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Internal and Brownian mode-coupling effects in the theory of magnetic relaxation and ferromagnetic resonance of ferrofluids

W T Coffey and P C Fannin

Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Republic of Ireland

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Abstract

It is shown how the Langevin equation for the motion of the magnetization of a ferrofluid particle with uniaxial anisotropy in a strong uniform applied field reduces to those governing the Néel (i.e. the solid-state or internal) mechanism of reorientation of the magnetic moment in the non-axially symmetric potential created when a field is applied at an angle to the easy axis and a Larmor-like equation for the transverse motion. The field angle, unlike in the solid-state problem, is a function of the time due to the torques imposed by the fluid carrier. The Langevin equation for the Brownian rotational motion of the particle itself reduces to that describing Debye relaxation in the applied field but is coupled to the magnetic motion via the external field. The results indicate that the dissipation parameter of the internal solid-state mechanism is augmented by the external stochastic torques imposed by the carrier. However, the effect appears to be negligible because of the ratio of the Brownian (Debye) time to the free Néel diffusion time. Furthermore, just as in the pure solid-state process, pronounced precession-aided longitudinal relaxation and ferromagnetic resonance effects, having their origin in the breaking of the axial symmetry due to the strong field, will occur. The precession-aided relaxation disappears for weak fields since the potential becomes axially symmetric. Moreover, the equations of motion of the magnetic moment and the particle completely decouple and the overall decay function is simply the product of the decay functions of the internal (Néel) and Debye processes. It appears that the ferromagnetic resonance in this instance is accurately described by the known solid-state results, since the Brownian relaxation time greatly exceeds the effective relaxation times of the internal dipole and quadrupole modes associated with the ferromagnetic resonance. This conclusion is reinforced by the favourable agreement of the weak-field result with experimental observations of the complex susceptibility of four ferrofluid samples.

1. Introduction

A long-standing problem in the theory of magnetic relaxation of ferrofluids is how the solid-state or Néel (longitudinal) mechanism of relaxation of internal rotation of the magnetic dipole moment with respect to the crystalline axes inside the particle, the associated transverse modes (which may give rise to ferromagnetic resonance) and the mechanical Brownian relaxation due to physical rotation of the ferrofluid particle in the carrier fluid may be treated in the context of a *single* model comprising both relaxation processes. (We recall that the slowest mode of the longitudinal relaxation process describes the reversal of the magnetization over the potential barrier created by the internal anisotropy of the particle which of course will be modified by an external applied field. The time taken to cross the barrier is known as the Néel relaxation time and follows the Arrhenius law.)

The question posed above was answered in part by Shliomis and Stepanov [1]. They showed that for uniaxial anisotropy, for weak applied magnetic fields and in the non-inertial limit, the equations of motion of the ferrofluid particle incorporating both the internal and the Brownian relaxation processes decouple from each other. Thus the reciprocal of the greatest relaxation time is the sum of the reciprocals of the Néel and Brownian relaxation times of both processes considered *independently*, that is those of a *frozen Néel* and a *frozen Brownian* mechanism! In this instance the joint probability of the orientations of the magnetic moment and the particle in the fluid, i.e. the crystallographic axes, is the product of the individual probability distributions of the orientations of the axes and the particle, so the underlying Fokker–Planck equation for the joint probability distribution also factorizes as do the statistical moments. Thus the internal and Debye processes are statistically independent. If the applied field is sufficiently strong, however, no such decoupling can take place.

The Shliomis–Stepanov approach to the ferrofluid relaxation problem, which is based on the Fokker–Planck equation, has come to be known as the egg model. Yet another treatment has recently been given by Scherer and Matuttis [2] using a generalized Lagrangian formalism; however, in the discussion of the applications of their method they limited themselves to a frozen Néel and a frozen Brownian mechanism respectively.

Here we re-examine the egg model (a form [3] of the itinerant oscillator model) noting the ratio of the free Brownian diffusion (Debye) time to the free Néel diffusion time and discarding the assumption of a weak applied field. The results will then be used to demonstrate how the ferrofluid magnetic relaxation problem in the non-inertial or high-mechanical-friction limit is essentially similar to the Néel relaxation in a uniform magnetic field applied at an oblique angle to the easy axis of magnetization [4–8]. Unlike in the solid-state mechanism however, the orientation of the field with respect to the easy axis is now a function of the time due to the physical rotation of the crystallographic axes [1] arising from the ferrofluid. The fact that the behaviour is essentially similar in all other respects to the solid-state oblique-field problem suggests that a strong *intrinsic* dependence of the greatest relaxation time on the damping (independent of that due to the free diffusion time) arising from the coupling between longitudinal and transverse modes occurs. Alternatively, the set of eigenvalues which characterize the longitudinal relaxation now depends strongly on the damping, unlike in axial symmetry. This *precession-aided* (so called because the influence of the precessional term is proportional to the inverse of the damping coefficient) longitudinal relaxation is absent in the weak-field case [1]. Here the equations of motion decouple into those describing a frozen Néel (pure Debye or Brownian) and a frozen Brownian (pure Néel) mechanism of relaxation, respectively. Thus the Néel or longitudinal relaxation is governed by an axially symmetric potential. Hence no *intrinsic* dependence of the greatest relaxation time on the damping exists. Moreover the longitudinal set of eigenvalues is *independent* of the damping, the damping

entering [9] via the free (Néel) diffusion time only. It follows that, in the linear response to a weak applied field, the only effect of the fluid carrier is to further dampen, according to a Debye or Rocard (inertia-corrected Debye) [10] mechanism, both the longitudinal and transverse responses of the solid-state mechanism. Furthermore, it will be demonstrated that in this case *the transverse relaxation process in the ferrofluid, which may give rise to ferromagnetic resonance, may be accurately described by the solid-state transverse result for axial symmetry* because the Brownian relaxation time greatly exceeds the characteristic relaxation times of all the transverse modes. The latter conclusion is reinforced by the favourable agreement of the linear response result with experimental observations of the complex susceptibility of four ferrofluid samples, which is presented in section 6 of the paper.

In order to illustrate how precession-aided relaxation effects may manifest themselves in a ferrofluid, it will be useful to briefly summarize the differences in relaxation behaviour between the cases of axially symmetric and non-axially symmetric potentials of the magnetocrystalline anisotropy and applied field, when the Brownian relaxation mode is frozen. Thus only the solid-state (Néel) mechanism is operative; that is, the magnetic moment of the single-domain particle may reorientate only with respect to the crystalline axes.

2. Langevin equation formalism

Our starting point is [8–11] the Landau–Lifshitz or Gilbert (LLG) equation for the dynamics of the magnetization $\boldsymbol{M}$ of a single-domain ferromagnetic particle, namely

$$2\tau_N \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{M} = \beta(\alpha^{-1}M_s[\boldsymbol{M}\times\boldsymbol{H}] + [[\boldsymbol{M}\times\boldsymbol{H}]\times\boldsymbol{M}]), \tag{1}$$

where

$$\tau_N = \frac{\beta(1+\alpha^2)M_s}{2\gamma\alpha} \tag{2}$$

is the free (solid-state mechanism) diffusion time (Néel diffusion time) of the magnetic moment, α is the dimensionless damping (dissipation) constant, M_s is the saturation magnetization, γ is the gyromagnetic ratio, $\beta = v_m/(kT)$, v_m is the volume (domain volume) of the particle and α^{-1} determines the magnitude of the precession term. The magnetic field $\boldsymbol{H}$ consists of applied fields (Zeeman term), the anisotropy field $\boldsymbol{H}_a$, and a random white-noise field accounting for the thermal fluctuations of the magnetization of an individual particle.

Equation (1) is [8–11] the Langevin equation of the solid-state orientation process. The field $\boldsymbol{H}$ may be written as

$$\boldsymbol{H} = \boldsymbol{H}_{ef} + \boldsymbol{H}_n(t) \tag{3}$$

here

$$\boldsymbol{H}_{ef} = -\frac{\partial V}{\partial \boldsymbol{M}} = -\frac{\partial U}{\partial \boldsymbol{m}} \tag{4}$$

is the conservative part of $\boldsymbol{H}$, which is determined from the free energy density V (U is the free energy, $m = M_s v_m$ is the magnitude of the magnetic moment $\boldsymbol{m}$ of the single-domain particle). The random field $\boldsymbol{H}_n(t)$ has the following properties (the angular braces denote the statistical average over the realizations of $\boldsymbol{H}_n(t)$):

$$\langle \boldsymbol{H}_n(t)\rangle = 0 \tag{5}$$

$$\langle H_n^{(i)}(t)H_n^{(j)}(t')\rangle = \frac{2kT\alpha}{\gamma M_s v_m}\delta_{ij}\delta(t-t'). \tag{6}$$

Here δ_{ij} is Kronecker's delta; $i, j = 1, 2, 3$ correspond to Cartesian (the crystalline) axes; $\delta(t)$ is the Dirac delta function. The random variable $\boldsymbol{H}_n(t)$ must also obey Isserlis's theorem [10]. By introducing [1] the dipole vector

$$\boldsymbol{e} = \frac{\boldsymbol{M}}{M_s} = \frac{\boldsymbol{m}}{m} \tag{7}$$

we find that equation (1) becomes

$$\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}t} = \frac{\gamma}{1+\alpha^2}(\boldsymbol{e} \times \boldsymbol{H}) + \frac{\alpha\gamma}{1+\alpha^2}(\boldsymbol{e} \times \boldsymbol{H}) \times \boldsymbol{e}. \tag{8}$$

Equation (8) has the form [1] of a kinematic relation involving the angular velocity $\boldsymbol{\omega}_e$ of the dipole vector $\boldsymbol{e}$:

$$\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}t} = \boldsymbol{\omega}_e \times \boldsymbol{e} = (\boldsymbol{\omega}_L + \boldsymbol{\omega}_R) \times \boldsymbol{e}. \tag{9}$$

Here

$$\boldsymbol{\omega}_L = -\frac{\gamma \boldsymbol{H}}{1+\alpha^2} = -\frac{\gamma(\boldsymbol{H}_{ef} + \boldsymbol{H}_n(t))}{1+\alpha^2} \tag{10}$$

$$\boldsymbol{\omega}_R = \frac{\gamma\alpha}{1+\alpha^2}(\boldsymbol{e} \times \boldsymbol{H}). \tag{11}$$

$\boldsymbol{\omega}_L$ is the angular velocity of free (Larmor) precession of $\boldsymbol{m}$ in the field $\boldsymbol{H}_{ef}$ superimposed on which is the rapidly fluctuating $\boldsymbol{H}_n(t)$; $\boldsymbol{\omega}_R$ is the *relaxational* component of $\boldsymbol{\omega}_e$. Equations (10) and (11) differ from equations (8) and (9) of Shliomis and Stepanov [1] because they contain the noise field and the factor $(1+\alpha^2)^{-1}$, since the Gilbert equation is used rather than the Landau–Lifshitz equation. The kinematic relation, equation (9), and the coupled Langevin equations, equations (10) and (11), are stochastic differential equations describing the motion of the dipole vector $\boldsymbol{e}$ *relative to the crystallographic axes*, that is the *internal* or solid-state relaxation. Differential recurrence relations (equivalent to the Fokker–Planck equation) for the statistical moments governing the dynamical behaviour of $\boldsymbol{e}$ may be deduced from equations (9)–(11) as described in [6, 7, 10]. If we now, following [1] and allowing for the factor $(1+\alpha^2)$, introduce the magnetic viscosity

$$\mu = \frac{M_s}{6\alpha\gamma}(1+\alpha^2), \tag{12}$$

equation (11) becomes

$$6\mu v_m \boldsymbol{\omega}_R = \boldsymbol{m} \times \left(-\frac{\partial U}{\partial \boldsymbol{m}}\right) + \boldsymbol{m} \times \boldsymbol{H}_n(t). \tag{13}$$

Equation (13) will be the key equation in our discussion of precession-aided Néel relaxation.

3. Precession-aided effects in Néel relaxation

The discussion given above holds for arbitrary free energy U. We now specialize our discussion to a particle with uniaxial anisotropy, such that

$$v_m V(\boldsymbol{M}) = U = -mH_0(\boldsymbol{e} \cdot \boldsymbol{h}) - Kv_m(\boldsymbol{e} \cdot \boldsymbol{n})^2 \tag{14}$$

$$\boldsymbol{h} = \frac{\boldsymbol{H}_0}{H_0}. \tag{15}$$

H_0 is the amplitude of the external uniform magnetic field (the polarizing field), $K > 0$ is the constant of the effective magnetic anisotropy, $\boldsymbol{n}$ is a unit vector along the easy

magnetization axis. The fact that $\boldsymbol{h}$ is not necessarily parallel to $\boldsymbol{n}$ means that the *axial symmetry* characteristic of uniaxial anisotropy will be broken. Thus equation (13) becomes

$$6\mu v_m \boldsymbol{\omega}_R - mH_0[\boldsymbol{e}\times\boldsymbol{h}] - 2Kv_m(\boldsymbol{e}\cdot\boldsymbol{n})[\boldsymbol{e}\times\boldsymbol{n}] = \boldsymbol{m}\times\boldsymbol{H}_n(t) = \lambda_R(t), \tag{16}$$

say. Next we write U explicitly as

$$U = -mH_0\cos\Theta + Kv_m\sin^2\vartheta, \tag{17}$$

where

$$\cos\Theta = \cos\vartheta'\cos\vartheta + \sin\vartheta\sin\vartheta'\cos(\varphi-\varphi'). \tag{18}$$

Here ϑ, φ are the polar angles of $\boldsymbol{e}$ with respect to the easy axis, which is the polar axis; ϑ', φ' are the polar angles of the external field direction $\boldsymbol{h}$ again with respect to the easy axis which in the solid-state problem are constants independent of the time. Analytic expressions for the greatest relaxation time τ in the bistable potential given by equation (17) in the intermediate-to-high-damping case (IHD) (where α is such that the energy loss per cycle of the motion of the magnetization at the saddle point energy trajectory, $\Delta E \gg kT$) may be obtained using Langer's theory [12, 13] of the decay of metastable states applied to the two-degree-of-freedom system specified by ϑ and ϕ, since in the solid-state case ϑ' and ϕ' are fixed. Likewise, the Kramers energy-controlled diffusion method [12, 14] may be used to obtain τ in the very-low-damping (VLD) case where $\Delta E \ll kT$.

We summarize as follows [8]. The free energy $v_m V(\boldsymbol{M})$, equation (14), has a bistable structure with minima at $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ separated by a potential barrier containing a saddle point [8, 15] at $\boldsymbol{n}_0$. If $(\alpha_1^{(i)}, \alpha_2^{(i)}, \alpha_3^{(i)})$ denote the direction cosines of $\boldsymbol{M}$ and $\boldsymbol{M}$ is close to a stationary point $\boldsymbol{n}_i$ of the free energy, then $V(\boldsymbol{M})$ can be approximated to second order in $\alpha^{(i)}$ as (see [9, 12, 15])

$$V = V_i + \tfrac{1}{2}[c_1^{(i)}(\alpha_1^{(i)})^2 + c_2^{(i)}(\alpha_2^{(i)})^2]. \tag{19}$$

The relevant Fokker–Planck equation may then be solved near the saddle point yielding [12, 15]

$$\tau = \tau_{IHD} \sim \left\{\frac{\Omega_0}{2\pi\omega_0}[\omega_1 \mathrm{e}^{\beta(V_1-V_0)} + \omega_2 \mathrm{e}^{\beta(V_2-V_0)}]\right\}^{-1}, \tag{20}$$

(equations for the expansion coefficients $c_i^{(j)}$ and V_i for the potential given by equation (17) are given elsewhere [12, 15]);

$$\omega_1^2 = \gamma^2 M_s^{-2} c_1^{(1)} c_2^{(1)}, \qquad \omega_2^2 = \gamma^2 M_s^{-2} c_1^{(2)} c_2^{(2)}, \qquad \omega_0^2 = -\gamma^2 M_s^{-2} c_1^{(0)} c_2^{(0)} \tag{21}$$

are the squares of the well and saddle angular frequencies, respectively, and

$$\Omega_0 = \frac{\beta}{4\tau_N}\Big[-c_1^{(0)} - c_2^{(0)} + \sqrt{(c_2^{(0)} - c_1^{(0)})^2 - 4\alpha^{-2} c_1^{(0)} c_2^{(0)}}\,\Big]. \tag{22}$$

Equation (22) is effectively the smallest positive (unstable barrier crossing mode) eigenvalue of the noiseless Langevin equation (equation (8) omitting the $\boldsymbol{H}_n(t)$ term) linearized in terms of the direction cosines about the saddle point. We remark that the influence of the precessional term on the longitudinal relaxation is represented by the α^{-2} term in equation (22). Furthermore, the relative magnitudes of the precessional and aligning terms in the Langevin equations are determined by α^{-1}, so equations (20)–(22), and (23) below, describe *precession-aided* longitudinal relaxation.

Equation (20) applies when $\Delta E \gg kT$ (IHD). If $\Delta E \ll kT$, we have for the escape from a single well [8, 12]

$$\tau = \tau_{LD} \sim \frac{\pi kT}{\omega_1 \Delta E}\mathrm{e}^{\beta(V_0-V_1)} \tag{23}$$

where $\Delta E \approx \alpha V_m |V_0|$. The IHD and VLD limits correspond to $\alpha \geqslant 1$ and $\alpha \leqslant 0.01$, respectively. However, for crossover values of α (around $\alpha \approx 0.1$), neither equation (20) nor (23) yields reliable quantitative estimates. Thus a more detailed analysis is necessary [12]. The most striking aspect of the precession-aided relaxation is the behaviour of the complex susceptibility for a small ac field superimposed on the strong field $\boldsymbol{H}_0$. This is particularly sensitive to the longitudinal and transverse mode coupling, exhibiting [8] a strong dependence of the high-frequency ferromagnetic resonant modes (characterized by $\boldsymbol{\omega}_L$) on the aligning (Néel) mode characterized by $\boldsymbol{\omega}_R$ and vice versa. Furthermore, suppression of the barrier crossing mode in favour of the fast relaxation modes in the wells of the bistable potential given by equation (17), occurs if the applied field is sufficiently strong. In terms of the differential recurrence relations generated by the Langevin or Fokker–Planck equations by means of a Fourier expansion in the spherical harmonics $Y_l^m(\vartheta, \phi)$, the coupling effect manifests itself in recurrence relations *inextricably* mixed in the characteristic numbers l and m, unlike in axial symmetry.

Finally, we remark on the asymptote for axial symmetry which arises if $\boldsymbol{H}_0$ is reversed, or is applied parallel to the easy axis $\boldsymbol{n}$. In the axially symmetric case ($\boldsymbol{H}_0 = 0$), τ is given by Brown's asymptotic expression [11] for simple uniaxial anisotropy:

$$\tau \sim \frac{\tau_N \sqrt{\pi}}{2\sigma^{3/2}} \exp \sigma, \qquad \sigma > 2, \tag{24}$$

where $\sigma = \beta K$. Thus, τ normalized by τ_N, unlike equations (21)–(23), is *independent* of α, so the mode-coupling effect completely disappears. Bridging formulae, which illustrate how the asymptotic equations (20) and (23) join smoothly onto the asymptotic equation (24) in the limit of small $\boldsymbol{H}_0$, have been extensively discussed in [12].

4. The effect of the fluid carrier (i) response for zero or very weak applied field

Let the crystallographic axes now rotate with angular velocity $\boldsymbol{\omega}_n$ corresponding to *physical rotation* of the ferrofluid particle due to the stochastic torques imposed by the liquid and the aligning action of $\boldsymbol{H}_0$ (we now have five degrees of freedom: the dipole angles ϑ, ϕ as before and the Euler angles ϑ', ϕ', ψ' which instead of being constant are now functions of the time due to the physical rotation of the easy axis). The relative angular velocity of the dipole and easy axis is then $\boldsymbol{\omega}_R - \boldsymbol{\omega}_n$, so equation (16), describing the motion of $\boldsymbol{m}$, must be modified to

$$6\mu v_m(\boldsymbol{\omega}_R - \boldsymbol{\omega}_n) - mH_0[\boldsymbol{e} \times \boldsymbol{h}] - 2Kv_m(\boldsymbol{e} \cdot \boldsymbol{n})[\boldsymbol{e} \times \boldsymbol{n}] = \boldsymbol{\lambda}_R(t). \tag{25}$$

The corresponding mechanical equation of motion of the particle is (the particle is treated as a rigid sphere, I is the moment of inertia of the sphere about a diameter) by Newton's third law

$$I\dot{\boldsymbol{\omega}}_n + 6\mu v_m(\boldsymbol{\omega}_n - \boldsymbol{\omega}_R) + 6\eta v\boldsymbol{\omega}_n - 2Kv_m(\boldsymbol{e} \cdot \boldsymbol{n})[\boldsymbol{n} \times \boldsymbol{e}] = \boldsymbol{\lambda}_n(t) - \boldsymbol{\lambda}_R(t), \tag{26}$$

where

$$6\eta v = \zeta \tag{27}$$

is the mechanical drag coefficient of the particle in the fluid, v is its hydrodynamic volume, η is the viscosity of the fluid. Thus, by addition of equations (25) and (26) we have the mechanical equation

$$I\dot{\boldsymbol{\omega}}_n + 6\eta v\boldsymbol{\omega}_n - mH_0[\boldsymbol{e} \times \boldsymbol{h}] = \boldsymbol{\lambda}_n(t), \tag{28}$$

where the white-noise $\boldsymbol{\lambda}_n(t)$ torque arising from the fluid carrier obeys

$$\langle \boldsymbol{\lambda}_n(t) \rangle = 0 \tag{29}$$

$$\langle \lambda_n^{(\alpha)}(t)\lambda_n^{(\beta)}(t') \rangle = 2kT\zeta\delta_{\alpha\beta}\delta(t - t'). \tag{30}$$

$\alpha, \beta = 1, 2, 3$ refer to the orientation of the crystallographic axes relative to Cartesian axes fixed in the liquid. The $\boldsymbol{\lambda}_n(t)$ again obey Isserlis's theorem [10], and we shall suppose that $\boldsymbol{\lambda}_n(t)$ and $\boldsymbol{\lambda}_R(t)$ are uncorrelated.

Equations (25) and (28) in general are coupled to each other inextricably by the external field term $\boldsymbol{e} \times \boldsymbol{h}$. If that vanishes, however, with the result that U depends only on $\boldsymbol{e} \cdot \boldsymbol{n}$ [2], they become

$$6\mu v_m(\boldsymbol{\omega}_R - \boldsymbol{\omega}_n) - 2K v_m(\boldsymbol{e} \cdot \boldsymbol{n})[\boldsymbol{e} \times \boldsymbol{n}] = \boldsymbol{\lambda}_R(t), \tag{31}$$

$$I\dot{\boldsymbol{\omega}}_n + 6\eta v \boldsymbol{\omega}_n = \boldsymbol{\lambda}_n(t). \tag{32}$$

The equations thus separate into the equation of motion of $\boldsymbol{m}$ relative to the easy axis, equation (31), and the equation of motion of the easy axis itself, equation (32). The mechanical equation (32) is governed by two characteristic times [12]: the Brownian diffusion or Debye relaxation time

$$\tau_B = \frac{3\eta v}{kT} \tag{33}$$

and the frictional time

$$\tau_\eta = \frac{I}{6\eta v}. \tag{34}$$

Thus the dynamical behaviour of equation (32) is governed by the inertial parameter

$$a = \frac{\tau_\eta}{\tau_B} = \frac{kT}{3\eta v}\frac{I}{6\eta v}. \tag{35}$$

If $a \to 0$, we have the non-inertial response. This is treated by Shliomis and Stepanov [1] who were able to factorize the joint distribution of the dipole and easy axis orientations in the Fokker–Planck equation into the product of the two separate distributions. Thus as far as the internal relaxation process is concerned, the axially symmetric treatment of Brown [11] applies. Hence intrinsically no coupling between the transverse and longitudinal modes exists, i.e. the eigenvalues of the longitudinal relaxation process are independent of α. The distribution function of the easy axis orientations $\boldsymbol{n}$ is simply that of a free Brownian rotator excluding inertial effects.

The picture in terms of the decoupled Langevin equations (31) and (32) above (omitting the inertial term $I\dot{\boldsymbol{\omega}}_n$ in equation (32)) is that the orientational correlation functions of the longitudinal and transverse components of the magnetization in the axially symmetric potential, $K v_m \sin^2 \vartheta$, are simply multiplied by the liquid-state factor, $\exp(-t/\tau_B)$, of the Brownian (Debye) relaxation of the ferrofluid stemming from equation (32). As far as the ferromagnetic resonance is concerned, we shall presently demonstrate that this factor is irrelevant.

We summarize as follows: the longitudinal and transverse magnetic susceptibilities characterizing the solid-state process are approximately described by [16]

$$\chi_\parallel(\omega) = \frac{\chi'_\parallel(0)}{1 + \mathrm{i}\omega\tau} \tag{36}$$

$$\chi_\perp(\omega) = \frac{\chi'_\perp(0)[(1 + \mathrm{i}\omega\tau_2) + \Delta]}{(1 + \mathrm{i}\omega\tau_2)(1 + \mathrm{i}\omega\tau_\perp) + \Delta} \tag{37}$$

$$\Delta = \frac{\sigma\tau_2}{\alpha^2\tau_N^2}(\tau_N - \tau_\perp). \tag{38}$$

In equations (36) and (37), $\chi'_\parallel(0)$, $\chi'_\perp(0)$ are the static susceptibilities parallel and perpendicular to the easy axis and τ is rendered accurately [17] by Brown's expression, equation (24), if $\sigma \geqslant 2$. Furthermore, the transverse susceptibility, equation (37), which is derived by truncating

the infinite hierarchy of differential recurrence relations for the correlation functions (with $U = K v_m \sin^2 \vartheta$) at the quadrupole term using the effective eigenvalue method, yields an accurate result for the transverse response provided that [18] $\sigma \ll 1$, or $\sigma \geqslant 5$. The effective eigenvalue solution, equation (37), fails [18] for σ in the range of 1–5 (where equations (24) and (36) also cease to be entirely reliable), since at small to moderate barrier heights a spread of the precession frequencies of the magnetization in the anisotropy field exists. Thus the hierarchy must be solved exactly using matrix continued fractions. In equation (37) $\tau_\perp$ is the effective relaxation time of the autocorrelation functions of the components $\sin\vartheta\cos\phi$, $\sin\vartheta\sin\phi$ (which are linear combinations of the autocorrelation functions of $Y_1^1(\vartheta,\phi)$ and $Y_1^{-1}(\vartheta,\phi)$) of the dipole moment relaxation mode, while τ_2 is the effective relaxation time of the quadrupole moment relaxation mode, which is a linear combination of the autocorrelation functions of $Y_2^1(\vartheta,\phi)$ and $Y_2^{-1}(\vartheta,\phi)$. The effective relaxation times τ_2 and $\tau_\perp$ may both be expressed [16] in terms of Dawson's integral and decrease monotonically with σ, each having asymptotes

$$\frac{\tau_N}{\sigma}, \qquad \sigma \gg 1. \tag{39}$$

Now according to linear response theory

$$\chi_{\parallel,\perp} = f_{\parallel,\perp}(0) - \mathrm{i}\omega \int_0^\infty f_{\parallel,\perp} \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t = \tilde{f}_{\parallel,\perp}(0) - \mathrm{i}\omega \tilde{f}_{\parallel,\perp}(\omega) \tag{40}$$

where $f_{\parallel,\perp}(t)$ are the longitudinal and transverse after-effect functions, e.g.

$$f_\parallel(t) \cong \chi'_\parallel(0) \exp(-t/\tau), \qquad \sigma \geqslant 2 \tag{41}$$

Moreover, in the frequency domain (the tilde denoting the one-sided Fourier transform)

$$\tilde{f}_\parallel(\omega) = \frac{\chi'_{||}(0)}{\mathrm{i}\omega + 1/\tau} \tag{42}$$

$$\tilde{f}_\perp(\omega) = \frac{\chi'_\perp(0)(\mathrm{i}\omega + 1/\tau_2)}{(\mathrm{i}\omega + 1/\tau_2)(\mathrm{i}\omega + 1/\tau_\perp) + (\sigma/\tau_N\alpha^2)(1/\tau_\perp - 1/\tau_N)}. \tag{43}$$

We note that both the effective relaxation times and the zero-frequency susceptibilities may be written in terms of Dawson's integral. The detailed expressions are given in [16].

The complex susceptibility of a ferrofluid in a weak applied field may be written directly from equations (42), (43) and the Langevin equations (31) and (32) (taking note of equation (35)) using the shift theorem for one-sided Fourier transforms, namely

$$\Phi\{\mathrm{e}^{-\lambda t} f(t)\} = \tilde{f}(\mathrm{i}\omega + \lambda).$$

Thus

$$\chi_\parallel(\omega) = \frac{\chi_\parallel{}'(0)}{1 + \mathrm{i}\omega T_\parallel}, \qquad \sigma \geqslant 2 \tag{44}$$

with the Néel relaxation time modified to

$$T_\parallel = \frac{\tau\tau_B}{\tau + \tau_B}. \tag{45}$$

Moreover [16], provided σ is not in the range 1–5 so that the effective eigenvalue truncation of the hierarchy of recurrence relations for the statistical moments is valid,

$$\chi_\perp(\omega) = \frac{\chi'_\perp(0)[\mathrm{i}\omega T_2 + 1 + \Delta T_\perp T_2/\tau_\perp\tau_2]}{(\mathrm{i}\omega T_2 + 1)(\mathrm{i}\omega T_1 + 1) + \Delta T_\perp T_2/\tau_\perp\tau_2}. \tag{46}$$

Thus the effective relaxation time of the dipole mode is modified to

$$T_\perp = \frac{\tau_\perp\tau_B}{\tau_\perp + \tau_B} \tag{47}$$

and that of the quadrupole mode becomes

$$T_2 = \frac{\tau_2 \tau_B}{\tau_2 + \tau_B}. \tag{48}$$

In a weak measuring field the particle anisotropy axes are oriented in a random fashion. Hence [1, 19] the susceptibility (averaged over particle orientations) is given by

$$\chi = \tfrac{1}{3}(\chi_\parallel + 2\chi_\perp). \tag{49}$$

Now [20] in ferrofluids where the Néel mechanism is blocked, $\sigma \gtrsim 8$, and so we will have in equation (45) $\tau \gg \tau_B$; thus

$$T_\parallel \cong \tau_B. \tag{50}$$

Furthermore, in equations (47) and (48) we may use the fact [16] that $\tau_\perp$ and τ_2 are *monotonic decreasing functions* of σ, and also that usually [19], for the ratio of the free diffusion times,

$$\frac{\tau_N}{\tau_B} \sim 10^{-2},$$

in order to ascertain which times may be neglected in equation (46). Thus we deduce that in equation (46) for all σ

$$T_\perp \cong \tau_\perp \tag{51}$$

$$T_2 \cong \tau_2. \tag{52}$$

Hence we may conclude, recalling the exact [18] transverse relaxation solution for $\chi_\perp$ from the Fokker–Planck equation, that the *solid-state effective eigenvalue solution embodied in equation (37) can also accurately describe the ferromagnetic resonance in ferrofluids* except in the range of σ from 1 to 5. Then the exact solid-state solution based on matrix continued fractions must be used. The conclusion appears to be in agreement with that of Fannin [21] and Fannin *et al* [22] who have extensively analysed experimental data on ferrofluids using equation (37). By way of illustration, a detailed comparison with experimental data for four colloidal suspensions is given in section 6. We also remark that the very-large-σ (high barrier) limit of equation (46) (the Landau–Lifshitz limit) agrees with the result of Scaife [20] who analysed the problem using an entirely different method. In the limit of high damping where $\alpha \gg 1$, equation (46) reduces to a pure relaxation equation in complete agreement with Shliomis and Stepanov [1], namely their equations (31) and (32).

Having explained how the FMR effect in ferrofluids consisting of uniaxial particles, subjected to a weak external field, may be accurately described by the solid-state response (that is, the factor $\exp(-t/\tau_B)$ arising from the mechanical motion may be discounted in the transverse response), we shall now very briefly describe inertial effects arising from the term $I\dot{\omega}_n$ in equation (32). Furthermore, we shall justify the neglect of this term as far as ferrofluid relaxation is concerned.

If inertial effects are included, the correlation functions pertaining to longitudinal and transverse motions will still be the product of the correlation functions of the free Brownian motion of a sphere [23] and the solid-state correlation functions $\langle \cos\vartheta(0) \cos\vartheta(t)\rangle_0$, etc; however, the composite expressions will be much more complicated for an arbitrary inertial parameter a [23]. The reason is that the orientational correlation functions for the Brownian motion of a sphere may only be expressed exactly as the inverse Laplace transform of an infinite continued fraction in the frequency domain. The parameter a has however been evaluated by Raikher and Shliomis [19] for typical values of ferrofluid parameters and is of the order of 10^{-5}. Hence, one may entirely neglect inertial effects unlike [10] in polar dielectrics, where the inertial effects become progressively more important at high frequencies. We remark that our treatment will apply not only to uniaxial anisotropy but also to an *arbitrary* non-axially

symmetric potential $U(\boldsymbol{e}\cdot\boldsymbol{n},t)$ of the magnetocrystalline anisotropy. Since the potential is a function of $\boldsymbol{e}\cdot\boldsymbol{n}$ only, the autocorrelation functions of the overall process (e.g. cubic anisotropy) will be the product of the individual orientational autocorrelation functions of the freely rotating sphere and the solid-state mechanism. However, unlike the case for uniaxial anisotropy, even though the correlation functions still factorize, substantial coupling between the transverse and longitudinal modes (which now have α-dependent eigenvalues; cf equations (20), (23)) will exist. The reason is that the non-axial symmetry is now an intrinsic property of the particles. This phenomenon should be observable in measurements of the complex susceptibility of such particles.

5. The effect of the fluid carrier (ii) mode–mode coupling effects for particles with uniaxial anisotropy in a strong applied field

We commence by recalling equations (25) and (28). In the non-inertial limit equation (28) becomes

$$6\eta v\boldsymbol{\omega}_n - mH_0[\boldsymbol{e}\times\boldsymbol{h}] = \boldsymbol{\lambda}_n(t), \tag{53}$$

and on eliminating $\boldsymbol{\omega}_n$ in equation (25) with the aid of equation (53):

$$\boldsymbol{\omega}_R - mH_0[\boldsymbol{e}\times\boldsymbol{h}]\left(\frac{1}{6\mu v_m}+\frac{1}{6\eta v}\right) - \frac{K}{3\mu}(\boldsymbol{e}\cdot\boldsymbol{n})[\boldsymbol{e}\times\boldsymbol{n}] = \frac{\boldsymbol{\lambda}_R(t)}{6\mu v_m}+\frac{\boldsymbol{\lambda}_n(t)}{6\eta v}. \tag{54}$$

Equation (54) is of the same form as equation (16) describing the motion of the dipole moment with a frozen ($\eta\to\infty$) Brownian mechanism in the presence of a field $\boldsymbol{H}_0$ at an oblique angle to the easy axis. It immediately follows that the effect of the fluid on the solid-state or internal mechanism of relaxation is to alter the magnetic drag coefficient ζ_m of the solid-state process such that

$$\frac{1}{\zeta_m} = \frac{1}{6\mu v_m}+\frac{1}{6\eta v}. \tag{55}$$

The corresponding change in the dimensionless damping coefficient α of the solid-state process is

$$\alpha' = \alpha\left(1+\frac{\mu v_m}{\eta v}\right) = \alpha\left(1+\frac{\tau_N}{\tau_B}\right). \tag{56}$$

Here the ratio τ_N/τ_B represents the coupling between the magnetic and mechanical motions arising from the non-separable nature of the Langevin equations (53), (54). Thus the correction to the solid-state result imposed by the fluid is once again of the order 10^{-2}. Hence we may conclude, despite the non-separability of the equations of motion, that the Néel relaxation time of the ferrofluid particle should still be accurately represented in the IHD and VLD limits by the solid-state relaxation time formulae, equations (20)–(23). Furthermore, equation (54) should be closely approximated by the solid-state relaxation equation

$$\boldsymbol{\omega}_R - mH_0(\boldsymbol{e}\times\boldsymbol{h})\frac{1}{6\mu v_m} - \frac{K}{3\mu}(\boldsymbol{e}\cdot\boldsymbol{n})(\boldsymbol{e}\times\boldsymbol{n}) = \frac{\boldsymbol{\lambda}_R(t)}{6\mu v_m}. \tag{57}$$

Hence just as in the solid-state problem one would also expect the following effects to occur [8] in a ferrofluid for a large dc bias field superimposed on which is a small ac field:

(a) A strong dependence of τ/τ_N on α (i.e. a frictional dependence of the smallest non-vanishing eigenvalue) unlike in the weak-field case (axial symmetry), which is a signature of the coupling between the longitudinal and transverse modes.

(b) Suppression of the Néel and barrier crossing modes in favour of the fast relaxation modes in the deep well of the bistable potential created by equation (17), if the reduced [8] bias field h_c exceeds a certain critical value. This gives rise to a high-frequency Debye-like relaxation band [4, 8].
(c) A very-high-frequency FMR peak due to excitation of the transverse modes having frequencies close to the precession frequency.

In the longitudinal response however, guided by equation (45), it will be necessary to have particles with $\tau < \tau_B$ so that the characteristic α dependence of the response is not masked by the Brownian process due to the damping imposed by the fluid.

We now return to the mechanical equation, (28), of motion of the particles, which for small damping (if the small inertial term is retained) predicts a damped oscillation of fundamental frequency [19]

$$\omega_0 = \sqrt{\frac{mH_0}{I}} \tag{58}$$

which would appear in the spectrum as a high-frequency resonant absorption, as has been verified [24, 25] in the theory of dielectric relaxation. In ferrofluids however it has been estimated [19] that fields of order of magnitude 10^7 Oe are needed for oscillatory effects, which is higher than any which may be obtained under terrestrial conditions. Hence one may rule out this resonant mode of the motion.

It remains to discuss the influence of $\boldsymbol{H}_0$ on the mechanical relaxation modes. An estimate of this may be made by recalling that equation (28) is basically the equation of motion of a rigid dipole in a strong constant external field. Moreover, if inertial effects are neglected, it has been shown in [10, 26] that the longitudinal and transverse effective relaxation times decrease monotonically with field strength from τ_B, having asymptotic behaviour

$$\tau_{\parallel} \sim \frac{\tau_B}{\xi}, \qquad \tau_{\perp} \sim \frac{2\tau_B}{\xi} \tag{59}$$

where

$$\xi = \frac{vM_sH_0}{kT} \gg 1. \tag{60}$$

Thus, the principal effect of the external field in equation (53) is to reduce the Brownian relaxation time.

Since detailed experimental data for ferrofluid susceptibilities in a strong oblique polarizing field (of intensity 10 T and higher), superimposed on which is a weak ac field, are not yet readily available, we shall in the next section confine ourselves to an illustration of how the weak-ac-field susceptibilities, equations (44), (46), (49) which incorporate the effect of the fluid carrier, compare favourably with experiment. We shall also demonstrate the effect which a weak polarizing field $\boldsymbol{H}_0$ (0–100 kA m^{-1}) has on the susceptibility profiles (figures 1–3) below. Furthermore, we shall show how to determine the average value of the internal field of a particle, the anisotropy constant and the gyromagnetic ratio.

6. Comparison with experimental observations of the complex susceptibility data

In order to support our theoretical discussions, we now present room temperature, complex susceptibility ($\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$) data, for four colloidal suspensions, samples 1–4. In all of the samples the surfactant is oleic acid.

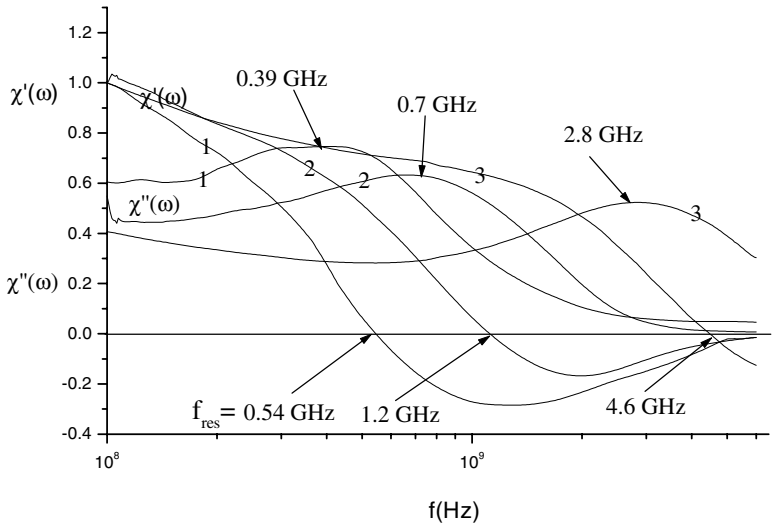

Figure 1. Normalized plots of $\chi'(\omega)$ and $\chi''(\omega)$ against f (Hz) for samples 1, 2 and 3 over the frequency range 100 MHz–6 GHz.

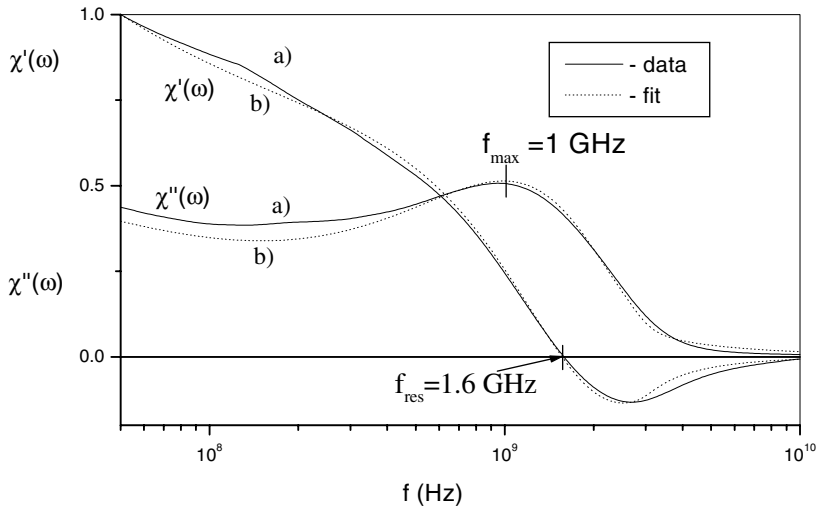

Figure 2. (a) Normalized plots of $\chi'(\omega)$ and $\chi''(\omega)$ and (b) the corresponding fits using equations (44), (46), (49), for sample 4.

The samples are as follows:

- Sample 1 is a 150 G (0.015 T) fluid consisting of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles suspended in a low-vapour-pressure hydrocarbon (Isopar M). The particles have a median diameter of 9 nm and a bulk saturation magnetization of 0.15 T.
- Sample 2 is a 300 G (0.03 T) fluid consisting of $Mn_{0.66}Zn_{0.34}Fe_2O_4$ particles suspended in Isopar M. The particles have a median diameter of 9 nm and a bulk saturation magnetization of 0.31 T.
- Sample 3 is a 400 G (0.04 T) fluid consisting of cobalt particles suspended in a di-ester carrier. The particles have a median diameter of 7.8 nm and a bulk saturation magnetization of 1 T.

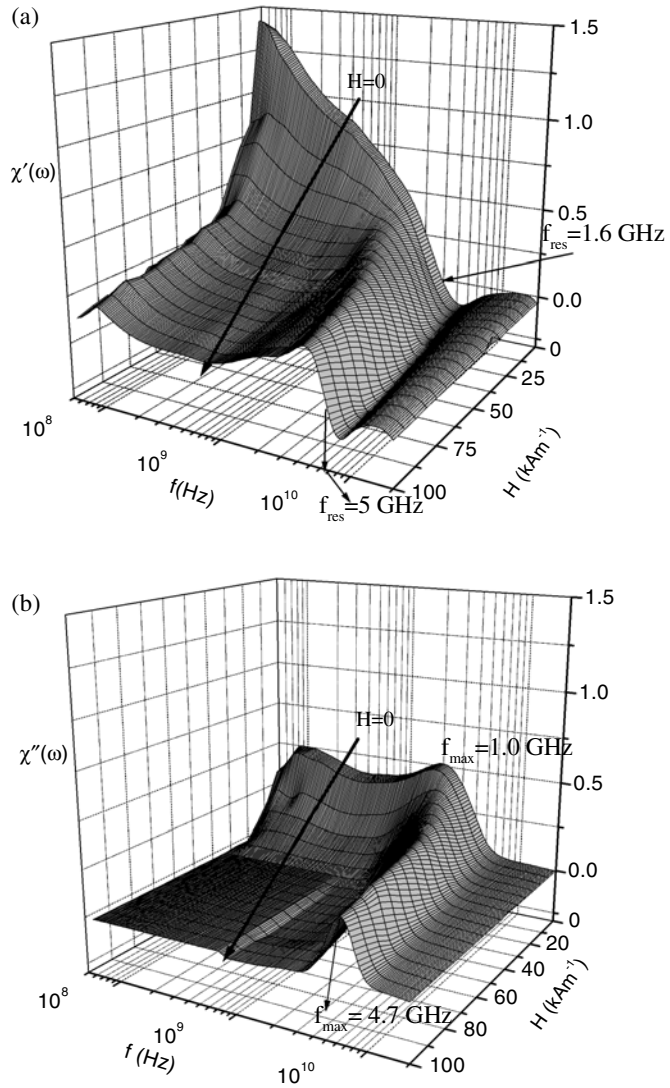

Figure 3. (*a*) A three-dimensional plot of $\chi'(\omega)$ against f (Hz) for sample 4 over the frequency range 100 MHz–15 GHz for 17 values of polarizing field, H_0, over the range 0–100 kA m^{-1}. (*b*) A three-dimensional plot of $\chi''(\omega)$ against f (Hz) for sample 4 over the frequency range 100 MHz–15 GHz for 17 values of the polarizing field, H_0, over the range 0–100 kA m^{-1}.

- Sample 4 is a 760 G (0.076 T) fluid consisting of magnetite particles suspended in Isopar M. The particles have a median diameter of 9 nm and a bulk saturation magnetization of 0.4 T.

For samples, 1–3, figure 1 shows the results obtained for the real ($\chi'(\omega)$) and imaginary ($\chi''(\omega)$) susceptibility components over the frequency range 100 MHz–6 GHz. It is apparent that a resonant-like profile, indicated by the $\chi'(\omega)$ component changing sign, at a frequency f_{res}, is characteristic for all the samples. f_{res} is seen to vary from 0.54 GHz for sample 1 to 4.4 GHz for sample 3. As $2\pi f_{res} = \gamma \bar{H}_A = \gamma 2\bar{K}/M_s$ (where $\bar{H}_A$ and $\bar{K}$ are average values of the particle internal field and anisotropy constant, respectively), this result is a signature of the

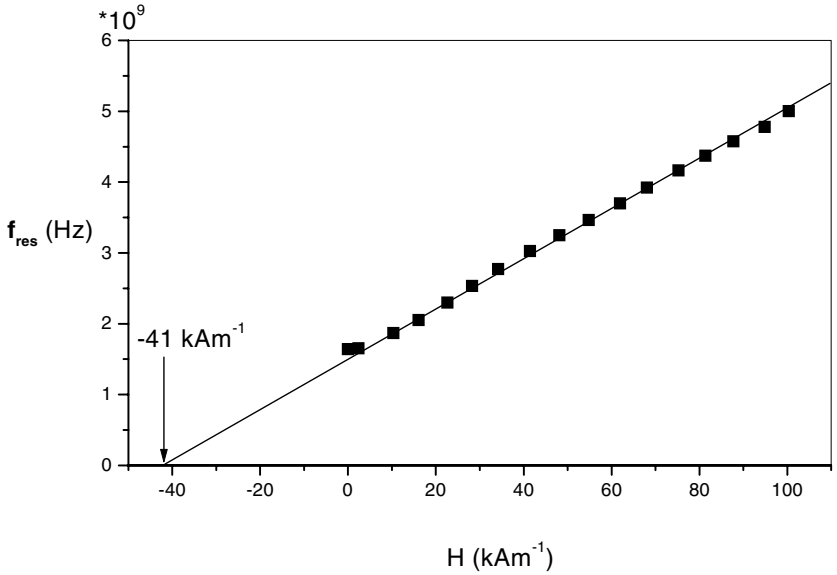

Figure 4. A plot of f_{res} against H_0 for sample 4 used in determining the average value of the internal field, $\bar{H}_A = 41$ kA m^{-1}.

difference in internal field and anisotropy constant of the particles. The susceptibility profiles have the same resonant form as was obtained for sample 4 (see figure 2), which proved to have a profile of the form predicted by equations (44), (46), (49). Furthermore, the actual values of $\bar{H}_A$ and $\bar{K}$ can be determined by means of polarized measurements as will be demonstrated now for sample 4.

Plot (a) of figure 2 shows the susceptibility components obtained for sample 4 over the wider frequency range of 50 MHz–10 GHz, whilst plot (b) shows the fit obtained using equations (44), (46), (49). As magnetic fluids have a distribution of particle shape and size, these parameters are accounted for by modifying the above equations to include a normal distribution of the anisotropy constant, $\bar{K}$, and a Nakagami distribution [21, 22] of radii, r. Here the fit was obtained for a mean $\bar{K} = 1.1 \times 10^4$ J m^{-3} with a standard deviation of 6×10^3 and a Nakagami distribution of radii, r, with a width factor $\beta = 4$, a mean particle radius $\bar{r} \approx 4.5$ nm, and a saturation magnetization of 0.4 T. The value used for α, the damping parameter, was 0.1, a figure within the range of values normally quoted [22] for α.

As far as measurements with a weak polarizing field are concerned, we remark that variation of the polarizing field, $\boldsymbol{H}_0$, over the range 0–100 kA m^{-1}, results in f_{res} increasing from 1.6 to 5.0 GHz. However, a much clearer understanding of the effect of $\boldsymbol{H}_0$ on $\chi'(\omega)$ and $\chi''(\omega)$ can be gleaned from a three-dimensional representation of the spectra as illustrated in figure 3(a) for the $\chi''(\omega)$ component and figure 3(b) for the $\chi''(\omega)$ component. Initially both components reduce with increasing $\boldsymbol{H}_0$, this effect being a manifestation of the contribution of the relaxational components to the susceptibility. Beyond approximately 400 MHz a relaxation to the resonance transition occurs with the $\chi'(\omega)$ component going through zero at the resonant frequency f_{res}.

A plot of f_{res} against $\boldsymbol{H}_0$ for the sample is shown in figure 4 and, as $\omega_{res} = 2\pi f_{res} = \gamma(H_0 + \bar{H}_A)$, the value of $\bar{H}_A$ is determined from the intercept of figure 4 and is found to be 41 kA m^{-1}, corresponding to a mean value of the anisotropy constant, $\bar{K}$, at room temperature and bulk M_s of 0.4 T, of 8.2×10^3 J m^{-3}. The gyromagnetic ratio, γ, is found

to be 2.26×10^5 S^{-1} A^{-1} m from the slope of figure 4 and is in close agreement with the theoretical value of 2.21×10^5 S^{-1} A^{-1} m.

Similar polarized studies undertaken [27,28] on samples 1–3 produced approximate $\bar{H}_A$-values of 1.6, 27 and 114 kA m^{-1}, respectively. The corresponding values of $\bar{K}$ were 120, 4×10^3 and 6×10^4 J m^{-3}.

7. Conclusions

The approach to the combined mechanical and magnetic motions of a ferrofluid particle and their mutual behaviour, which is based on rearrangement of the Langevin equations and a consideration of the various characteristic timescales, indicates how the physical effects of the fluid carrier on the magnetic relaxation may be explained without elaborate and detailed solution (which will always involve supermatrix continued fractions) of the various equations describing the system. The relative orders of magnitude of the timescales involved determine which of the existing independent internal and Brownian mode solutions may be applied to the ferrofluid particle in any given situation. These considerations hold even in the strong-field case, where the variables cannot be separated in the underlying Langevin equations. In particular, for zero or very weak external fields, we have shown that the high-frequency behaviour may be accurately modelled by the solid-state result equation (37), as the Brownian relaxation time τ_B simply cancels out of equation (46) due to the relative orders of magnitude of the various timescales. These are dictated by the ratio of the free diffusion times and the monotonic decrease of the effective relaxation times with barrier height which is a consequence of Dawson's integral. This appears to be the explanation for the success of equation (37) in explaining the experimental results of section 6 and of Fannin *et al* [22,27]. We further remark that no assumptions beyond that of the effective eigenvalue truncation of the set of differential recurrence relations have been made to obtain this result, since for zero or weak field the Langevin equations will always decouple. Furthermore, in the σ-range 1–5, where the effective eigenvalue solution is not [18] an accurate representation of the exact transverse susceptibility solution, that solution may always be found from the underlying set of differential recurrence relations by using matrix continued fractions.

The experimental data on the linear response, that is, the weak-ac-field susceptibility and the effect of a weak polarizing field, which we have presented in section 6, strongly support our conjectures concerning the application of the solid-state transverse response result equation (37) to magnetic fluids.

Finally, although the equations of motion do not separate in a strong bias field, it has been shown by considering the ratio of the free diffusion times that the relaxation behaviour is essentially similar to the Néel relaxation in an oblique field. Thus one would expect, because all the eigenvalues now depend strongly on the damping, various precession-aided relaxation and resonant effects to appear in ferrofluids just as in the solid state. The precession-aided relaxation is also of interest in connection with the stochastic resonance phenomenon [29,30]. This phenomena automatically appears in bistable potentials such as equation (17) and should be acutely sensitive to the magnitude and direction of the bias field because of the depletion effect produced by such a field in the shallower of the two wells of the potential [31–34]. The stochastic resonance effect should also be acutely sensitive to the weak ac field if the bias field is near to the critical value at which the switch of the greatest relaxation time from Arrhenius to non-Arrhenius-like behaviour takes place.

We finally remark that a detailed review of matrix continued fraction methods for the solution of differential recurrence relations is available in [35], while a detailed account of the rotational Brownian motion of the sphere is available in [36].

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