Coupled physical and magnetodynamic rotational diffusion of a single-domain ferromagnetic nanoparticle suspended in a liquid

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A concise operator form of the Fokker-Planck equation agreeing with that proposed by Weizenecker [Phys. Med. Biol. **63**, 035004 (2018)] for the joint orientational distribution of the coupled physical and magnetodynamic rotational diffusion of a single-domain ferromagnetic nanoparticle suspended in a liquid is written from the postulated Langevin equations for the stochastic dynamics. Series expansion of its solution in a complete set yields, using the theory of angular momentum, differential-recurrence equations for statistical moments for coupled motion with uniaxial symmetry of the internal anisotropy-Zeeman energy of a nanoparticle. The numerical results via the matrix iteration method suggest that the susceptibility is adequately approximated by a *single* Lorentzian with peak frequency given by the *inverse integral relaxation time* and are discussed in relation to those of the well-known "egg model".

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I. INTRODUCTION

Appropriate modeling of the stochastic dynamics of the suspended nanoparticles is important in nanoparticle imaging and other medical applications [1,2]. In such *ferrofluids* (i.e., colloidal suspensions of single-domain ferromagnetic nanoparticles) the overall change in magnetization of the magnetic suspension following the alteration of an externally applied magnetic field stems from two *distinct* sources. These are the physical or Debye-like *Brownian rotation* of the nanoparticle (treated as a sphere) in space [3] and the rotation of the magnetization inside it, i.e., the Néel *magnetodynamic* mechanism [4], consisting of noise-assisted escape over the anisotropy-Zeeman energy barrier inside the particle, i.e., reversal of its magnetic moment. A long-standing issue in the magnetic relaxation of ferrofluids is how these two stochastic rotations may be treated in a single model comprising both relaxation processes. In modeling the phenomenon, the limiting cases of *frozen* Néel or *frozen* Debye mechanisms may *individually* be well described using either the appropriate Langevin equation or its accompanying Fokker-Planck equation (FPE). Consequently, both limits have been thoroughly examined [5,6] as far as their characteristic relaxation times and susceptibilities are concerned leading to viable approximate formulas. However, the corresponding investigations for *coupled* vector Langevin equations for *both* the Debye-like physical rotation of a magnetic nanoparticle in the noninertial limit and for the rotational magnetodynamics of its internal magnetization vector are relatively few.

From a *mathematical* point of view, the description of the dynamics of the magnetization of a suspended particle belongs to the class of problems pertaining to the dynamics of two coupled entities (particle and magnetization). However various *physical* interpretations of such pair interactions when coupled to a bath exist. The simplest models consider only interactions between two entities embedded in a bath via the deterministic (mutual) interaction potential so that the stochastic interaction of the other with the bath does not influence the former at all and vice versa. This condition is reflected in the respective Langevin equation for each entity and the accompanying FPE for the joint probability density function. Another more complicated but more intuitive model is termed the egg model, which, in addition to the deterministic interaction cited above accounts for the mutual stochastic interaction between them. For example, the internal frictional torque acting on the eggshell is now proportional to the difference between yolk and shell angular velocities counteracted as usual by the appropriate white noise torques. Thus, Shliomis and Stepanov [7,8] successfully used the egg model (a form of the itinerant oscillator model [9]) to simultaneously explain the Brownian and Néel relaxation in ferrofluids [8]. The motion of the magnetic moment corresponds to the rotation of the yolk and the hydrodynamic drag is due to the white. Using this model, they showed that for uniaxial particles (for very weak externally applied magnetic fields so that linear response theory is valid) 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

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the greatest relaxation time is the sum of the reciprocals of the Néel and Brownian relaxation times of both processes considered *independently*, and the joint probability distribution of the orientations of the magnetic moment and the particle in the fluid is the product of each individual one. Hence, the internal and Debye processes are statistically independent for linear response to the applied field. Such a decoupling of the equations of motion is also possible for a massive particle, which rotates almost independently of the internal dynamics of the magnetization. If the applied field is sufficiently strong, however, no such decoupling can take place for the egg model.

Scherer and Matuttis [10] have given yet another treatment using a generalized Lagrangian formalism, however in applying their method they again limited themselves to a frozen Néel and a frozen Brownian mechanism, respectively. The egg model [11] was later revisited in Ref. [9], showing how the ferrofluid magnetic relaxation in the noninertial or high hydrodynamical 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 [12,13], which now depends on time due to the physical rotation of the particle [7]. Hence a strong intrinsic dependence of the relaxation time on the magnetic damping was predicted. Models very similar to the egg model were used in [14,15] to simulate magnetization hysteresis curves in oscillating external fields and magnetization relaxation of suspended multicore particles, respectively. A critical analysis of the egg model and an alternative consideration of the combined Brownian and Néel relaxation dynamics of ferrofluids is available in Ref. [16].

The difference in the physical interpretation of the coupling leads to different forms of the Langevin equations and the corresponding FPEs. Thus, for the simplest model, where the interaction of the two entities is considered only via the mutual potential energy, the FPE separates into two sets of differential operators that describe the particle rotation and magnetization dynamics, respectively. The coupling manifests itself through the mutual potential energy that is present in both sets. This is not so for the egg model, where for linear response the product of operators acting on the particle and the magnetization variables is available.

It is our purpose here to examine the *coupled* physical and magnetodynamic rotational diffusion of a single domain ferromagnetic nanoparticle suspended in a liquid and give an exact numerical solution for relevant quantities such as the complex magnetic susceptibility and the relaxation time. First, we commence with coordinate systems designed so as to simplify the Euler-Langevin and Landau-Lifshitz-Gilbert equations underlying the calculations. Next, we show how a FPE can be written from these coupled Langevin equations and corresponds to that given in Ref. [17]. An alternative equation for the joint distribution function of the orientations of the anisotropy axes and magnetic moments of the particles was examined in Refs. [18,19]. We proceed by rewriting the FPE using a Fourier series expansion (in a manner long familiar for coupled spin systems in quantum mechanics) of the joint distribution function of the orientations of the magnetization and easy axis vectors as a hierarchy of linear differential-recurrence equations. These ultimately yield the statistical moments and are solved via the computationally efficient method of matrix iteration [5,6]. Hence the average

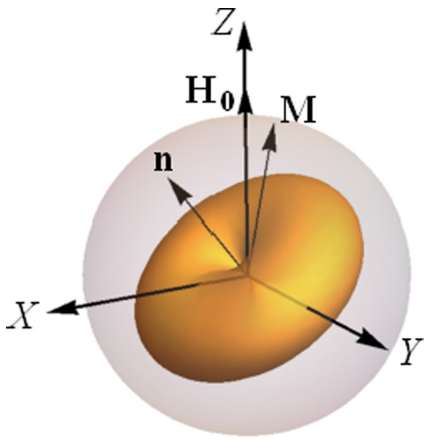


FIG. 1. Geometry of the task: spherical particle, its internal uniaxial magneto crystalline potential with easy axis $\mathbf{N} = N\mathbf{n}$ and magnetization vector $\mathbf{M}$. The external field $\mathbf{H}_0 = H\mathbf{e}_Z$ is directed along the Z axis of the laboratory coordinate system.

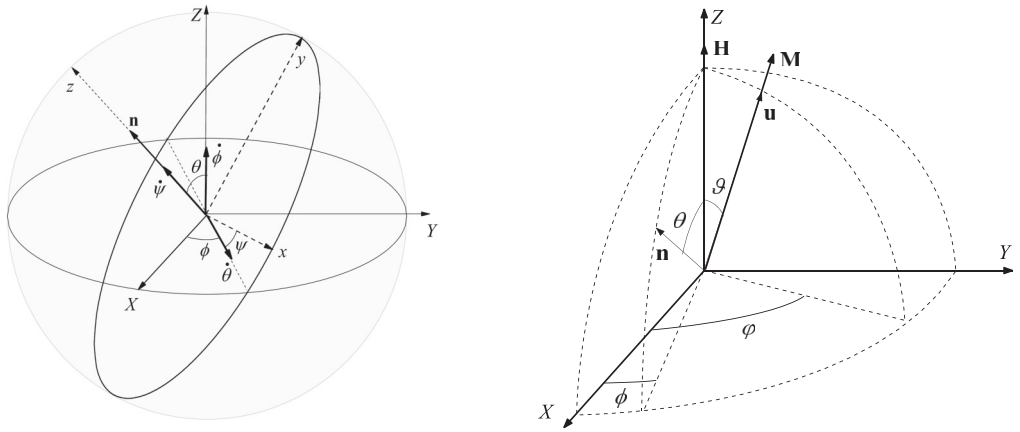
(observed) magnetization of a suspension of noninteracting ferromagnetic nanoparticles and its magnetic susceptibility can be determined. The various limiting cases (Néel, pure Brownian rotation) are discussed. The exact solution of the FPE even for the simplest possible coupling of the Debye and magnetic processes is a significant difference between this work and numerous considerations of suspensions via numerical simulations. Moreover, the method based on the use of compact matrix iterations for solving differential-recurrence relations vastly simplifies the analysis of the dynamics of magnetization of complex systems in comparison with the results of Refs. [17,18]. The calculations may also be extended in an obvious way to cover both the nonlinear ac and step responses for the model.

II. SYSTEM OF LANGEVIN EQUATIONS FOR COMBINED ROTATIONAL DIFFUSION

We consider a single domain ferromagnetic nanoparticle with a magnetization $\mathbf{M}$ suspended in a fluid carrier. Suppose that the particle possesses internal uniaxial anisotropy. The direction of the easy axis $\mathbf{n}$ of the internal magnetocrystalline anisotropy potential is *fixed* in the body of the particle, which can also *physically* rotate relative to the surrounding fluid matrix (see Fig. 1). In a spatially uniform external magnetic field $\mathbf{H}_0$, the normalized magnetic energy density E of the nanoparticle is defined by [5,6,17,18]:

$$E = -\sigma(\mathbf{u}\cdot\mathbf{n})^2 - \xi(\mathbf{u}\cdot\mathbf{e}_Z), \tag{1}$$

where $\mathbf{u}$, $\mathbf{n}$ and $\mathbf{e}_Z$ are unit vectors specifying the magnetization $\mathbf{M} = M_S\mathbf{u}$ (M_S is the saturation magnetization), easy axis $\mathbf{N} = N\mathbf{n}$, and the externally applied magnetic field $\mathbf{H}_0 = H_0\mathbf{e}_Z$ orientations (see Fig. 1), $\sigma = vK/(kT)$ and $\xi = v\mu_0 M_S H_0/(kT)$ are the dimensionless anisotropy and applied field parameters, respectively, K is the anisotropy constant, v is the volume of the particle, $\mu_0 = 4\pi \times 10^{-7}\mathrm{JA}^{-2}\mathrm{m}^{-1}$ is the permeability of free space in SI units, and kT is the thermal energy. We suppose that $\mathbf{H}_0$ is directed along the Z axis of the laboratory coordinate system and that the dynamics of the magnetization vector $\mathbf{u} = \mathbf{M}/M_S$ *inside* the particle



(a) (b)

FIG. 2. The coordinate systems used: (a) Eulerian angles; (b) polar angles.

obey the magnetic Langevin equation. This is the Landau-Lifshitz-Gilbert equation augmented by a random field term, namely [5,6],

$$\dot{\mathbf{u}} = \frac{\gamma}{1+\alpha^2}[(\mathbf{H}+\mathbf{h})\times\mathbf{u}] + \frac{\gamma\alpha}{1+\alpha^2}[\mathbf{u}\times[(\mathbf{H}+\mathbf{h})\times\mathbf{u}]], \tag{2}$$

where γ is the gyromagnetic ratio for electrons, α is the phenomenological damping parameter representing the dissipation to the surroundings and the total deterministic field $\mathbf{H}$ is defined via

$$\mathbf{H} = -\frac{kT}{v\mu_0 M_S}\frac{\partial E}{\partial \mathbf{u}}, \tag{3}$$

and $\mathbf{h}$ is a random spatially uniform isotropic Gaussian white noise magnetic field imposed by the thermal bath. The Euler-Langevin equation for the physical (Debye) rotational Brownian motion of the suspended nanoparticle regarded as a sphere is [5]

$$\frac{d}{dt}\hat{\mathbf{I}}\omega_n(t) = -\varsigma\omega_n(t) + \mathbf{K}(t) + \lambda(t). \tag{4}$$

Here $\hat{\mathbf{I}}$ is the tensor of inertia of the particle, $\boldsymbol{\omega}_n(t)$ is the angular velocity of the sphere, $\mathbf{K}(t)$ is the *deterministic* torque acting on it, $-\varsigma\boldsymbol{\omega}_n(t)$ and $\boldsymbol{\lambda}(t)$ are the hydrodynamic damping and random white noise torques imposed by the thermal bath. The random field $\mathbf{h}(t)$ and torque $\boldsymbol{\lambda}(t)$ have zero averages $\overline{\lambda_i(t)} = \overline{h_i(t)} = 0$ and correlation functions

$$\overline{h_i(t_1)h_j(t_2)} = \frac{2\alpha kT}{v\gamma\mu_0 M_S}\delta_{ij}\delta(t_1-t_2),$$
$$\overline{\lambda_i(t_1)\lambda_j(t_2)} = 2kT\varsigma\delta_{ij}\delta(t_1-t_2). \tag{5}$$

Here the overbars mean the statistical averaging, δ_{ji} is Kronecker's delta and $i, j = X, Y, Z$ represent the Cartesian axes of the laboratory coordinate system.

In the noninertial limit, i.e., where the components of the inertia tensor $\hat{\mathbf{I}}$ all vanish, Eq. (4) becomes

$$\varsigma\boldsymbol{\omega}_n(t) = \mathbf{K}(t) + \boldsymbol{\lambda}(t). \tag{6}$$

Here we suppose that for a spherical particle the friction tensor $\boldsymbol{\varsigma}$ has similar components ($\varsigma_x = \varsigma_y = \varsigma_z = \varsigma$) in principal body axes. Expressions for the deterministic torque $\mathbf{K}(t)$ in Eq. (6) differ from author to author, e.g., in Ref. [17] the following expression for $\mathbf{K}(t)$ has been used:

$$\mathbf{K} = kT\left[\frac{\partial E}{\partial \mathbf{n}}\times\mathbf{n}\right], \tag{7}$$

while yet another expression was employed in Ref. [18], namely,

$$\mathbf{K} = kT\left(\left[\frac{\partial E}{\partial \mathbf{n}}\times\mathbf{n}\right] + \left[\frac{\partial E}{\partial \mathbf{u}}\times\mathbf{u}\right]\right). \tag{8}$$

Following the simplest model of interaction, we use $\mathbf{K}$ in the form of Eq. (7). Next, observe that the *physical rotation* of a particle about the easy axis of magnetization $\mathbf{n}$ should not affect the orientation of $\mathbf{M}$ at all. In this sense $\mathbf{M}$ behaves exactly as a compass needle, namely, *spatial,* i.e., *physical rotation of the compass frame itself cannot alter the orientation of the needle*, which may interact only with an external magnetic field. On the contrary, any physical rotation of a particle, *altering the orientation of* $\mathbf{n}$ *relative* to that of $\mathbf{M}$, will assuredly affect the orientation of $\mathbf{M}$ itself. Hence the angular velocity of rotation of the vector $\mathbf{u} = \mathbf{M}/M_S$ relative to the laboratory coordinate system *cannot be written as the sum* of its angular velocity in coordinates *fixed* in the particle and the angular velocity $\boldsymbol{\omega}_n(t)$ of rotation of the particle as a whole.

Considering the physical rotation, recall that the evolution equations for the Eulerian angles θ, ϕ, ψ [see Fig. 2(a)] are expressed in terms of the components of the angular velocity ω_x, ω_y, and ω_z presented in Cartesian axes x, y, z fixed in the nanoparticle (notation follows Landau and Lifshitz [20]), viz.

$$\dot\theta = \omega_x\cos\psi - \omega_y\sin\psi, \tag{9}$$

$$\sin\theta\dot\phi = \omega_x\sin\psi + \omega_y\cos\psi, \tag{10}$$

$$\dot\psi = \omega_z - \omega_x\sin\psi\cot\theta - \omega_y\cos\psi\cot\theta. \tag{11}$$

Equation (11) is superfluous and can be omitted because altering ψ does not affect the orientation of $\mathbf{u}$. Hence, with $\mathbf{n}(t) = \{1, 0, 0\}$ and $\dot{\mathbf{n}}(t) = \{0, \dot{\theta}, \sin\theta\dot{\phi}\}$ in the spherical coordinate system shown in Fig. 2, both Eqs. (9) and (10) represent a Langevin equation for the *physical rotation* of the easy axis vector $\mathbf{n}(t)$ itself

$$\dot{\mathbf{n}}(t) = [\boldsymbol{\omega}_n(t) \times \mathbf{n}(t)] = \frac{1}{\varsigma}\left[\left(kT\left[\frac{\partial E}{\partial \mathbf{n}} \times \mathbf{n}(t)\right] + \boldsymbol{\lambda}(t)\right) \times \mathbf{n}(t)\right]. \quad (12)$$

Thus, in the noninertial limit the rotation in space of the magnetic nanoparticle reduces to the rotation of its easy axis. Since the gradient operator on the unit sphere is defined as [21]

$$\frac{\partial E}{\partial \mathbf{n}} = \left(0, \frac{\partial E}{\partial \theta}, \frac{1}{\sin\theta}\frac{\partial E}{\partial \phi}\right), \quad (13)$$

we have Eq. (12) rendered as

$$\dot{\theta} = -\frac{1}{2\tau_{\mathrm{B}}}\frac{\partial E}{\partial \theta} + \frac{\Gamma_\phi}{\sqrt{2\tau_{\mathrm{B}}}}, \quad (14)$$

$$\dot{\phi} = -\frac{1}{2\tau_{\mathrm{B}}\sin^2\theta}\frac{\partial E}{\partial \phi} - \frac{\Gamma_\theta}{\sqrt{2\tau_{\mathrm{B}}}\sin\theta}. \quad (15)$$

Hence, the coupling to the magnetic system is manifested solely through E. Here $\Gamma_i = \lambda_i/\sqrt{kT\varsigma}$ and

$$\tau_{\mathrm{B}} = \frac{\varsigma}{2kT} \quad (16)$$

is the free diffusion (Debye) time of the Brownian rotation of the easy axis $\mathbf{n}$.

Likewise, the same is true for the magnetic Langevin Eq. (2) specifying the evolution of $\mathbf{M}$ inside the particle. Noticing that

$$\frac{\partial E}{\partial \mathbf{u}} = \left(0, \frac{\partial E}{\partial \vartheta}, \frac{1}{\sin\vartheta}\frac{\partial E}{\partial \varphi}\right), \quad (17)$$

we may also rewrite the magnetic Eq. (2) as [5,6]

$$2\tau_{\mathrm{N}}\dot{\vartheta} = -\frac{1}{\alpha\sin\vartheta}\frac{\partial E}{\partial \varphi} - \frac{\partial E}{\partial \vartheta} + \frac{2\tau_{\mathrm{N}}\gamma}{1+\alpha^2}h_\varphi + \frac{2\tau_{\mathrm{N}}\gamma}{\alpha^{-1}+\alpha}h_\vartheta, \quad (18)$$

$$2\tau_{\mathrm{N}}\sin\vartheta\dot{\varphi} = \frac{1}{\alpha}\frac{\partial E}{\partial \vartheta} - \frac{1}{\sin\vartheta}\frac{\partial E}{\partial \varphi} - \frac{2\tau_{\mathrm{N}}\gamma}{1+\alpha^2}h_\vartheta + \frac{2\tau_{\mathrm{N}}\gamma}{\alpha^{-1}+\alpha}h_\varphi. \quad (19)$$

Thus, the coupling to the physical system is again achieved solely through E. Here

$$\tau_{\mathrm{N}} = \frac{v\mu_0 M_S}{2kT\gamma}(\alpha^{-1}+\alpha) \quad (20)$$

is the free diffusion relaxation time. The system of coupled Langevin Eqs. (14), (15), (18), and (19) was proposed in [17] along with a very lengthy treatment of the FPE corresponding to them, most of which may be circumvented via the theory of angular momentum as described in the next section.

III. FOKKER-PLANCK EQUATION FOR COMBINED ROTATIONAL DIFFUSION

First observe that (as far as Langevin equations are concerned) the spatial rotation of two vectors in a potential is like that of rotation of coupled spins [22] or dipoles [23]. Such problems can always be reduced to solving differential-recurrence equations for the observables, which may then be accomplished via matrix continued fraction or by matrix iteration methods. The observation that coupling occurs only via E allows one to simplify the task by *separately* considering only the Brownian (Debye) rotation of $\mathbf{n}$ in E and the Néel rotation of $\mathbf{u}$ *also* in E. Hence the FPE for the distribution function $W(\theta, \phi, \vartheta, \varphi, t)$ may be written as

$$\frac{\partial W}{\partial t} = (\mathbf{L}^n_{FP} + \mathbf{L}^u_{FP})W. \quad (21)$$

Here $\mathbf{L}^n_{FP}$ and $\mathbf{L}^u_{FP}$ are the sets of differential operators generated by physical rotation of the body fixed vector $\mathbf{n}$ [Eqs. (14) and (15)] and magnetodynamic rotation of the magnetization vector $\mathbf{u}$ [Eqs. (18) and (19)] *separately*. However, we already have (see Eq. (1.15.9) of Ref. [5])

$$\mathbf{L}^n_{FP}W = \frac{1}{2\tau_{\mathrm{B}}}\left\{\Delta_{\theta\phi}W + \frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta W\frac{\partial E}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\left(W\frac{\partial E}{\partial\phi}\right)\right]\right\} \quad (22)$$

and (see Eq. (1.17.15) of Ref. [5])

$$\mathbf{L}^u_{FP}W = \frac{1}{2\tau_{\mathrm{N}}}\left\{\Delta_{\vartheta\varphi}W + \frac{1}{\alpha\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}\left(W\frac{\partial E}{\partial\varphi}\right) - \frac{\partial}{\partial\varphi}\left(W\frac{\partial E}{\partial\vartheta}\right)\right] + \frac{v}{\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}\left(\sin\vartheta W\frac{\partial E}{\partial\vartheta}\right) + \frac{1}{\sin\vartheta}\frac{\partial}{\partial\varphi}\left(W\frac{\partial E}{\partial\varphi}\right)\right]\right\}, \quad (23)$$

where

$$\Delta_{\beta\gamma} = \frac{1}{\sin\beta}\frac{\partial}{\partial\beta}\left(\sin\beta\frac{\partial}{\partial\beta}\right) + \frac{1}{\sin^2\beta}\frac{\partial^2}{\partial\gamma^2} \quad (24)$$

is the angular part of the Laplacian. The resulting FPE (21) with $\mathbf{L}^n_{FP}$ and $\mathbf{L}^u_{FP}$ given by Eqs. (22) and (23) coincides with that of Weizenecker [17]. Next by introducing the infinitesimal rotation operators [5,18]

$$\hat{\mathbf{J}}_n = \left[\mathbf{n} \times \frac{\partial}{\partial \mathbf{n}}\right] = \nabla_{\theta\phi}, \quad \hat{\mathbf{J}}_u = \left[\mathbf{u} \times \frac{\partial}{\partial \mathbf{u}}\right] = \nabla_{\vartheta\varphi} \quad (25)$$

and

$$\hat{\mathbf{J}}^2_n = \Delta_{\theta\phi}, \quad \hat{\mathbf{J}}^2_u = \Delta_{\vartheta\varphi}, \quad (26)$$

we may rewrite Eq. (21) in operator form as

$$\frac{\partial W}{\partial t} = \frac{1}{2\tau_{\mathrm{B}}}\{\hat{\mathbf{J}}^2_n W + \hat{\mathbf{J}}_n \cdot (W\hat{\mathbf{J}}_n E)\} + \frac{1}{2\tau_{\mathrm{N}}}\left\{\hat{\mathbf{J}}^2_u W + \hat{\mathbf{J}}_u \cdot (W\hat{\mathbf{J}}_u E) + \frac{1}{\alpha}([\hat{\mathbf{J}}_u W \times \hat{\mathbf{J}}_u E]\cdot\mathbf{u})\right\} \quad (27)$$

facilitating transformation of the FPE into differential-recurrence relations [5,6], because only products of spherical harmonics will be involved in the alignment term. Observe that Eq. (27) differs from the analogous Eq. (42) of [18] (see also Ref. [19]) due to the last (precessional) term which has been neglected in Ref. [18] because only frequencies well below the GHz regime are considered there. Moreover, we have taken $\mathbf{K}$ as Eq. (7) instead of Eq. (8), so the operator $\hat{\mathbf{J}}_n^2$ must be replaced in the treatment of Refs. [18,19] by the operator $\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}_n^2 + \hat{\mathbf{J}}_u^2$.

Now for a frozen particle the (Debye) time of the Brownian rotation $\tau_B \to \infty$. Hence $\mathbf{n}$ is then *fixed* in space, say along axis Z of the laboratory coordinate system ($\theta, \phi = \text{const} = 0$). Thus, only the Néel, i.e., the magnetic relaxation over a barrier mechanism, remains and so

$$\frac{\partial}{\partial t} W(\vartheta, \varphi, t) = \mathbf{L}_{FP}^{u} W(\vartheta, \varphi, t) \tag{28}$$

with normalized energy [5,6]

$$E(\vartheta) = -\sigma \cos^2 \vartheta - \xi \cos \vartheta. \tag{29}$$

Vice versa, if the magnetization is frozen inside the particle, say along the easy axes ($\vartheta = \theta$, $\varphi = \phi$), the diffusion time of the Néel rotation $\tau_N \to \infty$. Hence only the physical (Debye) rotation with permanent dipole moment $\mathbf{M}$ ($|\mathbf{M}| = M_S$) subjected to an external field now remains and so

$$\frac{\partial}{\partial t} W(\theta, \phi, t) = \mathbf{L}_{FP}^{n} W(\theta, \phi, t) \tag{30}$$

with the energy of the particle E given as [5]

$$E(\theta) = -\xi \cos \theta. \tag{31}$$

Both limiting cases have been exhaustively treated [5].

Next consider the relaxation of the magnetization after switching off the external field $\mathbf{H}_0$. The normalized energy of the free (i.e., without an external field) rotation of the two coupled vectors $\mathbf{n}$ and $\mathbf{u}$ is then

$$E = -\sigma (\mathbf{u} \cdot \mathbf{n})^2, \tag{32}$$

which is now symmetrical under the interchange $\mathbf{u} \leftrightarrow \mathbf{n}$ (or $\{\vartheta, \varphi\} \leftrightarrow \{\theta, \phi\}$). Moreover, one can by considering *low frequencies only* entirely neglect the precessional term in Eq. (27). Hence both operators $\mathbf{L}_{FP}^{n}$ and $\mathbf{L}_{FP}^{u}$ are now *similar* in form, viz.

$$\mathbf{L}_{FP}^{n,u} W = \frac{1}{2\tau_{B,N}} \left\{ \hat{\mathbf{J}}_{n,u}^2 W + \hat{\mathbf{J}}_{n,u} \cdot (W \hat{\mathbf{J}}_{n,u} E) \right\}. \tag{33}$$

However, with differing characteristic times $\tau_{B,N}$. Yet another specific case is switching between *arbitrary* values of the external field $\mathbf{H}_0$ with the potential given by the general Eq. (1). Thus, the action of the operators $\mathbf{L}_{FP}^{n}$ and $\mathbf{L}_{FP}^{u}$ on E now differs. Accurate numerical determination of the overall relaxation time $\tau_r(\tau_B, \tau_N)$ comprising the combined relaxation processes is the prime object of the following section.

IV. DIFFERENTIAL RECURRENCE RELATION FOR STATISTICAL MOMENTS

The solution of the FPE (21) rests on a series expansion of the joint distribution function $W(\theta, \phi, \vartheta, \varphi, t)$ via a complete set of functions reducing that task to solving a system of ordinary differential-recurrence equations for the (observables) coefficients of the series (i.e., the statistical moments). First recall the quantum mechanical treatment of coupled spins [20], viz., if *individual uncoupled* spins I and II say, *separately* have wave functions ψ_I and ψ_{II}, the wave function of the system of two *coupled* spins may be sought as a linear combination of the products $\psi_I \psi_{II}$. Now recall that in *pure Néel* relaxation (immobile $\mathbf{n}$) the distribution function $W_N(\vartheta, \varphi, t)$ is expanded in a complete set (Fourier-Laplace series) of the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ [5,6], while in *pure Brownian* (or Debye) relaxation (immobile $\mathbf{u}$) the distribution function $W_B(\theta, \phi, t)$ is also expanded in spherical harmonics $Y_{lm}(\theta, \phi)$ [5]. Hence for *coupled* rotational diffusion the *joint* distribution function $W(\theta, \phi, \vartheta, \varphi, t)$ may be expanded as a linear combination of products of the form $Y_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\vartheta, \varphi)$ (the method of separation of the variables is used). However, the potential E from Eq. (1) in the coordinates chosen has the separable into products form, viz.,

$$\begin{aligned} E &= -\sigma (\sin\theta \sin\vartheta \cos(\phi - \varphi) + \cos\theta \cos\vartheta)^2 - \xi \cos\vartheta \\ &= -\sigma \frac{8\pi}{15} \sum_{k=-2}^{2} (-1)^k Y_{2-k}(\theta, \phi) Y_{2k}(\vartheta, \varphi) \\ &\quad - 2\xi \sqrt{\frac{\pi}{3}} Y_{10}(\vartheta, \varphi) - \frac{\sigma}{3}, \end{aligned} \tag{34}$$

which only depends on the three angles θ, ϑ and the difference of azimuths $\phi - \varphi$, suggesting that we may then expand the joint distribution $W(\theta, \vartheta, \phi - \varphi, t)$ as the *simplified* series, namely,

$$W(\theta, \vartheta, \phi - \varphi, t) = \sum_{l_1, l_2, m} f_{l_1 l_2 m}(t) Y_{l_1 - m}(\theta, \phi) Y_{l_2 m}(\vartheta, \varphi). \tag{35}$$

The expansion coefficients in Eq. (35), namely, the statistical moments,

$$\begin{aligned} f_{l_1 l_2 m}(t) = \int_{\Omega_n} \int_{\Omega_u} & Y_{l_1 m}(\theta, \phi) Y_{l_2 - m}(\vartheta, \varphi) \\ & \times W(\theta, \vartheta, \phi - \varphi, t) d\Omega_n d\Omega_u \end{aligned} \tag{36}$$

represent the moment system (i.e., ensemble averages of the functions $Y_{l_1 m}(\theta, \phi) Y_{l_2 - m}(\vartheta, \varphi)$ over W). Here $d\Omega_n = \sin\theta d\theta d\phi$ and $d\Omega_u = \sin\vartheta d\vartheta d\varphi$ are surface elements on the unit sphere for $\mathbf{n}$ and $\mathbf{u}$. Clearly the particular expansion, i.e., Eq. (35) incorporates the dependence of W on $\phi - \varphi$ because $Y_{l_1 - m}(\theta, \phi) Y_{l_2 m}(\vartheta, \varphi) \sim e^{-im(\phi - \varphi)}$. The calculation of the moments posed as Eq. (36) was used in Refs. [22,23] dealing with the interacting two spin problem. An analogous expansion was also presented in Ref. [17], however, in the much more complicated (four indices instead of three) form of products $Y_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\vartheta, \varphi)$, so that the ensuing recurrence equations have also four indexes and are much harder to solve. Our expansion (35) also differs from those of Ref. [18], where the transformation to $\hat{\mathbf{J}}_u^2$ representation was used. This procedure involves additional nonessential and

nontrivial recalculations, nevertheless finally leading to three-index differential-recurrence equations just as expansion (35) does.

We can neglect the precessional term in Eq. (27), because the condition for noninertial motion of the magnetic nanoparticle used throughout is always fulfilled at low frequencies, lying well below the GHz regime, so that the precessional term is also negligible (typical frequencies of precessional motion correspond to GHz and higher). By substituting Eq. (35) into the FPE (21) we then have the differential-recurrence equations for the $f_{l_1 l_2 m}(t)$ rendered in three recurring index $(l_1 l_2 m)$ form:

$$\tau_{\mathrm{D}}\frac{d}{dt}f_{l_1l_2m} = -\frac{1}{2}(\eta_1 l_1(l_1+1)+\eta_2 l_2(l_2+1))f_{l_1l_2m} + \xi\eta_2\left(\frac{l_2+1}{2}\sqrt{\frac{(l_2-m)(l_2+m)}{(2l_2-1)(2l_2+1)}}f_{l_1l_2-1m} - \frac{l_2}{2}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}f_{l_1l_2+1m}\right) + \sum_{\substack{l_1'=-2\\ \Delta l_1'=2}}^{2}\sum_{\substack{l_2'=-2\\ \Delta l_2'=2}}^{2}\sum_{j=-2}^{2} d^{l_1,l_2,m}_{l_1+l_1',l_2+l_2',m+j} f_{l_1+l_1'l_2+l_2'm+j}, \tag{37}$$

where we have introduced the overall characteristic free diffusion time τ_{D} defined via $\tau_{\mathrm{D}}^{-1} = \tau_{\mathrm{B}}^{-1} + \tau_{\mathrm{N}}^{-1}$, and associated ratios $\eta_1 = \tau_{\mathrm{D}}/\tau_{\mathrm{B}}$ and $\eta_2 = \tau_{\mathrm{D}}/\tau_{\mathrm{N}}$ and

$$d^{l_1,l_2,m}_{l_1+l_1',l_2+l_2',m+j} = \sigma(-1)^j\sqrt{\frac{(2l_1+2l_1'+1)(2l_2+2l_2'+1)}{(2l_1+1)(2l_2+1)}}C^{l_10}_{l_1+l_1'020}C^{l_1m}_{l_1+l_1'-m-j2j}C^{l_20}_{l_2+l_2'020}C^{l_2-m}_{l_2+l_2'm+j2-j} \times\frac{1}{6}\{\eta_1[6+l_1(l_1+1)-(l_1+l_1')(l_1+l_1'+1)]+\eta_2[6+l_2(l_2+1)-(l_2+l_2')(l_2+l_2'+1)]\}. \tag{38}$$

The coefficients in Eq. (37) are obtained via the theory of angular momentum (see Refs. [5,6,21]) following lengthy manipulations, allowing one to express them [cf. third line of Eq. (37)] in terms of the Clebsch-Gordan coefficients $C^{LM}_{lml'm'}$, Eq. (38). These coefficients are readily available (e.g., in Mathematica ®) and vastly simplify the presentation (e.g., compare Eq. (37) with the very lengthy equations of Ref. [17]).

To determine the magnetization response $M_Z(t)$ following an arbitrary steplike alteration of the external dc magnetic field from say $\mathbf{H}_{\mathrm{I}}(t)$ to $\mathbf{H}_{\mathrm{II}}(t)$ we introduce the relaxation functions $c_{l_1l_2m}(t) = f_{l_1l_2m}(t) - f^{\mathrm{II}}_{l_1l_2m}$ of the combined two (**n** and **u**) vector system with $c_{l_1l_2m}(0) = f^{\mathrm{I}}_{l_1l_2m} - f^{\mathrm{II}}_{l_1l_2m}$. Here I and II correspond to the *equilibrium* states of the suspended particles before and after alteration of the external field. Now the $c_{l_1l_2m}(t)$ must also satisfy the differential-recurrence relation (37) because the equilibrium averages $f^{\mathrm{I}}_{l_1l_2m}$ and $f^{\mathrm{II}}_{l_1l_2m}$ satisfy the homogeneous recurrence relation (37), namely

$$\frac{d}{dt}f^{\mathrm{I,II}}_{l_1l_2m}(0) = 0. \tag{39}$$

The *equilibrium* states are described by Boltzmann distributions (i.e., corresponding to the stationary solutions of the homogeneous equation $\mathbf{L}^{n,u}_{FP}W = 0$), viz.,

$$W_{\mathrm{I,II}}(\theta,\vartheta,\phi-\varphi) = Z^{-1}_{\mathrm{I,II}}\exp[\sigma(\sin\theta\sin\vartheta\cos(\phi-\varphi) + \cos\theta\cos\vartheta)^2 + \xi_{\mathrm{I,II}}\cos\vartheta], \tag{40}$$

where $Z_{\mathrm{I,II}}$ are the partition functions (normalization constants). Hence the initial $f^{\mathrm{I}}_{l_1l_2m}$ and final $f^{\mathrm{II}}_{l_1l_2m}$ values can be calculated as

$$f^{\mathrm{I,II}}_{l_1l_2m} = \int_{\Omega_n}\int_{\Omega_u} Y_{l_1m}(\theta,\phi)Y_{l_2-m}(\vartheta,\varphi) \times W_{\mathrm{I,II}}(\theta,\vartheta,\phi-\varphi)d\Omega_n d\Omega_u. \tag{41}$$

In general, the response of the magnetization $M_Z(t)$ following a steplike alteration of the field is represented via the normalized relaxation function

$$f(t) = \frac{\langle M_Z\rangle(t) - \langle M_Z\rangle_{\mathrm{II}}}{\langle M_Z\rangle_{\mathrm{I}} - \langle M_Z\rangle_{\mathrm{II}}} = \frac{c_{010}(t)}{c_{010}(0)}. \tag{42}$$

Therefore, with $c_{l_1l_2m}(t)$ as obtained from the solution of Eq. (37), we also have the *integral relaxation time* τ_{int} [5], namely the area under the decay curve $f(t)$ [5,6]

$$\tau_{\mathrm{int}} = \int_0^\infty f(t)dt. \tag{43}$$

In general, $f(t)$ characterizes *nonlinear response*. Nevertheless as a special case it contains the *linear response* to *infinitesimally* small steplike changes in the magnitude of the (arbitrarily) strong applied dc field $\mathbf{H}^{\mathrm{I}}_Z$, i.e., for $\mathbf{H}^{\mathrm{II}}_Z = \mathbf{H}^{\mathrm{I}}_Z - \boldsymbol{\kappa}$ as $\boldsymbol{\kappa}\to\mathbf{0}$, where $\boldsymbol{\kappa}$ is regarded as a small external perturbation. Hence $f(t)$ then coincides with the normalized longitudinal dipole equilibrium correlation function $C_\parallel(t)$, that is

$$\lim_{\kappa\to 0} f(t) = C_\parallel(t) = \frac{\langle M_Z(0)M_Z(t)\rangle_{\mathrm{II}} - \langle M_Z(0)\rangle^2_{\mathrm{II}}}{\langle M^2_Z(0)\rangle_{\mathrm{II}} - \langle M_Z(0)\rangle^2_{\mathrm{II}}}. \tag{44}$$

Thus according to linear response theory (see, e.g., Ref. [6]), via the one-sided Fourier transform $\tilde{C}_\parallel(i\omega)$ of $C_\parallel(t)$, we have the correlation time $\tau = \tilde{C}_\parallel(0)$, and also the

normalized dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ [5] since

$$\frac{\chi(\omega)}{\chi} = 1 - i\omega\tilde{C}_{\parallel}(i\omega). \tag{45}$$

Here χ is the static susceptibility. Furthermore, the asymptotic behavior of $\chi(\omega)$ in the extrema of very low and very high frequencies is explicitly given by [5,6]

$$\frac{\chi(\omega)}{\chi} \sim \begin{cases} 1 - i\omega\tau_{\rm int} + ..., & \omega \to 0, \\ -i\left(\omega\tau_{\parallel}^{ef}\right)^{-1} + ..., & \omega \to \infty, \end{cases} \tag{46}$$

which serves as a check on the accuracy of the numerical calculation. In Eq. (46)

$$\tau_{\rm ef} = -1/\dot{C}_{\parallel}(0) \tag{47}$$

is the *effective* relaxation time governing the initial decay of $C_{\parallel}(t)$. Here $\tau_{\rm int}$ and $\tau_{\rm ef}$ [5,6] characterize the global and the short-time behavior of $C_{\parallel}(t)$, respectively.

V. SYMBOLIC SOLUTION OF THE FPE

To determine the statistical moments $c_{l_1 l_2 m}(t)$ from Eq. (37), we first introduce the column vectors composed of them, viz.,

$$\mathbf{C}_n(t) = \begin{pmatrix} \mathbf{c}_{2n-1\,0}(t) \\ \mathbf{c}_{2n-2\,1}(t) \\ \vdots \\ \mathbf{c}_{0\,2n-1}(t) \\ \mathbf{c}_{2n\,0}(t) \\ \mathbf{c}_{2n-1\,1}(t) \\ \vdots \\ \mathbf{c}_{0\,2n}(t) \end{pmatrix}, \quad \mathbf{c}_{nn'}(t) = \begin{pmatrix} c_{nn'-r}(t) \\ c_{nn'-r+1}(t) \\ \vdots \\ c_{nn'\,r}(t) \end{pmatrix}, \tag{48}$$

($r = \min[n, n']$). Thus Eq. (37) obviously becomes the five-term vector recurrence relation, viz.,

$$\tau_{\rm D}\frac{d}{dt}\mathbf{C}_n(t) = \mathbf{Q}_n^{--}\mathbf{C}_{n-2}(t) + \mathbf{Q}_n^{-}\mathbf{C}_{n-1}(t) + \mathbf{Q}_n\mathbf{C}_n(t) + \mathbf{Q}_n^{+}\mathbf{C}_{n+1}(t) + \mathbf{Q}_n^{++}\mathbf{C}_{n+2}(t), \tag{49}$$

with $\mathbf{C}_0(t) = 0$. The supermatrix coefficients $\mathbf{Q}_n$, $\mathbf{Q}_n^{\pm}$, $\mathbf{Q}_n^{\pm\pm}$ are explicitly given in the Appendix. Equation (49), then yields via the matrix iterative method described in Ref. [6] the formal solution for the Laplace transform $\tilde{\mathbf{C}}_1(s)$, namely

$$\tilde{\mathbf{C}}_1(s) = \int_0^{\infty} \mathbf{C}_1(t)e^{-st}dt = \tau_{\rm D}\mathbf{R}_1. \tag{50}$$

In this equation the vector $\mathbf{R}_n$ is defined as

$$\mathbf{R}_n = [s\tau_{\rm D}\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^{++}\mathbf{T}_{n+2} - (\mathbf{Q}_n^{+} + \mathbf{Q}_n^{++}\mathbf{S}_{n+2})\mathbf{S}_{n+1}]^{-1} \times [\mathbf{C}_n(0) + (\mathbf{Q}_n^{+} + \mathbf{Q}_n^{++}\mathbf{S}_{n+2})\mathbf{R}_{n+1} + \mathbf{Q}_n^{++}\mathbf{R}_{n+2}] \tag{51}$$

and the matrices $\mathbf{S}_n$ and $\mathbf{T}_n$ are defined [6] by the inhomogeneous algebraic recurrence equations

$$\mathbf{S}_n = [s\tau_{\rm D}\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^{++}\mathbf{T}_{n+2} - (\mathbf{Q}_n^{+} + \mathbf{Q}_n^{++}\mathbf{S}_{n+2})\mathbf{S}_{n+1}]^{-1} \times [\mathbf{Q}_n^{-} + (\mathbf{Q}_n^{+} + \mathbf{Q}_n^{++}\mathbf{S}_{n+2})\mathbf{T}_{n+1}], \tag{52}$$

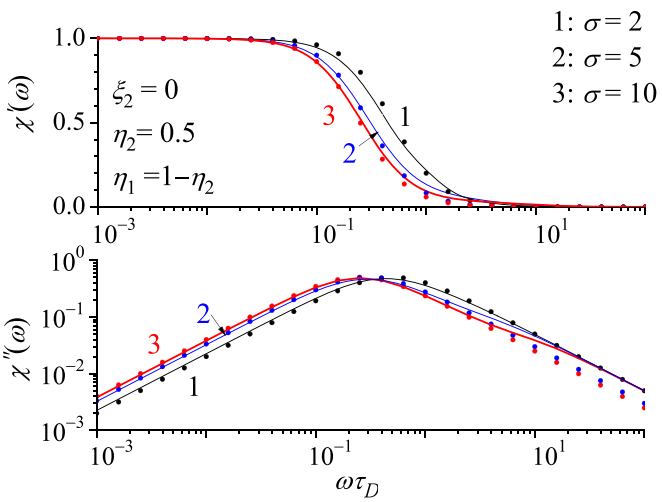


FIG. 3. Real and imaginary parts of complex susceptibility $\chi(\omega)$ vs $\omega\tau_D$ for $\xi_2 = 0$, $\xi_1 = \xi_2 + 0.0001$ (linear response), $\eta_1 = \eta_2 = 0.5$ and various barrier heights σ. Solid lines: exact numerical solution from Eqs. (42), (44), and (45). Circles: approximate Eq. (54).

$$\mathbf{T}_n = [s\tau_{\rm D}\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^{++}\mathbf{T}_{n+2} - (\mathbf{Q}_n^{+} + \mathbf{Q}_n^{++}\mathbf{S}_{n+2})\mathbf{S}_{n+1}]^{-1}\mathbf{Q}_n^{--}. \tag{53}$$

The initial value column vector $\mathbf{C}_n(0)$ in Eq. (51) can also be calculated via the homogeneous form of the algebraic recurrence equation [6] (see Appendix). In calculating $\tilde{\mathbf{C}}_1(s)$ via Eq. (50) the iterative procedure is implemented starting by arbitrarily selecting a number $n_{\rm max}$ large enough for convergence. For the parameters used $n_{\rm max} = 15$ is sufficient to arrive at an accuracy of not less than five significant digits in the majority of cases.

VI. RESULTS AND DISCUSSIONS

We now describe the results of the calculation of the susceptibility of the suspension. The role played by the barrier height σ (inverse temperature) in the behavior of the real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of the dynamic susceptibility $\chi(\omega)$ is illustrated in Fig. 3, while the effect of the external magnetic field on $\chi(\omega)$ is illustrated in Fig. 4. For nanoparticles fixed in space [frozen $\mathbf{n}(t)$] one would expect that two distinct peaks would appear in the spectra of the magnetic loss $\chi''(\omega)$ [5,6]. The high-frequency peak is due to the fast near-degenerate intrawell modes, while the low-frequency one is due to the slow interwell mode. However, in Figs. 3 and 4 only one peak is clearly visible. This can be attributed to reorientation of the magnetic moments of the nanoparticles after switching the field.

Regarding numerical comparison of the results of the egg model and that of Ref. [17] as treated here this is possible if a correspondence is established between the respective time scales. For example, consider the case $\tau_u = 2kT/\kappa_u = \tau_N$ and $\tau_n = 2kT/\kappa_n = \tau_B$, where κ_u and κ_n are the respective hydrodynamic drag coefficients of the egg and its yolk in the egg model [19]. Qualitatively speaking susceptibility for both models can be closely approximated by the single Lorentzian

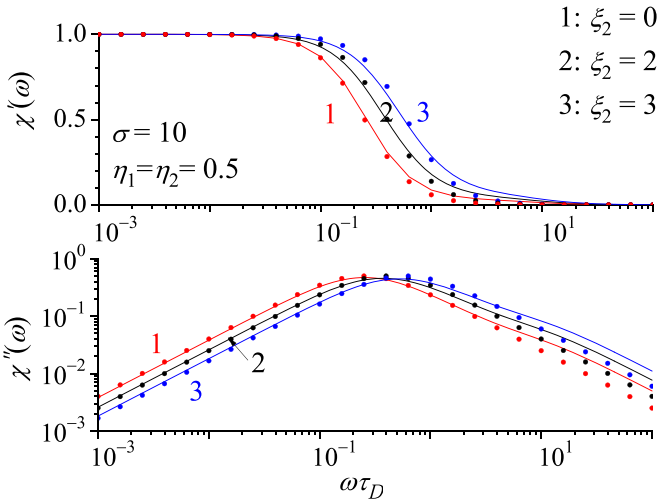


FIG. 4. Real and imaginary parts of complex susceptibility $\chi(\omega)$ vs $\omega\tau_D$ for $\sigma = 10$, $\xi_1 = \xi_2 + 0.0001$, $\eta_1 = \eta_2 = 0.5$ and various values ξ_2. Solid lines: exact numerical solution from Eqs. (42), (44), and (45). Circles: approximate Eq. (54).

(Debye-like formula) (see Figs. 3–5 and results of Ref. [18])

$$\frac{\chi(\omega)}{\chi} = \frac{1}{1 + i\omega/\omega_{\max}}. \tag{54}$$

Here $\omega_{\max}$ is the frequency of the peak of the magnetic loss $\chi''(\omega)$. However, $\omega_{\max}$ in Eq. (54) is estimated in different ways in each model. In the model of a suspended nanoparticle considered [Eqs. (14), (15), (18), and (19)], the fast intrawell modes still manifest themselves at relatively high frequencies, in so far as the single Lorentzian behavior of the susceptibility is slightly violated (see Figs. 3 and 4). However, even this behavior can be explained because in marked

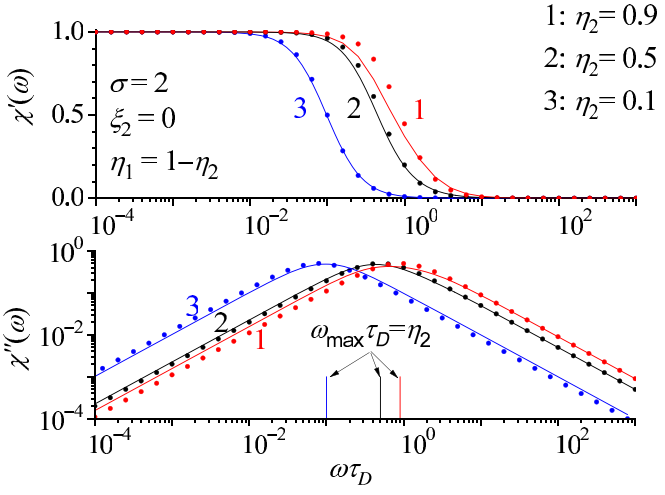


FIG. 5. Real and imaginary parts of complex susceptibility $\chi(\omega)$ vs $\omega\tau_D$ for barrier height (inverse temperature) $\sigma = 2$, $\xi_2 = 0$, $\xi_1 = \xi_2 + 0.0001$ (linear response), $\eta_1 = 1 - \eta_2$ and various values of η_2. The maxima of $\chi''(\omega)$ are determined by the Neél relaxation time, namely $\omega_{\max} \sim 1/\tau_N$, in this low barrier instance. Solid lines: exact numerical solution from Eqs. (42), (44), and (45). Circles: approximate Eq. (54).

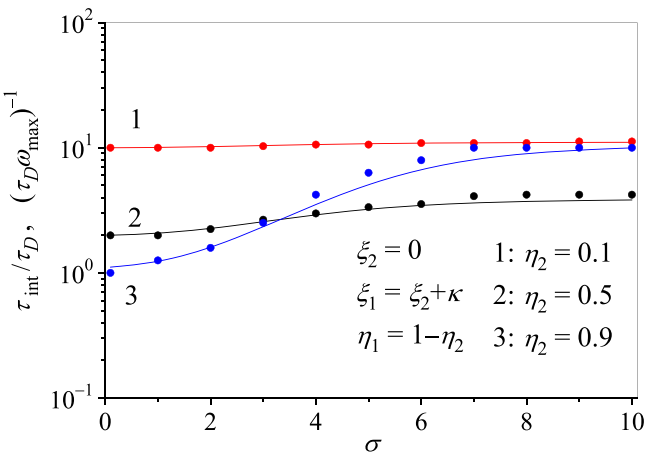


FIG. 6. Normalized integral relaxation time $\tau_{\rm int}/\tau_D$ (solid lines) and the inverse frequency of the maximum of the imaginary part of the susceptibility $(\tau_D\omega_{\max})^{-1}$ (circles) vs the anisotropy (or inverse temperature) parameter σ for $\xi_1 = \xi_2 + 0.0001$, $\xi_2 = 0$ and various values η_2 ($\eta_1 = 1 - \eta_2$). Solid lines: numerical solution from Eqs. (42), (44), and (45).

contrast to completely *fixed* nanoparticles, nanoparticles in *suspensions* can rotate relatively freely and thus have an arbitrary orientation in space. Consequently, the applied field does not directly affect the nanoparticles (only via its action on the magnetic moment, which is coupled to the particle). Moreover, in such a model, there is no coupling between the precessional motion of the magnetization and the rotation of the particle. Nevertheless, increase of the inverse temperature parameter σ leads to a decrease of $\omega_{\max}$, while in contrast increase in the external magnetic field leads to an increase of $\omega_{\max}$.

The role of the ratio of free diffusion times $\tau_B/\tau_N = \eta_2/\eta_1$ in the behavior of the dynamic susceptibility is shown in Fig. 5. Clearly for relatively low barriers ($\sigma = 2$) the position

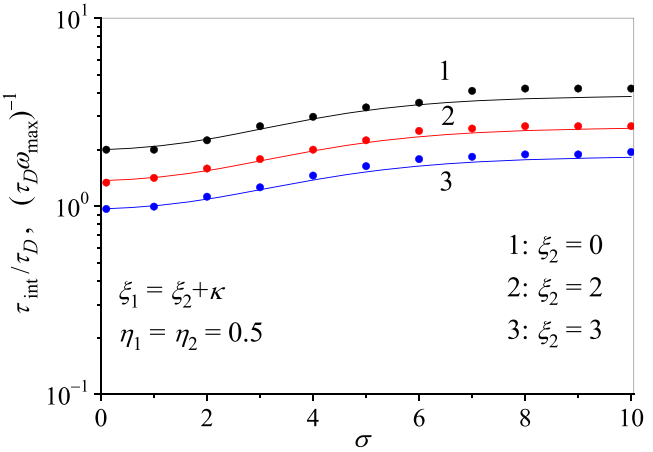


FIG. 7. Normalized integral relaxation time $\tau_{\rm int}/\tau_D$ (solid lines) and the inverse frequency of the maximum of the imaginary part of the susceptibility $(\tau_D\omega_{\max})^{-1}$ (circles) vs the anisotropy (or inverse temperature) parameter σ for $\xi_1 = \xi_2 + 0.0001$, $\eta_1 = \eta_2 = 0.5$ and various values ξ_2. Solid lines: numerical solution from Eqs. (42), (44), and (45).

of $\omega_{\max}$ is mainly determined by $\omega_{\max} \sim \tau_N^{-1}$. This approximation is violated for high barriers, where $\omega_{\max}$ deviates from the value τ_N^{-1} (see Fig. 3). Returning to the comparison of the models in the egg one $\omega_{\max} \sim \tau_{\rm D}^{-1}$ [18], while in that of Ref. [17] both $\omega_{\max}$ and the coupling of Brown and Néel rotations cannot be, in general, described by the effective relaxation time $\tau_{\rm D}^{-1} = \tau_{\rm B}^{-1} + \tau_{\rm N}^{-1}$ (see Fig. 5). This conclusion is consistent with the results of Ref. [17]. The difference with the egg model stems from the neglect of the internal stochastic torques as described in the Introduction (see also the difference in the formulas for $\mathbf{K}(t)$ [Eqs. (7) and (8)].

Figure 6 shows the *integral relaxation time* $\tau_{\rm int}$ and the inverse frequency of the maximum of the imaginary part of susceptibility $\tau = 1/\omega_{\max}$ vs the anisotropy (or inverse temperature) parameter σ. Obviously if the Brownian diffusion is fast, i.e., $\eta_2 \ll \eta_1$, the spatial reorientation of the particle itself determines the relaxation of the magnetization and the over barrier transition barely influences this process, so that the dependence of $\tau_{\rm int}$ on σ is *negligible*. In contrast if $\eta_2 > \eta_1$ we see a *significant increase* in $\tau_{\rm int}$ which increases with σ. However this dependence is not as pronounced as that for a completely fixed particle [6], because reorientations of the particle can still contribute. The integral relaxation time $\tau_{\rm int}$ is again closly approximated by the maximum of the imaginary part of susceptibility $\tau = 1/\omega_{\max}$.

Figure 7 shows the effect of the external field parameter ξ on $\tau_{\rm int}$. Obviously $\tau_{\rm int}$ decreases as the external field increases, while $\tau_{\rm int}$ and $\tau = 1/\omega_{\max}$ again almost coincide.

APPENDIX: MATRICES $\mathbf{Q}_n$ AND $\mathbf{Q}_n^{\pm}$ AND INITIAL VALUE VECTOR $\mathbf{C}_n(0)$

The various matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, $\mathbf{Q}_n^-$ in the five-term recurrence Eq. (49) have the general form (representing a generalization of a method of treating pentadiagonal recurrence relations due to Risken (see Ref. [24], p. 200))

$$\mathbf{Q}_n^- = \begin{pmatrix} \mathbf{V}_{2n-1} & \mathbf{R}_{2n-1} \\ \mathbf{0} & \mathbf{V}_{2n} \end{pmatrix}, \quad \mathbf{Q}_n = \begin{pmatrix} \mathbf{P}_{2n-1} & \mathbf{S}_{2n-1} \\ \mathbf{R}_{2n} & \mathbf{P}_{2n} \end{pmatrix}, \quad \mathbf{Q}_n^+ = \begin{pmatrix} \mathbf{U}_{2n-1} & \mathbf{0} \\ \mathbf{S}_{2n} & \mathbf{U}_{2n} \end{pmatrix}$$

$$\mathbf{Q}_n^{--} = \begin{pmatrix} \mathbf{Z}_{2n-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{Z}_{2n} \end{pmatrix}, \quad \mathbf{Q}_n^{++} = \begin{pmatrix} \mathbf{W}_{2n-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{W}_{2n} \end{pmatrix}.$$

The elements of these subsidiary matrices are themselves matrices with the following forms:

$$\mathbf{P}_n = \begin{pmatrix} \mathbf{p}_{n0} & 0 & \bar{\bar{\mathbf{p}}}_{n0} & \ddots & \mathbf{0} \\ 0 & \mathbf{p}_{n-11} & 0 & \ddots & \ddots \\ \bar{\mathbf{p}}_{n-22} & 0 & \ddots & \ddots & \bar{\bar{\mathbf{p}}}_{2n-2} \\ \ddots & \ddots & \ddots & \ddots & 0 \\ \mathbf{0} & \ddots & \bar{\mathbf{p}}_{0n} & 0 & \mathbf{p}_{0n} \end{pmatrix}, \quad \mathbf{R}_n = \begin{pmatrix} \mathbf{0} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{r}_{n-11} & \mathbf{0} & \ddots & \ddots \\ \mathbf{0} & \mathbf{r}_{n-22} & \ddots & \mathbf{0} \\ \ddots & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \mathbf{0} & \mathbf{r}_{0n} \end{pmatrix},$$

$$\mathbf{S}_n = \begin{pmatrix} \mathbf{0} & \mathbf{s}_{n0} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{s}_{n-11} & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \mathbf{0} & \mathbf{0} & \mathbf{s}_{0n} \end{pmatrix}, \quad \mathbf{V}_n = \begin{pmatrix} \mathbf{v}_{n0} & \mathbf{0} & \ddots & \mathbf{0} \\ 0 & \mathbf{v}_{n-11} & \ddots & \ddots \\ \bar{\mathbf{v}}_{n-22} & 0 & \ddots & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{v}}_{n-33} & \ddots & \mathbf{v}_{2\,n-2} \\ \ddots & \ddots & \ddots & 0 \\ \mathbf{0} & \ddots & \mathbf{0} & \bar{\mathbf{v}}_{0n} \end{pmatrix},$$

$$\mathbf{U}_n = \begin{pmatrix} \bar{\mathbf{u}}_{n0} & \mathbf{0} & \mathbf{u}_{n0} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{u}}_{n-11} & \mathbf{0} & \mathbf{u}_{n-11} & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \mathbf{0} & \bar{\mathbf{u}}_{0n} & \mathbf{0} & \mathbf{u}_{0n} \end{pmatrix}, \quad \mathbf{Z}_n = \begin{pmatrix} \ddots & \ddots & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \ddots & \ddots & \mathbf{0} \\ \mathbf{z}_{n-22} & \mathbf{0} & \ddots & \ddots \\ \mathbf{0} & \mathbf{z}_{n-33} & \ddots & \ddots \\ \ddots & \mathbf{0} & \ddots & \mathbf{0} \\ \ddots & \ddots & \ddots & \mathbf{z}_{2n-2} \\ \mathbf{0} & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \ddots & \ddots \end{pmatrix},$$

$$\mathbf{W}_n = \begin{pmatrix} \ddots & \mathbf{0} & \mathbf{w}_{n0} & \mathbf{0} & \ddots & \ddots & \mathbf{0} & \mathbf{0} \\ \ddots & \ddots & \mathbf{0} & \mathbf{w}_{n-11} & \mathbf{0} & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \mathbf{0} & \mathbf{0} & \ddots & \ddots & \mathbf{0} & \mathbf{w}_{0n} & \mathbf{0} & \ddots \end{pmatrix}.$$

Two particular matrices $\mathbf{r}_{nn'}$, $\mathbf{s}_{nn'}$ occurring above are single-diagonal ones, namely, $[\mathbf{r}_{nn'}]_{mk} = r_{nn'm}\delta_{mk}$ and $[\mathbf{s}_{nn'}]_{mk} = s_{nn'm}\delta_{mk}$. These have the following matrix elements:

$$s_{l_1 l_2 m} = -\xi\eta_2 \frac{l_2}{2}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}, \quad r_{l_1 l_2 m} = \xi\eta_2 \frac{l_2+1}{2}\sqrt{\frac{(l_2-m)(l_2+m)}{(2l_2-1)(2l_2+1)}}.$$

All the remaining matrices $\mathbf{x} = \mathbf{p}, \bar{\mathbf{p}}, \bar{\bar{\mathbf{p}}}, \mathbf{v}, \bar{\mathbf{v}}, \mathbf{u}, \bar{\mathbf{u}}, \mathbf{z}, \mathbf{w}$ are five-diagonal, namely, of the general form $[\mathbf{x}_{nn'}]_{mk} = \sum_{j=-2}^{2} x^j_{nn'm}\delta_{mk+j}$. In these the matrix elements $x^j_{nn'm}$ are of the following explicit form:

$$p^j_{l_1 l_2 m} = -\tfrac{1}{2}(\eta_1 l_1(l_1+1) + \eta_2 l_2(l_2+1))\delta_{j0} + d^{l_1 l_2 m}_{l_1 l_2 m+j}, \quad \bar{p}^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1+2\, l_2-2\, m+j}, \quad \bar{\bar{p}}^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1-2\, l_2+2\, m+j},$$
$$v^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1-2\, l_2\, m+j}, \bar{v}^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1\, l_2-2\, m+j}, \quad u^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1\, l_2+2\, m+j}, \bar{u}^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1+2\, l_2\, m+j},$$
$$z^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1-2\, l_2-2\, m+j}, \quad w^j_{l_1 l_2 m} = d^{l_1 l_2 m}_{l_1+2\, l_2+2\, m+j}.$$

Now all the matrices have the same number of rows, namely, $2\min[n, n'] + 1$, however, each one has its own particular number of columns which can be determined as $2r_x + 1$, where r_x takes on specific values as follows:

$$r_p = \min[n, n'], \quad r_{\bar{p}} = \min[n+2, n'-2], \quad r_{\bar{\bar{p}}} = \min[n-2, n'+2],$$
$$r_s = \min[n, n'+1], \quad r_r = \min[n, n'-1], \quad r_z = \min[n-2, n'-2], \quad r_w = \min[n+2, n'+2],$$
$$r_v = \min[n-2, n'], \quad r_{\bar{v}} = \min[n, n'-2], r_u = \min[n, n'+2], \quad r_{\bar{u}} = \min[n+2, n'].$$

The details of the formation of these matrices for the analogous two interacting spin problem are discussed in Refs. [22,23].

Finally, the initial value vectors $\mathbf{C}_n(0)$ are calculated as

$$\mathbf{C}_n(0) = \mathbf{F}^{\mathrm{I}}_n - \mathbf{F}^{\mathrm{II}}_n,$$

where the column vectors $\mathbf{F}^{\mathrm{I,II}}_n$ are

$$\mathbf{F}^{\mathrm{I,II}}_n = \begin{pmatrix} \mathbf{f}^{\mathrm{I,II}}_{2n-1\,0} \\ \mathbf{f}^{\mathrm{I,II}}_{2n-2\,1} \\ \vdots \\ \mathbf{f}^{\mathrm{I,II}}_{0\,2n-1} \\ \mathbf{f}^{\mathrm{I,II}}_{2n\,0} \\ \mathbf{f}^{\mathrm{I,II}}_{2n-1\,1} \\ \vdots \\ \mathbf{f}^{\mathrm{I,II}}_{0\,2n} \end{pmatrix}_{4n^2+2n+1}, \quad \mathbf{f}^{\mathrm{I,II}}_{nn'} = \begin{pmatrix} f^{\mathrm{I,II}}_{nn'-r} \\ f^{\mathrm{I,II}}_{nn'-r+1} \\ \vdots \\ f^{\mathrm{I,II}}_{nn'r} \end{pmatrix},$$

and $r = \min[n, n']$. The column vector elements $f^{\mathrm{I}}_{l_1 l_2 m}$ and $f^{\mathrm{II}}_{l_1 l_2 m}$ are determined from Eq. (41). An alternative method of calculation of the initial value vectors $\mathbf{C}_n(0)$ yielding exactly the same result is to find the vectors $\mathbf{F}^{\mathrm{I,II}}_n$ from the homogeneous matrix recursion formula (the time-independent version of Eq. (49) $\dot{\mathbf{C}}_n = 0$)]

$$\mathbf{Q}^{--}_n \mathbf{F}^{\mathrm{I,II}}_{n-2} + \mathbf{Q}^{-}_n \mathbf{F}^{\mathrm{I,II}}_{n-1} + \mathbf{Q}_n \mathbf{F}^{\mathrm{I,II}}_n + \mathbf{Q}^{+}_n \mathbf{F}^{\mathrm{I,II}}_{n+1} + \mathbf{Q}^{++}_n \mathbf{F}^{\mathrm{I,II}}_{n+1} = \mathbf{0}$$

(see the matrix iteration method of [6]). Here the dependence of the elements of the matrices $\mathbf{Q}_n$, $\mathbf{Q}^{\pm}_n$, $\mathbf{Q}^{\pm\pm}_n$ on ξ_{I} (for $\mathbf{F}^{\mathrm{I}}_n$) and ξ_{II} (for $\mathbf{F}^{\mathrm{I,II}}_n$) must be accounted for.

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