N)/4I_R I_N ,$$

and so

$$r(t) = \langle \dot{\phi}_R(0)\dot{\phi}_R(t)\rangle_0 = \frac{kT}{I_R + I_N}\left[e^{-\beta t} + \frac{I_N}{I_R}\exp(-\tfrac{1}{2}\beta t)\left[\cos\Omega_1 t - \frac{\beta}{2\Omega_1}\sin\Omega_1 t\right]\right] . \quad \text{(A3)}$$

To calculate orientational correlation functions, we make use of a theorem concerning characteristic functions of Gaussian random variables, namely [15]

$$\langle \exp(iX)\rangle = \exp[i\langle X\rangle - \tfrac{1}{2}(\langle X^2\rangle - \langle X\rangle^2)] . \quad \text{(A4)}$$

Because the noise torques acting on the system have Gaussian distributions and because the equations of motion of ψ in the harmonic approximation are linear, ψ will be a Gaussian random variable (linear transformations of Gaussian random variables are themselves Gaussian) and Φ is automatically a Gaussian random variable because the equation of motion of Φ contains no external torques apart from those due to the Brownian movement.

Returning now to our original variable, we wish to calculate the magnetic moment autocorrelation function $\rho(t)$. We have, by definition,

$$\rho(t) = \mu^2 \langle \cos\phi_R(0)\cos\phi_R(t)\rangle_0 . \quad \text{(A5)}$$

We now write Eq. (A5) in terms of the independent random variables Φ and ψ as

$$\rho(t) = \langle \cos\Phi(0)\cos\Phi(t)\rangle_0 \times\{\mu^2[\langle \cos[a\psi(0)]\cos[a\psi(t)]\rangle_0 + \langle \sin[a\psi(0)]\sin[a\psi(t)]\rangle_0]\} . \quad \text{(A6)}$$

In writing Eq. (A6) we have recalled that ψ and Φ are independent random variables; thus averages like

$$\langle \cos\Phi(0)\cos\Phi(t)\cos[a\psi(0)]\cos[a\psi(t)]\rangle_0$$

may be written

$$\langle \cos\Phi(0)\cos\Phi(t)\rangle_0 \langle \cos[a\psi(0)]\cos[a\psi(t)]\rangle_0 ,$$

while averages like

$$\langle \cos\Phi(0)\sin\Phi(t)\cos[a\psi(0)]\sin[a\psi(t)]\rangle_0$$

all vanish. We have also used the fact that for the free rotator

$$\langle \cos\Phi(0)\cos\Phi(t)\rangle_0 = \langle \sin\Phi(0)\sin\Phi(t)\rangle_0 .$$

We now write Eq. (A6) in a form in which the Gaussian theorem given above may be used. We first define

$$\Delta\psi = \psi(t) - \psi(0)$$

and write

$$\langle \cos[a\psi(0)]\cos[a\psi(t)]\rangle_0 + \langle \sin[a\psi(0)]\sin[a\psi(t)]\rangle_0 = \langle \cos[a\psi(0)]\cos[a\psi(0) + a\Delta\psi]\rangle_0 + \langle \sin[a\psi(0)]\sin[a\psi(0) + a\Delta\psi]\rangle_0 ,$$

$$\langle \cos(a\Delta\psi)\rangle_0 = \text{Re}[\langle \exp(ia\Delta\psi)\rangle_0] = g(t) . \quad \text{(A7)}$$

$\psi(t)$ and $\psi(0)$ are Gaussian random variables; therefore $\Delta\psi$ is a Gaussian random variable. We may therefore write

$$g(t)=\mathrm{Re}(\exp\{ia\langle\Delta\psi\rangle_0-\tfrac{1}{2}a^2[\langle(\Delta\psi)^2\rangle_0-\langle\Delta\psi\rangle_0^2]\})\ .$$

By stationarity

$$\langle\psi(0)\rangle_0=0\ .$$

Thus $\Delta\psi$ is a *centered* random variable, whence

$$g(t)=\exp[-\tfrac{1}{2}a^2\langle(\Delta\psi)^2\rangle_0]\ . \tag{A8}$$

Thus we write $g(t)$ by knowing $\langle(\Delta\psi)^2\rangle_0$ only. To use the results of Ref. [17] it is convenient to substitute for $\langle(\Delta\psi)^2\rangle_0$, so that Eq. (A8) becomes

$$\exp\{-\tfrac{1}{2}a^2[\langle\psi^2(0)+\psi^2(t)-2\psi(0)\psi(t)\rangle_0]\}=\exp[-a^2\langle\psi^2(0)\rangle_0]\exp[a^2\langle\psi(0)\psi(t)\rangle_0]\ , \tag{A9}$$

because $\langle\psi^2(0)\rangle_0=\langle\psi^2(t)\rangle_0$ by stationarity. Thus

$$\rho(t)=\rho_\Phi(t)\{\mu^2\exp(-a^2\langle\psi^2\rangle_0)\exp[a^2\langle\psi(0)\psi(t)\rangle_0]\}\ . \tag{A10}$$

$\rho_\Phi(t)$ is the autocorrelation function $\langle\cos\Phi(0)\cos\Phi(t)\rangle_0$ for rotation about a space-fixed axis. The value of this is [5]

$$\tfrac{1}{2}\exp\left[-\frac{kT}{(I_R+I_N)\beta^2}(\beta t-1+e^{-\beta t})\right]\ . \tag{A11}$$

We now evaluate $\langle\psi(0)\psi(t)\rangle_0$. We again use the results of Ref. [17] for the harmonic oscillator model in the underdamped case. Thus

$$\langle\psi(0)\psi(t)\rangle_0=\gamma_1x(t)\ ,$$

where

$$x(t)=\exp(-\beta t/2)[\cos\Omega_1t-(\beta/2\Omega_1)\sin\Omega_1t] \tag{A12}$$

and

$$\gamma_1=\frac{\langle\dot\psi^2\rangle_0}{\Omega^2}\ .$$

Equation (A10) when Fourier transformed leads to a very complicated expression [14]. Equations (60) and (61), however, may be derived simply as follows. We first consider the plane rotator of moment of inertia I specified by the angular coordinate θ. The angular-velocity autocorrelation function of this is [5,6]

$$\langle\dot\theta(0)\dot\theta(t)\rangle_0=(kT/I)e^{-\beta t} \tag{A13}$$

and (L denoting the Laplace transform)

$$L\{\langle\dot\theta(0)\dot\theta(t)\rangle_0\}=(kT/I)/(s+\beta)\ . \tag{A14}$$

Also with

$$\begin{aligned}&\Delta\theta=\theta(t)-\theta(0)\ ,\\&\langle\tfrac{1}{2}(\Delta\theta)^2\rangle_0=(kT/I\beta^2)(\beta t-1+e^{-\beta t})\ ,\end{aligned} \tag{A15}$$

the complex susceptibility is

$$\frac{\chi_\parallel(s)}{\chi_\parallel(0)}=-\int_0^\infty\frac{d}{dt}\left[\exp\left\{-\frac{\langle(\Delta\theta)^2\rangle_0}{2}\right\}\right]e^{-st}dt \tag{A16}$$

$$=-sL\left\{\sum_{n=1}^{\infty}\frac{\langle(\Delta\theta)^2\rangle_0}{2^n}\frac{(-1)^n}{n!}\right\}\ . \tag{A17}$$

If we truncate this equation at $n=1$, we have

$$\frac{\chi_\parallel(s)}{\chi_\parallel(0)}=sL\left\{\frac{\langle(\Delta\theta)^2\rangle_0}{2}\right\}=\frac{kT}{I}\frac{1}{s(s+\beta)} \tag{A18}$$

$$=\frac{kT}{I}\frac{1}{s}L\{\langle\dot\theta(0)\dot\theta(t)\rangle_0\}\ . \tag{A19}$$

Equation (A19) is singular at $s=0$ and so cannot hold at low frequencies. Let us, however, shift the s^{-1} term in that equation by the inverse of $\tau_D=I\beta/kT$. Equation (A19) then becomes

$$\frac{\chi_\parallel(s)}{\chi_\parallel'(0)}=\frac{kT}{I}\frac{1}{(s+kT/I\beta)(s+\beta)}\ . \tag{A20}$$

Equation (A19) is the Rocard equation [5,16]. It accurately represents the susceptibility of the free rotator if $\gamma\leq0.05$. Equation (A20) is valuable insofar as it provides a simple connection between the complex susceptility and the angular-velocity correlation function and also allows the Rocard equation to be easily derived. An analogous, simple way of treating the itinerant oscillator also exists [15], as our approximate formula (A20) may be derived from the analogous high-frequency formula for the itinerant oscillator, namely,

$$\frac{\chi_\parallel(s)}{\chi_\parallel'(0)}=(1/s)L\{\langle\dot\phi_R(0)\dot\phi_R(t)\rangle_0\}\ , \tag{A21}$$

by simply writing $s\to s+kT/[I_N\beta(1+I_r^{-1})]$ in the leading term in (A21). We can now calculate the complex polarizability directly from the Laplace transform of the angular velocity autocorrelation function. The high-frequency susceptibility in terms of the Φ and ψ variables is

$$\frac{\chi_\parallel(s)}{\chi_\parallel'(0)}=\frac{1}{s}L\{\langle\dot\Phi(0)\dot\Phi(t)\rangle_0+a^2\langle\dot\psi(0)\dot\psi(t)\rangle_0\} \tag{A22}$$

$$=\frac{kT}{I_R+I_N}\frac{1}{s}\left[\frac{1}{s+\beta}+\frac{I_N}{I_R}\frac{s}{s^2+\beta s+\Omega^2}\right]\ . \tag{A23}$$

We shift the s^{-1} term by $1/\tau_D$. The resulting equation, which is the same as Eq. (59), is (the reader is referred to [15] for more details)

$$\frac{\chi_\parallel(s)}{\chi_\parallel'(0)}=\frac{kT}{I_R+I_N}\frac{1}{(s+1/\tau_D)}\times\left[\frac{1}{s+\beta}+\frac{I_N}{I_R}\frac{s}{s^2+\beta s+\Omega^2}\right]\ . \tag{A24}$$

Equation (A24) is the Rocard equation, added to which is the response of a damped harmonic oscillator of a natural angular frequency Ω filtered by a Debye process.

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