Nonlinear response of a dipolar system with rotational diffusion to a rotating field

B. U. Felderhof*
Institut für Theoretische Physik A, RWTH Aachen, Templergraben 55, 52056 Aachen, Germany
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The rotational diffusion equation for a dipole in the presence of a rotating field is solved by expansion of the orientational distribution function in terms of spherical harmonics. For the stationary solution, the distribution function rotates bodily in angular space. The magnitude of the average dipole moment and the lag angle are studied as functions of field strength and frequency. A comparison is made with the nonlinear response calculated from approximate macroscopic relaxation equations, proposed by Shliomis [Zh. Eksp. Teor. Fiz. **61**, 2611 (1972) [Sov. Phys. JETP **34**, 1291 (1972)]] and by Martsenyuk *et al.* [Zh. Eksp. Teor. Fiz. **65**, 834 (1973) [Sov. Phys. JETP **38**, 413 (1974)]]. Shliomis found that for sufficiently high field, the lag angle and the absorption are multivalued functions of frequency. This is not the case for the exact solution of the rotational diffusion equation presented here. The response of a macroscopic system of interacting dipoles is calculated in a mean-field approximation for a spherical sample.

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I. INTRODUCTION

It was found experimentally by Moskowitz and Rosensweig [1] that a rotating magnetic field acting on a ferrofluid can set the fluid into rotational motion. It was later established by Rosensweig *et al.* [2] that the motion of the fluid as a whole is dominated by surface effects, and that the sense of rotational motion depends on the curvature of the meniscus. A ferrofluid filling its container and satisfying stick boundary conditions will remain at rest, and only the magnetization will rotate, lagging the magnetic field by a certain angle.

In the following, we do not consider macroscopic motion, but rather the rotation of magnetization in a volume element in which the fluid is at rest. We study the dependence of amplitude and lag angle on field strength and frequency for a dilute suspension on the basis of the Smoluchowski equation describing the rotational diffusion of individual dipoles.

The rotation of magnetization in a rotating magnetic field was investigated by Shliomis [3,4] on the basis of a macroscopic relaxation equation for the magnetization, involving a single relaxation time [5]. He showed that the lag angle and the torque exerted on a particle are multivalued functions of frequency, if the field is sufficiently strong. We show in the following that this is not the case for the solution of the Smoluchowski equation. Both lag angle and torque are single-valued functions of frequency at any field strength. This suggests that the multivalued behavior found by Shliomis is a peculiarity of his relaxation equation. Experimental study of the behavior of the magnetization as a function of frequency would provide a critical test. We find that a second macroscopic relaxation equation, proposed by Martsenyuk *et al.* [6], approximates the behavior found from the Smoluchowski equation quite well, and does not lead to multivalued behavior.

Our solution of the Smoluchowski equation is based on the observation that in a rotating magnetic field the stationary orientational distribution function rotates bodily in angular space at the same frequency. The stationary distribution is expanded in spherical harmonics, and the equations for the coefficients are solved numerically after truncation at sufficiently high order. The expansion converges rapidly, even for strong field. Mathematically the solution is simpler than for an oscillating field [7–11], where a double expansion in Legendre polynomials and harmonics in time is required. We compare in detail with the macroscopic relaxation equation of Martsenyuk *et al.* [6]. We discuss entropy, free energy, and dissipation for both the Smoluchowski equation and the macroscopic relaxation equation.

Finally, we study the behavior of the magnetization of interacting dipoles filling a closed spherical container uniformly. With the assumption that the correlations between the dipoles can be neglected, and that the local field acting on a dipole can be approximated by the Lorentz local field, it follows that the behavior of magnetization and corresponding torque is identical to that for a dilute system. It would be of interest to study this geometry experimentally or in computer simulation also for dense suspensions, particularly in view of Shliomis' prediction of multivalued behavior. An experiment of this type was suggested earlier by Henjes [12].

All our considerations apply equally to electric and magnetic dipoles. For definiteness, we use language and notation corresponding to the magnetic case.

II. DIPOLES IN ROTATING FIELD

We consider a system of magnetic dipoles of dipole moment $\boldsymbol{\mu}=m\boldsymbol{u}$, where $\boldsymbol{u}$ is a unit vector, driven by an applied rotating magnetic field. We assume that the system has reached a stationary state in which in the volume element under consideration, the Maxwell magnetic field, and the magnetization rotate with frequency ω in the x-y plane. The x,y components of the field $\boldsymbol{H}(t)$ are given by

$$H_x(t)=H\cos\omega t, \quad H_y=H\sin\omega t. \tag{1}$$

The magnetization $\boldsymbol{M}(t)$ rotates at the same frequency, but lags behind the field. Thus, putting $\boldsymbol{M}(t)=nm\boldsymbol{F}(t)$, where n is the number density, we may write

$$F_x(t)=F\cos(\omega t-\alpha), \quad F_y=F\sin(\omega t-\alpha). \tag{2}$$

*Electronic address: ufelder@physik.rwth-aachen.de

Both the amplitude F and the lag angle α depend on the magnetic field strength H and the frequency ω. The mean torque exerted by the field on a dipole is in the z direction, and in dimensionless units has the magnitude

$$\mathcal{T}=F\xi\sin\alpha, \tag{3}$$

with dimensionless field $\xi=mH/kT_0$, where k is Boltzmann's constant and T_0 is the temperature.

We analyze the situation, in particular, for a dilute system of dipoles subject to rotational Brownian motion due to interaction with a heat bath at temperature T_0. The distribution function of orientations $f(\boldsymbol{u},t)$ is assumed to satisfy the Smoluchowski equation [13]

$$\frac{\partial f}{\partial t}=D_R\boldsymbol{L}\cdot[\boldsymbol{L}f+\beta(\boldsymbol{L}\varepsilon)f], \tag{4}$$

where D_R is the rotational diffusion coefficient, $\boldsymbol{L}$ is the rotation operator

$$\boldsymbol{L}=\boldsymbol{u}\times\frac{\partial}{\partial\boldsymbol{u}}, \tag{5}$$

and $\beta=1/kT_0$. The potential energy of a dipole with direction $\boldsymbol{u}=(\theta,\varphi)$ in the field $\boldsymbol{H}(t)$ is

$$\varepsilon(\boldsymbol{u},t)=-mH\sin\theta\cos(\varphi-\omega t). \tag{6}$$

It is natural to assume that the stationary solution of Eq. (4) has the form

$$f(\boldsymbol{u},t)=f(\theta,\phi), \tag{7}$$

with phase angle

$$\phi=\varphi-\omega t. \tag{8}$$

We find that the stationary solution $f(\theta,\phi)$ satisfies the equation in two variables,

$$\begin{aligned}-\omega\tau_R\frac{\partial f}{\partial\phi}=&\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}\\&+\xi\left[2\sin\theta\cos\phi\,f-\cos\theta\cos\phi\frac{\partial f}{\partial\theta}\right.\\&\left.+\frac{\sin\phi}{\sin\theta}\frac{\partial f}{\partial\phi}\right],\end{aligned} \tag{9}$$

with relaxation time $\tau_R=1/D_R$. By expansion in spherical harmonics [14], we can write the solution

$$f(\theta,\phi)=\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}C_{\ell m}Y_\ell^m(\theta,\phi). \tag{10}$$

The x,y components of the magnetization are then given by

$$\begin{aligned}F_x(t)&=\sqrt{\frac{8\pi}{3}}[-C'_{11}\cos\omega t-C''_{11}\sin\omega t],\\F_y(t)&=\sqrt{\frac{8\pi}{3}}[C''_{11}\cos\omega t-C'_{11}\sin\omega t],\end{aligned} \tag{11}$$

where C'_{11},C''_{11} are the real and imaginary parts of the complex coefficient C_{11}. As a consequence

$$F=\sqrt{\frac{8\pi}{3}}|C_{11}|,\quad \alpha=\arctan\frac{C''_{11}}{C'_{11}}. \tag{12}$$

Hence the mean torque is given by

$$\mathcal{T}(\xi,\omega)=-\sqrt{\frac{8\pi}{3}}\xi C''_{11}. \tag{13}$$

We solve Eq. (9) by noting that the last term on the right-hand side can be expressed as the action of a linear operator V on the distribution function $f(\theta,\phi)$ of the form

$$Vf=\xi\left[2\sin\theta\cos\phi-\cos\theta L_y+\sin\theta\sin\phi\frac{\partial}{\partial\phi}\right]f. \tag{14}$$

Using known properties of the spherical harmonics [15], we find that the action of the operator V on the spherical harmonic Y_ℓ^m is given by

$$\begin{aligned}VY_\ell^m=&\frac{1}{2}\xi[(\ell-1)v_{\ell m}Y_{\ell-1}^{m-1}-(\ell-1)w_{\ell m}Y_{\ell-1}^{m+1}+(\ell\\&+2)w_{\ell+1,m-1}Y_{\ell+1}^{m-1}-(\ell+2)v_{\ell+1,m+1}Y_{\ell+1}^{m+1}],\end{aligned} \tag{15}$$

with coefficients

$$v_{\ell m}=\sqrt{\frac{(\ell+m)(\ell+m-1)}{(2\ell+1)(2\ell-1)}},\quad w_{\ell m}=v_{\ell,-m}. \tag{16}$$

Substituting Eq. (10) into Eq. (9), we find therefore that the coefficients $\{C_{\ell m}\}$ satisfy the set of coupled equations,

$$\begin{aligned}im\omega\tau_R C_{\ell m}=&\ell(\ell+1)C_{\ell m}-\frac{1}{2}\xi[\ell v_{\ell+1,m+1}C_{\ell+1,m+1}\\&-\ell w_{\ell+1,m-1}C_{\ell+1,m-1}+(\ell+1)w_{\ell m}C_{\ell-1,m+1}\\&-(\ell+1)v_{\ell m}C_{\ell-1,m-1}].\end{aligned} \tag{17}$$

By normalization of the distribution function, the coefficient C_{00} is given by

$$C_{00}=\frac{1}{\sqrt{4\pi}}. \tag{18}$$

The remaining coefficients $C_{\ell m}$ are determined from the set of linear equations (17). The equations can be solved by truncation at sufficiently large ℓ. For given ξ and ω, one

finds that the coefficients $C_{\ell m}$ tend to zero rapidly with increasing ℓ, so that it is not difficult to achieve convergence.

III. LIMITING CASES AND MACROSCOPIC RELAXATION EQUATION

It is of interest to compare the exact solution obtained above with the approximate solutions found in the limits of low frequency and weak field. We shall also compare the exact solution for the magnetization with that obtained in the so-called effective field approximation [6,16].

In the limit of low frequency, the solution will be well approximated by a quasiequilibrium solution, corresponding to the thermal equilibrium in the instantaneous field. We call this the adiabatic approximation. The corresponding distribution function is

$$f_{ad}(\theta,\phi)=\exp[\xi\sin\theta\cos\phi]/Z(\xi), \tag{19}$$

with normalization factor

$$Z(\xi)=\frac{4\pi\sinh\xi}{\xi}. \tag{20}$$

The corresponding magnetization components are

$$F_x(t)=L(\xi)\cos\omega t, \quad F_y(t)=L(\xi)\sin\omega t, \tag{21}$$

where $L(\xi)$ is the Langevin function

$$L(\xi)=\coth\xi-\frac{1}{\xi}. \tag{22}$$

Thus for the adiabatic solution, the amplitude F takes the equilibrium value $L(\xi)$, as if the field were static, and the lag angle α vanishes.

For weak field, Eq. (9) can be solved by perturbation expansion in powers of ξ. Thus we put

$$f(\theta,\phi)=f_0+f_1+f_2+\cdots, \tag{23}$$

where the subscript denotes the order in ξ. From Eq. (9), one finds

$$f_0=\frac{1}{4\pi},$$

$$f_1(\theta,\phi)=\frac{1}{4\pi}\xi\cos\alpha_1\sin\theta\cos(\phi+\alpha_1), \tag{24}$$

with phase angle

$$\alpha_1=\arctan\left(\frac{\omega}{2D_R}\right). \tag{25}$$

The corresponding amplitude F is to first order in ξ,

$$F_w=\frac{1}{3}\xi\cos\alpha_1. \tag{26}$$

It turns out that Eq. (24) provides a good approximation at high frequency. At high frequency, the field is weak effectively, since the dipoles cannot follow the field.

In a constant field ξ, the time-independent equilibrium distribution is

$$f_{eq}(x)=\exp(\xi x)/Z(\xi). \tag{27}$$

The corresponding equilibrium magnetization is

$$F_{eq}(\xi)=L(\xi). \tag{28}$$

In the effective field approximation [6,16], it is assumed that the distribution function has the equilibrium form

$$f_e(\theta,\varphi,t)=\exp[\boldsymbol{u}\cdot\boldsymbol{\xi}_e(t)]/Z(\xi_e) \tag{29}$$

at all times with field $\boldsymbol{\xi}_e(t)$ in the direction of the magnetization $\boldsymbol{M}(t)$ with magnitude $\xi_e(t)$ given by $F=L(\xi_e)$, as in Eq. (28). The magnetization itself is assumed to follow from a macroscopic relaxation equation. The latter is derived as a moment equation of Eq. (4), on the assumption that the distribution has the form (29). We denote the approximate reduced magnetization by $\boldsymbol{F}_M(t)$ and the corresponding effective field by $\boldsymbol{\xi}_{eM}(t)$. Martsenyuk *et al.* [6] derived the macroscopic equation

$$\frac{d\boldsymbol{F}_M}{dt}=-D_R\left[2\frac{L(\xi_{eM})}{\xi_{eM}}(\boldsymbol{\xi}_{eM}-\boldsymbol{\xi})+\frac{3L(\xi_{eM})-\xi_{eM}}{\xi_{eM}^3}\boldsymbol{\xi}_{eM}\times(\boldsymbol{\xi}\times\boldsymbol{\xi}_{eM})\right]. \tag{30}$$

As we shall see, the macroscopic relaxation equation provides quite a good approximation to the actual magnetization.

By substitution of Eqs. (1) and (2), with F replaced by F_M and α replaced by α_M, into Eq. (30) one finds that the equation is satisfied provided ξ_{eM} and α_M satisfy the pair of equations

$$\xi_{eM}=\xi\cos\alpha_M,$$

$$\tan\alpha_M=\omega\tau_R\frac{L(\xi_{eM})}{\xi_{eM}-L(\xi_{eM})}. \tag{31}$$

It is easily checked that these equations are consistent with the behavior found above for low frequency and for weak field. It is of interest to compare the behavior predicted by Eq. (31) with that found from Shliomis' relaxation equation [3,4]. We denote the corresponding reduced magnetization as $\boldsymbol{F}_S(t)$. Shliomis' relaxation equation reads in present notation as

$$\frac{d\boldsymbol{F}_S}{dt}=\boldsymbol{\Omega}_{pS}\times\boldsymbol{F}_S-2D_R\left[\boldsymbol{F}_S-\frac{L(\xi)}{\xi}\boldsymbol{\xi}\right], \tag{32}$$

with angular velocity vector $\boldsymbol{\Omega}_{pS}$ given by

$$\boldsymbol{\Omega}_{pS}=D_R\boldsymbol{\mathcal{T}}_S, \tag{33}$$

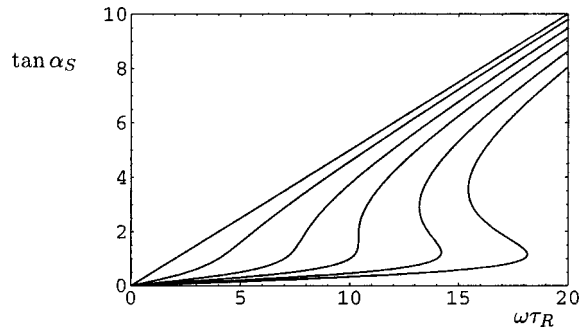

FIG. 1. Plot of $\tan\alpha_S(\xi,\omega)$, following from Shliomis' equations (34) and (35), as a function of $\omega\tau_R$ for values $\{0+,2,5,8,12,16\}$ of $P_S(\xi)$ (from left to right).

with mean torque $\boldsymbol{\mathcal{T}}_S=\boldsymbol{F}_S(t)\times\boldsymbol{\xi}(t)$ in dimensionless units. The solution is of the form (2) with amplitude F_S and lag angle α_S given by the pair of equations

$$F_S=L(\xi)\cos\alpha_S,$$

$$\tan\alpha_S=\frac{1}{2}(\omega\tau_R-\xi F_S\sin\alpha_S). \tag{34}$$

With the abbreviations $x_S=\tan\alpha_S$ and $P_S=\frac{1}{2}\xi L(\xi)$, this leads to the cubic equation

$$x_S^3-\frac{1}{2}\omega\tau_R x_S^2+(P_S+1)x_S-\frac{1}{2}\omega\tau_R=0. \tag{35}$$

In Fig. 1, we plot $\tan\alpha_S(\xi,\omega)$ as a function of $\omega\tau_R$ for the values $\{0+,2,5,8,12,16\}$ of $P_S(\xi)$. This corresponds approximately to the values $\{0+,5,11,17,25,33\}$ of the field ξ. In Fig. 2, we plot the ratio $\mathcal{T}_S(\xi,\omega)/\omega\tau_R$ as a function of $\omega\tau_R$ for the same values of $P_S(\xi)$. These functions are multivalued for $P_S(\xi)>8$. In Fig. 3, we plot $\tan\alpha(\xi,\omega)$ and $\tan\alpha_M(\xi,\omega)$ as functions of $\omega\tau_R$ for the same values of $P_S(\xi)$ as previously. In Fig. 4, we plot the ratios $\mathcal{T}(\xi,\omega)/\omega\tau_R$ and $\mathcal{T}_M(\xi,\omega)/\omega\tau_R$. It is evident from Figs. 3 and 4 that these functions are single valued. Figure 3 shows that the values of $\tan\alpha(\xi,\omega)$ are given only approximately by the macroscopic equation. It is shown in Fig. 4 that the values of the torque are reproduced much better by the approximate equation.

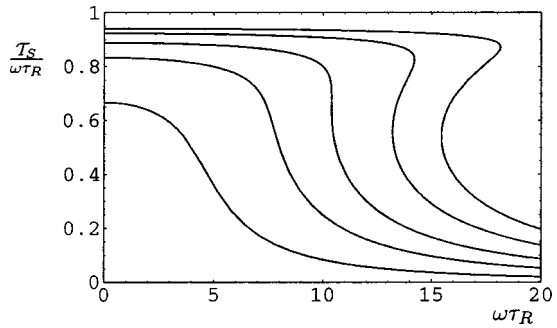

FIG. 2. Plot of the ratio $\mathcal{T}_S(\xi,\omega)/\omega\tau_R$, following from Shliomis' equations (34) and (35), as a function of $\omega\tau_R$ for values $\{2,5,8,12,16\}$ of $P_S(\xi)$ (from left to right).

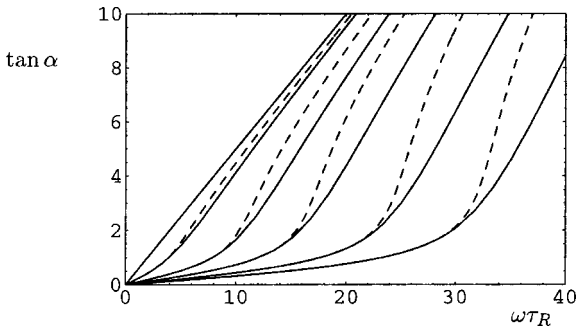

FIG. 3. Plot of the exact values of $\tan\alpha(\xi,\omega)$ (solid curves), and of $\tan\alpha_M(\xi,\omega)$, following from Eq. (31), (dashed curves), as functions of $\omega\tau_R$ for values $\{0+,2,5,8,12,16\}$ of $P_S(\xi)$ (from left to right).

It is also of interest to compare the exact distribution with the one assumed in the effective field approximation. The distibution is given by a peak in the (θ,ϕ) plane centered about $\theta=\pi/2$ and $\phi_0=-\alpha(\xi,\omega)$. In Fig. 5, we compare the function $f(\pi/2,\phi)$ with the function $f_{eM}(\pi/2,\phi)$ corresponding to the field $\xi_{eM}(\xi,\omega)$ for $\xi=20$ and $\omega=18.689\,D_R$. In Fig. 6, we compare the function $f(\theta,\phi_0)$ with the function $f_{eM}(\theta,\phi_0)$ for the same values of (ξ,ω). The plot in Fig. 5 shows that the distribution is distorted considerably in the ϕ direction compared with the distribution of the effective field approximation.

IV. FIRST HARMONIC RESPONSE, ABSORPTION, AND TORQUE

A quantity of prime interest in the nonlinear response of the magnetization is the amplitude of the first harmonic, defined by

$$P(\xi,\omega)=\xi\omega\int_0^T[F_x(t)\cos\omega t+F_y(t)\sin\omega t]dt. \tag{36}$$

From Eq. (2), we find

$$P(\xi,\omega)=2\pi\xi F\cos\alpha. \tag{37}$$

From Eq. (25) and (26) we find for weak field

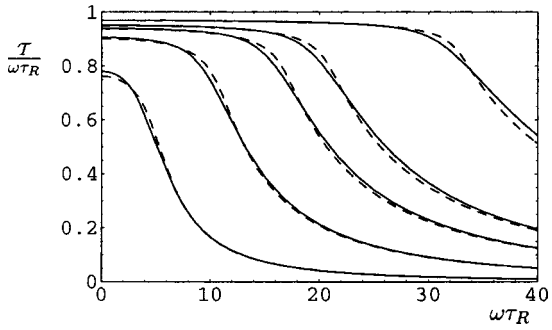

FIG. 4. Plot of the exact values of $\mathcal{T}(\xi,\omega)/\omega\tau_R$ (solid curves), and of $\mathcal{T}_M(\xi,\omega)/\omega\tau_R$, following from Eq. (31), (dashed curves), as functions of $\omega\tau_R$ for values $\{2,5,8,12,16\}$ of $P_S(\xi)$ (from left to right).

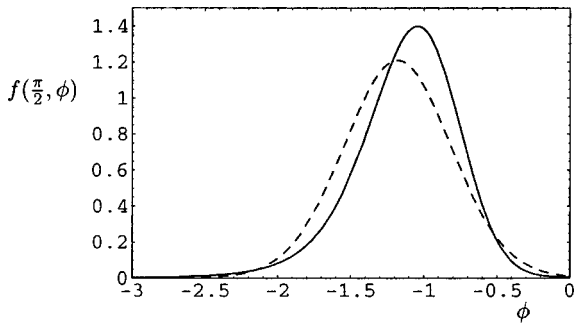

FIG. 5. Plot of the stationary distribution function $f(\pi/2,\phi)$ in the rotating frame for $\xi=20$ and $\omega=18.689D_R$ (solid curve), compared with the distribution $f_{eM}(\pi/2,\phi)$ of the effective field approximation (dashed curve).

$$P_w(\xi,\omega)=\frac{2\pi}{3}\xi^2\cos^2\alpha_1=\frac{2\pi}{3}\xi^2\frac{4}{4+\omega^2\tau_R^2}. \tag{38}$$

In the zero frequency limit, one finds from Eq. (21)

$$P(\xi,0)=2\pi\xi L(\xi). \tag{39}$$

This differs significantly from the expression for oscillating field [11]. For small ξ, the expression reduces to $P_w(\xi,0)=2\pi\xi^2/3$, twice that for an oscillating field.

A second quantity of interest is the absorption, defined as the work done by the field in a period $T=2\pi/\omega$. In dimensionless units,

$$Q(\xi,\omega)=\xi\int_0^T\left[\frac{dF_x}{dt}\cos\omega t+\frac{dF_y}{dt}\sin\omega t\right]dt. \tag{40}$$

It follows from Eq. (2) that the exact absorption is

$$Q(\xi,\omega)=2\pi\xi F\sin\alpha. \tag{41}$$

To second order in ξ, the absorption is

$$Q_w(\xi,\omega)=\frac{2\pi}{3}\xi^2\sin\alpha_1\cos\alpha_1=\frac{2\pi}{3}\xi^2\frac{2\omega\tau_R}{4+\omega^2\tau_R^2}. \tag{42}$$

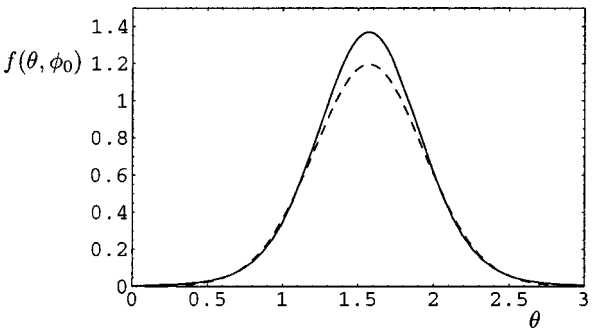

FIG. 6. Plot of the stationary distribution function $f(\theta,\phi_0)$ for $\phi_0=-\alpha(\xi,\omega)$ in the rotating frame for $\xi=20$ and $\omega=18.689D_R$ (solid curve), compared with the distribution $f_{eM}(\theta,\phi_{0M})$ for $\phi_{0M}=-\alpha_M(\xi,\omega)$ of the effective field approximation (dashed curve).

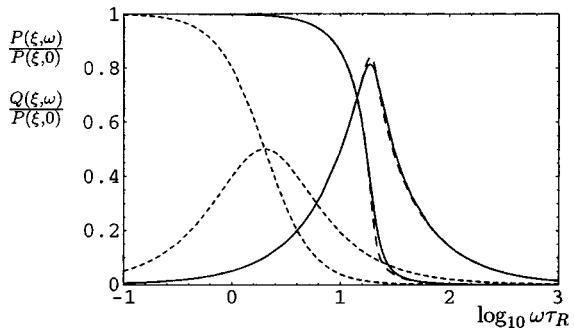

FIG. 7. Plot of the reduced functions $P(\xi,\omega)/P(\xi,0)$ and $Q(\xi,\omega)/P(\xi,0)$ as functions of $\log_{10}\omega\tau_R$ for $\xi=20$ (solid curves), compared with the quantities $P_w(\xi,\omega)/P_w(\xi,0)$ and $Q_w(\xi,\omega)/P_w(\xi,0)$ valid in the weak field limit (dotted curves), as well as with the quantities $P_M(\xi,\omega)/P(\xi,0)$ and $Q_M(\xi,\omega)/P(\xi,0)$ calculated from the effective field approximation (long dashes).

We can compare with the absorption $Q_S(\xi,\omega)$ calculated from the approximate magnetization $F_S(t)$, and similarly the absorption $Q_M(\xi,\omega)$ calculated from $F_M(t)$.

It follows from Eqs. (3) and (41) that absorption and torque are related by

$$Q=2\pi\mathcal{T}. \tag{43}$$

In other words, the work done per second equals $\omega\mathcal{T}$. Note that here the frequency ω, rather than the "angular velocity" $\Omega_p=D_R\mathcal{T}$, occurs. It has been suggested [17] in connection with Shliomis' relaxation equation to call $\Omega_p\mathcal{T}$ the coherent rate of dissipation, and the remainder $(\omega-\Omega_p)\mathcal{T}$ the incoherent rate of dissipation, but in the framework of the Smoluchowski equation there is no point in doing so.

The behavior of the quantities $P(\xi,\omega)$ and $Q(\xi,\omega)$ as functions of ω is qualitatively similar to that for oscillating field [11]. The absorption $Q_w(\xi,\omega)$ calculated from the linearized theory shows a resonance when plotted as a function of $\log_{10}\omega\tau_R$ with maximum at $\omega_{mw}=2/\tau_R$, corresponding to Debye relaxation time $\tau_D=1/2D_R$. In Fig. 7, we plot the reduced first harmonic response $P(\xi,\omega)/P(\xi,0)$ as a function of $\log_{10}\omega\tau_R$ for $\xi=20$, as well as the reduced absorption $Q(\xi,\omega)/P(\xi,0)$. We compare with the quantities $P_w(\xi,\omega)/P_w(\xi,0)$ and $Q_w(\xi,\omega)/P_w(\xi,0)$ valid in the weak field limit. The latter are related by Kramers-Kronig relations. The plot shows a significant qualitative difference for strong field. We also plot the corresponding quantities calculated from the macroscopic equation. The approximate theory performs quite well. At the maximum at $\omega_m=18.869D_R$, the exact value is $Q(20,\omega_m)=97.044$, whereas the approximate value is $Q_M(20,\omega_m)=100.221$. At high frequency both curves tend to the expression for weak field (4.7). This expression has its maximum $Q_w(20,2D_R)=418.88$ at $\omega_{mw}=2D_R$.

V. ENTROPY, FREE ENERGY, AND DISSIPATION

The entropy per particle in a state characterized by distribution $f(\boldsymbol{u},t)$ can be calculated from Boltzmann's expression

$$\mathcal{S}=-k\int f(\boldsymbol{u},t)\ln f(\boldsymbol{u},t)d\boldsymbol{u}. \tag{44}$$

The corresponding free energy per particle is

$$\mathcal{F}=\mathcal{U}-T_0\mathcal{S}, \tag{45}$$

where $\mathcal{U}$ is the mean potential energy.

In the stationary state, the distribution function rotates with constant angular velocity ω. Hence in the stationary state the free energy, the mean potential energy, and the entropy are constant. The distribution function differs from the equilibrium form, and there is a constant rate of dissipation. In the stationary state, the mean potential energy is

$$\mathcal{U}=-kT_0\xi F\cos\alpha. \tag{46}$$

By use of Eq. (37), we find the relation

$$\mathcal{U}=-\frac{kT_0}{2\pi}P(\xi,\omega). \tag{47}$$

The entropy must be calculated from Eq. (44) after substitution of Eq. (10).

The free energy is a functional $\mathcal{F}[f]$ of the distribution function. For general distribution $f(\boldsymbol{u},t)$, its rate of change is

$$\frac{d\mathcal{F}}{dt}=\int[\varepsilon(\boldsymbol{u},t)+kT_0\ln f]\frac{\partial f}{\partial t}d\boldsymbol{u}+\int\frac{\partial\varepsilon}{\partial t}f\,d\boldsymbol{u}. \tag{48}$$

Substituting Eq. (4) and performing an integration by parts, we transform this to

$$\frac{d\mathcal{F}}{dt}=-kT_0D_R\int\left[\frac{\partial}{\partial\boldsymbol{u}}(\ln f-\boldsymbol{\xi}(t)\cdot\boldsymbol{u})\right]^2 f(\boldsymbol{u},t)d\boldsymbol{u} - m\boldsymbol{F}(t)\cdot\frac{d\boldsymbol{H}}{dt}. \tag{49}$$

In the stationary state, the left-hand side vanishes, and the second term on the right is independent of time. Hence the first term on the right also does not depend on time, and we find the relation

$$\dot{\mathcal{D}}(\xi,\omega)=\frac{\omega}{2\pi}Q(\xi,\omega), \tag{50}$$

where $\dot{\mathcal{D}}(\xi,\omega)$ is the rate of dissipation given by

$$\dot{\mathcal{D}}(\xi,\omega)=D_R\int\left[\frac{\partial}{\partial\boldsymbol{u}'}(\ln f-\xi\sin\theta\cos\phi)\right]^2 f(\boldsymbol{u}')d\boldsymbol{u}', \tag{51}$$

where $\boldsymbol{u}'=(\theta,\phi)$ is the direction of the dipole in the rotating frame. Clearly the integrand is positive. Hence the rate of dissipation is positive. The relation (50) shows that the rate of dissipation is calculated conveniently from the absorption, i.e., from the work done on the system.

For a distribution of the exponential form (29), a so-called *e* distribution, the free energy becomes a functional $\mathcal{F}_e[\boldsymbol{F}]$ of the magnetization $\boldsymbol{F}$, or alternatively of the effective field $\boldsymbol{\xi}_e$ related to $\boldsymbol{F}$ by Eq. (28). By substitution of Eq. (29) into Eq. (44), one finds for the corresponding entropy

$$\mathcal{S}_e(\boldsymbol{F})=k\ln Z(\xi_e)-k\,\boldsymbol{\xi}_e\cdot\boldsymbol{F}. \tag{52}$$

Hence the free energy is

$$\beta\mathcal{F}_e(\boldsymbol{F},t)=(\boldsymbol{\xi}_e-\boldsymbol{\xi}(t))\cdot\boldsymbol{F}-\ln Z(\xi_e). \tag{53}$$

We see by use of the relation

$$\boldsymbol{F}=\frac{\partial\ln Z(\xi_e)}{\partial\boldsymbol{\xi}_e}, \tag{54}$$

equivalent to Eq. (28), that $\boldsymbol{\xi}_e$ is the thermodynamic force conjugate to $\boldsymbol{F}$,

$$\boldsymbol{\xi}_e=-\frac{1}{k}\frac{\partial\mathcal{S}_e(F)}{\partial\boldsymbol{F}}. \tag{55}$$

The entropy $\mathcal{S}_e(F)$ depends only on the magnitude F, and $\mathcal{S}_e(0)=k\ln 4\pi$. From Eqs. (52) and (53) we find

$$\boldsymbol{\xi}_e-\boldsymbol{\xi}(t)=\frac{\partial\beta\mathcal{F}_e}{\partial\boldsymbol{F}}. \tag{56}$$

If at time t the distribution has the exponential form assumed in Eq. (29), then the rate of change of the magnetization at that time is

$$\left.\frac{d\boldsymbol{F}}{dt}\right|_e=\int\boldsymbol{u}\frac{\partial f_e}{\partial t}d\boldsymbol{u}. \tag{57}$$

Substituting from Eq. (4), one finds

$$\left.\frac{d\boldsymbol{F}}{dt}\right|_e=D_R(\boldsymbol{\xi}(t)-\boldsymbol{\xi}_e)\cdot\langle\mathbf{1}-\boldsymbol{u}\boldsymbol{u}\rangle_{\xi_e}. \tag{58}$$

By use of Eq. (56), we can write

$$\left.\frac{d\boldsymbol{F}}{dt}\right|_e=-\boldsymbol{\gamma}(\boldsymbol{F})\cdot\beta\frac{\partial\mathcal{F}_e}{\partial\boldsymbol{F}} \tag{59}$$

with mobility tensor

$$\boldsymbol{\gamma}(\boldsymbol{F})=\gamma_\parallel(F)\hat{\boldsymbol{F}}\hat{\boldsymbol{F}}+\gamma_\perp(F)(\mathbf{1}-\hat{\boldsymbol{F}}\hat{\boldsymbol{F}}), \tag{60}$$

with Onsager coefficients

$$\gamma_\parallel(F)=2D_R\frac{L(\xi_e(F))}{\xi_e(F)},\qquad\gamma_\perp(F)=D_R\frac{\xi_e(F)-L(\xi_e(F))}{\xi_e(F)}. \tag{61}$$

One obtains the macroscopic relaxation equation Eq. (30) by postulating that

$$\frac{d\boldsymbol{F}_M}{dt} = -\boldsymbol{\gamma}(\boldsymbol{F}_M)\cdot\beta\frac{\partial\mathcal{F}_e}{\partial\boldsymbol{F}_M} \tag{62}$$

holds at all times. The above derivation throws new light on the macroscopic equation (30) of Martsenyuk *et al.* [6], and shows how this should be viewed in the framework of irreversible thermodynamics. The inverse expressions for $\tau_\parallel(F)=1/\gamma_\parallel(F)$ and $\tau_\perp(F)=1/\gamma_\perp(F)$ were derived by Martsenyuk *et al.* [6] in linear response theory. The mobility tensor $\boldsymbol{\gamma}(\boldsymbol{F})$ is symmetric, positive definite, and has trace

$$\gamma_\parallel(F)+2\gamma_\perp(F)=2D_R. \tag{63}$$

At vanishing magnetization, both coefficients $\gamma_\parallel(0),\gamma_\perp(0)$ equal $\frac{2}{3}D_R$. The longitudinal coefficient $\gamma_\parallel(F)$ decreases to zero with increasing magnetization. At the same time the transverse coefficient $\gamma_\perp(F)$ increases to its maximum value D_R. Thus at vanishing magnetization the mobility tensor is isotropic, and it becomes more and more anisotropic with increasing magnetization.

Multiplying Eq. (60) by $\boldsymbol{\xi}(t)-\boldsymbol{\xi}_e(t)$, we obtain by use of Eq. (56)

$$(\boldsymbol{\xi}(t)-\boldsymbol{\xi}_e(t))\cdot\frac{d\boldsymbol{F}_M}{dt}=\beta\frac{\partial\mathcal{F}_e}{\partial\boldsymbol{F}_M}\cdot\boldsymbol{\gamma}(\boldsymbol{F}_M)\cdot\beta\frac{\partial\mathcal{F}_e}{\partial\boldsymbol{F}_M}. \tag{64}$$

For the stationary process the term with $\boldsymbol{\xi}_e(t)$ on the left-hand side of this equation vanishes on account of Eq. (55), and the right-hand side is independent of time on account of Eq. (62), so that then the equation can be expressed as

$$Q_M(\xi,\omega)=\frac{2\pi}{\omega}\dot{\mathcal{D}}_M(\xi,\omega) \tag{65}$$

with the macroscopic rate of dissipation

$$\dot{\mathcal{D}}_M(\xi,\omega)=\beta\frac{\partial\mathcal{F}_e}{\partial\boldsymbol{F}_M}\cdot\boldsymbol{\gamma}(\boldsymbol{F}_M)\cdot\beta\frac{\partial\mathcal{F}_e}{\partial\boldsymbol{F}_M}. \tag{66}$$

It is evident that $\dot{\mathcal{D}}_M(\xi,\omega)$ provides a macroscopic approximation to the actual rate of dissipation $\dot{\mathcal{D}}(\xi,\omega)$, given by Eq. (51). The expression agrees with that for the rate of entropy production derived from irreversible thermodynamics and Maxwell's equations [18].

VI. INTERACTING DIPOLES IN SPHERICAL SAMPLE

Our study of the Smoluchowski equation applies to a dilute system of dipoles in which interactions can be neglected. The same calculation can be applied to a system of interacting dipoles distributed uniformly in a spherical container, provided correlations between dipoles are neglected, and the average local field acting on a dipole is approximated by the Lorentz local field. On the basis of these assumptions, we find that the single-particle distribution is given by the same expression as before.

The neglect of correlations between dipoles implies that the statistical behavior of the system is described by the single-particle distribution function. We consider a spherical sample placed in a uniform applied rotating field

$$\boldsymbol{H}_0(t)=H_0[\boldsymbol{e}_x\cos\omega t+\boldsymbol{e}_y\sin\omega t]. \tag{67}$$

The field induces a magnetization $\boldsymbol{M}(t)$ and a Maxwell field $\boldsymbol{H}(t)$, which are uniform throughout the sample. It follows from Maxwell's equations of magnetostatics that the Maxwell field inside the sphere is given by

$$\boldsymbol{H}(t)=\boldsymbol{H}_0(t)-\frac{4\pi}{3}\boldsymbol{M}(t), \tag{68}$$

where the last term is the demagnetizing field, in Gaussian units. The distribution function will rotate uniformly about the z axis. Quite generally, it can be assumed to satisfy the equation [19,20]

$$\frac{\partial f}{\partial t}=D_R\boldsymbol{L}\cdot[\boldsymbol{L}f+\beta(\boldsymbol{L}\varepsilon_{loc})f], \tag{69}$$

where $\varepsilon_{loc}(t)=-m\boldsymbol{u}\cdot\boldsymbol{H}_{loc}(t)$ is the potential energy of a dipole. By our assumption of statistical independence of dipoles, the local field $\boldsymbol{H}_{loc}(t)$ can be expressed in terms of the single-particle distribution function. We make the further assumption that the local field can be approximated by the Lorentz local field $\boldsymbol{H}_L(t)$ given by

$$\boldsymbol{H}_L(t)=\boldsymbol{H}(t)+\frac{4\pi}{3}\boldsymbol{M}(t). \tag{70}$$

Substituting Eq. (68), we see that for a spherical sample the Lorentz field $\boldsymbol{H}_L(t)$ is identical with the applied field $\boldsymbol{H}_0(t)$. Hence with this approximation for the local field, Eq. (69) reduces to Eq. (4) with H replaced by H_0, and all our earlier results apply.

The identification of the Lorentz local field with the applied field holds only for a spherical sample. In ellipsoidal or cylindrical geometry, the Maxwell field and the magnetization are again uniform, but the Lorentz local field differs from the applied field. Therefore in an applied rotating field the behavior of the magnetization will depend on the sample shape. Only for a spherical sample do we have a prediction for the magnetization. This can be used to test the validity of the theoretical assumptions in experiment or computer simulation. In computer simulation, it is not necessary to use a finite sample shape. One can employ periodic boundary conditions and mimic the sample shape by the choice of periodic Green's function [21].

VII. DISCUSSION

We have studied the nonlinear response of a dipolar system to a rotating field on the basis of Smoluchowski's rotational diffusion equation. For strong field the response differs markedly from that found by Shliomis [3] from a macroscopic relaxation equation. On the other hand, the effective field approximation of Martsenyuk *et al.* [6] leads to results qualitatively similar to those found from the Smoluchowski equation.

For the case of an applied oscillating field, we have found elsewhere [11] that the frequency-dependence of the nonlinear response violates the Kramers-Kronig relations. Though we have not demonstrated this in detail, the same is true for the response to a rotating field.

As discussed at the end of Sec. VI, it would be desirable to extend the calculation for interacting dipoles to cylindrical geometry. Also, it would be of interest to consider a superposition of two rotating fields, as studied by Gazeau *et al.* [22,23] experimentally and in linear response theory.

[1] R. Moskowitz and R.E. Rosensweig, Appl. Phys. Lett. **11**, 301 (1967).
[2] R.E. Rosensweig, J. Popplewell, and R.J. Johnston, J. Magn. Magn. Mater. **85**, 171 (1990).
[3] M.I. Shliomis, Dokl. Akad. Nauk. SSSR **218**, 1071 (1974) [Sov. Phys. Dokl. **19**, 686 (1975)].
[4] R.E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985).
[5] M.I. Shliomis, Zh. Eksp. Teor. Fiz. **61**, 2411 (1972) [Sov. Phys. JETP **34**, 1291 (1972)].
[6] M.A. Martsenyuk, Yu.L. Raikher, and M.I. Shliomis, Zh. Eksp. Teor. Fiz. **65**, 834 (1973) [Sov. Phys. JETP **38**, 413 (1974)].
[7] Y.L. Raikher, V.I. Stepanov, and S.V. Burylov, J. Colloid Interface Sci. **144**, 308 (1991).
[8] J.L. Déjardin and Yu.P. Kalmykov, Phys. Rev. E **61**, 1211 (2000).
[9] J.L. Déjardin and Yu.P. Kalmykov, J. Chem. Phys. **112**, 2916 (2000).
[10] J.L. Déjardin, Yu.P. Kalmykov, and P.M. Déjardin, Adv. Chem. Phys. **117**, 275 (2001).
[11] B.U. Felderhof and R.B. Jones, (unpublished).
[12] K. Henjes, J. Magn. Magn. Mater. **117**, L311 (1992).
[13] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1989), p. 295.
[14] A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1974).
[15] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1970), p. 187.
[16] Yu.L. Raikher and M.I. Shliomis, Adv. Chem. Phys. **87**, 595 (1994).
[17] R.E. Rosensweig, Magnitnaja Gidrodinamika **36**, 303 (2000).
[18] B.U. Felderhof and H.J. Kroh, J. Chem. Phys. **110**, 7403 (1999).
[19] B.J. Berne, J. Chem. Phys. **62**, 1154 (1975).
[20] M.P. Warchol, J. Chem. Phys. **71**, 502 (1979).
[21] B. Cichocki, B.U. Felderhof, and K. Hinsen, Phys. Rev. A **39**, 5350 (1989).
[22] F. Gazeau, B.M. Heegaard, J.-C. Bacri, A. Cebers, and R. Perzynski, Europhys. Lett. **35**, 609 (1996).
[23] F. Gazeau, C. Baravian, J.-C. Bacri, R. Perzynski, and M.I. Shliomis, Phys. Rev. E **56**, 614 (1997).