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Nonlinear response of a dipolar system with rotational diffusion to an oscillating field

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Abstract

The rotational diffusion equation for a dipole in the presence of an oscillating field is solved by expansion of the orientational distribution function in terms of Legendre polynomials and harmonics. The nonlinear response of the average dipole moment is studied as a function of field strength and frequency. Outside the linear regime the in-phase and out-of-phase response as functions of frequency do not satisfy Kramers–Kronig relations. A comparison is made with the nonlinear response calculated from approximate macroscopic relaxation equations proposed by Shliomis and by Martsenyuk *et al.* The response of a macroscopic system of interacting dipoles is calculated in the mean-field approximation for a spherical sample.

1. Introduction

The linear response of a dipolar system to an applied oscillating field was calculated by Debye [1] from a solution of the rotational diffusion equation for the orientational distribution function valid to first order in the field. In a strong oscillatory field it is necessary to calculate the nonlinear response of the system. Coffey and Paranjape [2] and Raikher and Stepanov [3] have evaluated the response up to cubic terms in the field. Morita and Watanabe [4, 5] proposed a general formal perturbation theory of the nonlinear response. Raikher *et al* [6] solved the equation for the orientational distribution function by expansion in Legendre polynomials and harmonics. In the following we use the same method. A more intricate solution in terms of matrix continued fractions was obtained recently by Déjardin and Kalmykov [7]. They suggested that their solution is more exact than the more direct solution of the linear system of equations obtained by truncation. Actually, numerical evaluation of the matrix continued fraction also involves truncation. Numerically both methods work equally well. The first method is more transparent, and both methods are equally exact. An extension of the theory to include the effect of polarizability [8] was reviewed recently by Déjardin *et al* [9].

In the following we discuss the solution of the rotational diffusion equation, and study the first-harmonic response and absorption in some detail. Raikher *et al* [6] restricted attention to the response of the order parameter and the corresponding birefringence. We compare our results with the approximate macroscopic description of Martsenyuk *et al* [10], and find that this description performs quite well.

We also compare our results with a calculation of first-harmonic response and absorption on the basis of the Shliomis macroscopic relaxation equation [11]. The earlier treatment of this problem by Rosensweig [12] involved an approximation.

For the Shliomis relaxation equation the nonlinear response is remarkably simple. The absorption resonance, as a function of frequency, is not shifted from the linear case, and is only reduced by a factor which depends on the field strength. The amplitude of oscillation is a single-valued function of frequency, unlike the response to a rotating field, where the Shliomis relaxation equation predicts a multivalued response [13, 14], typical of the response of a nonlinear oscillator [15, 16].

For the rotational diffusion equation the response is more complicated than for the Shliomis relaxation equation. With increasing field strength the absorption resonance is shifted significantly to higher frequency, and also becomes broader [7]. On the other hand, the response remains single-valued. Also, there is no transition to chaos, as is observed generically for nonlinear oscillators [16–20].

The frequency dependence of the response has a further remarkable feature. As is well known, the frequency-dependent susceptibility characterizing the linear response is a complex function of frequency, with real and imaginary parts related by Kramers–Kronig relations [21] as a consequence of causality. We find by explicit calculation that the complex function characterizing the nonlinear response does not have this feature. It is known in the context of quantum optics that Kramers–Kronig relations may be violated in nonlinear situations [22, 23].

We do not consider all complications of real ferrofluids; thus we assume that the particles have only a permanent dipole moment, and we neglect Néel relaxation. Also we assume the suspension to be monodisperse. For dilute suspensions polydispersity can be taken into account by an average of our results for the magnetization over the size distribution. The idealized model system can be studied in a computer simulation.

Finally, we show that the theory developed for the dilute system without dipolar interactions can be extended to dense systems by a proper choice of macroscopic geometry, provided that the acting local field can be approximated by the Lorentz local field. It follows from Maxwell's equations of electrostatics that for a spherical sample the latter is identical with the applied field.

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

2. Dipoles in an oscillating field

We consider a system of non-interacting dipoles performing orientational Brownian motion in the presence of an oscillating field. We shall consider magnetic dipoles of dipole moment $\boldsymbol{\mu} = m\mathbf{u}$, where \mathbf{u} is a unit vector, in the presence of the magnetic field $\mathbf{H}(t) = H_0\mathbf{e}_z \cos \omega t$ oscillating in the z -direction at frequency ω . Our considerations apply equally well to electric dipoles in an oscillating electrical field. The distribution function of orientations $f(\mathbf{u}, t)$ is assumed to satisfy the Smoluchowski equation

$$\frac{\partial f}{\partial t} = D_R \mathbf{L} \cdot [\mathbf{L}f + \beta(\mathbf{L}\boldsymbol{\varepsilon})f], \quad (2.1)$$

where D_R is the rotational diffusion coefficient, and L is the rotation operator

$$L = \mathbf{u} \times \frac{\partial}{\partial \mathbf{u}}. \tag{2.2}$$

The potential energy of a dipole in the field $\mathbf{H}(t)$ is

$$\varepsilon(\mathbf{u}, t) = -mH_0 \cos \theta \cos \omega t, \tag{2.3}$$

where $\cos \theta = \mathbf{u} \cdot \mathbf{e}_z$. The periodic solution of equation (2.1) will have the form $f(\theta, t)$, so that the equation can be simplified to

$$\frac{\partial f}{\partial t} = D_R \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} + \xi \cos \omega t \sin^2 \theta f \right) \right], \tag{2.4}$$

with the abbreviation $\xi = \beta m H_0$. In terms of the variable $x = \cos \theta$ this becomes

$$\frac{\partial f}{\partial t} = D_R \frac{\partial}{\partial x} \left[(1 - x^2) \frac{\partial f}{\partial x} - \xi \cos \omega t (1 - x^2) f \right]. \tag{2.5}$$

It is convenient to normalize to

$$\int_{-1}^1 f(x, t) dx = 1. \tag{2.6}$$

We solve equation (2.5) by expansion in Legendre polynomials and harmonics

$$f(x, t) = \frac{1}{2} + \sum_{\ell=1}^{\infty} \left[\sum_{n=0}^{\infty} A_{\ell n} \cos n\omega t + \sum_{n=1}^{\infty} B_{\ell n} \sin n\omega t \right] P_{\ell}(x). \tag{2.7}$$

Substituting the expansion into equation (2.5) we find the coupled set of equations

$$\begin{aligned} -n\omega A_{\ell n} &= D_R \left[-\ell(\ell+1)B_{\ell n} + \frac{1}{2}\xi \left(\frac{\ell(\ell+1)}{2\ell-1} (B_{\ell-1, n-1} + B_{\ell-1, n+1}) \right. \right. \\ &\quad \left. \left. - \frac{\ell(\ell+1)}{2\ell+3} (B_{\ell+1, n-1} + B_{\ell+1, n+1}) \right) \right], \\ n\omega B_{\ell n} &= D_R \left[-\ell(\ell+1)A_{\ell n} + \frac{1}{2}\xi \left(\frac{\ell(\ell+1)}{2\ell-1} ((1 + \delta_{n1})A_{\ell-1, n-1} + A_{\ell-1, n+1}) \right. \right. \\ &\quad \left. \left. - \frac{\ell(\ell+1)}{2\ell+3} ((1 + \delta_{n1})A_{\ell+1, n-1} + A_{\ell+1, n+1}) \right) \right] \end{aligned} \tag{2.8}$$

for $n \geq 1, \ell \geq 1$ with the convention

$$\begin{aligned} A_{00} &= \frac{1}{2}, & A_{0n} &= 0, \\ B_{\ell 0} &= 0, & B_{0n} &= 0. \end{aligned} \tag{2.9}$$

In addition, for $\ell \geq 1$

$$A_{\ell 0} = \frac{1}{2}\xi \left[\frac{1}{2\ell-1} A_{\ell-1, 1} - \frac{1}{2\ell+3} A_{\ell+1, 1} \right]. \tag{2.10}$$

The coefficient A_{00} occurs as an inhomogeneous term in the equation for B_{11} . For given (ξ, ω) the equations (2.8) and (2.10) can be solved by truncation at sufficiently large ℓ and n . One finds that the higher-order coefficients tend to zero rapidly. The equations have a symmetry which shows that

$$\begin{aligned} A_{\ell n} &= 0 & \text{for } \ell + n \text{ odd,} \\ B_{\ell n} &= 0 & \text{for } \ell + n \text{ odd.} \end{aligned} \tag{2.11}$$

We write the magnetization as

$$M(t) = nmF(t), \tag{2.12}$$

where n is the number density, and $F(t)$ is the moment

$$F(t) = \int_{-1}^1 x f(x, t) dx. \quad (2.13)$$

For brevity we shall call $F(t)$ the magnetization. From equation (2.7) we find

$$F(t) = \frac{2}{3} \sum_{n=1}^{\infty} [A_{1n} \cos n\omega t + B_{1n} \sin n\omega t]. \quad (2.14)$$

It follows from equation (2.11) that only harmonics with n odd contribute. A second moment of interest is the order parameter

$$S(t) = \int_{-1}^1 P_2(x) f(x, t) dx. \quad (2.15)$$

From equation (2.7) we find

$$S(t) = \frac{2}{5} \left[\sum_{n=0}^{\infty} A_{2n} \cos n\omega t + \sum_{n=1}^{\infty} B_{2n} \sin n\omega t \right]. \quad (2.16)$$

It follows from equation (2.11) that only harmonics with n even contribute.

3. Limiting cases and the macroscopic relaxation equation

It is of interest to compare the exact solution obtained above with the approximate solutions obtained in the limits of low frequency and weak field. We can also compare the exact solution for the magnetization with that obtained from the so-called effective field approximation [10, 24].

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

$$f_{ad}(x, t) = \exp[\xi \cos \omega t x] / Z(\xi \cos \omega t) \quad (3.1)$$

with the normalization factor

$$Z(\xi) = \frac{2 \sinh \xi}{\xi}. \quad (3.2)$$

For a weak field equation (2.5) can be solved by perturbation expansion in powers of ξ . Thus we put

$$f(x, t) = f_0 + f_1 + f_2 + \dots, \quad (3.3)$$

where the subscript denotes the order in ξ . From equation (2.5) one finds

$$\begin{aligned} f_0 &= \frac{1}{2}, \\ f_1(x, t) &= \frac{1}{2} \xi \cos \alpha \cos(\omega t - \alpha) x, \end{aligned} \quad (3.4)$$

with phase angle

$$\alpha(\omega) = \arctan\left(\frac{\omega}{2D_R}\right). \quad (3.5)$$

The second-order term is

$$f_2(x, t) = \frac{1}{12} \xi^2 \cos \alpha [\cos \alpha + \cos \alpha_2 \cos(2\omega t - \alpha - \alpha_2)] P_2(x) \quad (3.6)$$

with phase angle

$$\alpha_2(\omega) = \arctan\left(\frac{\omega}{3D_R}\right). \quad (3.7)$$

It turns out that equation (3.4) provides a good approximation at high frequency. At high frequency the field is effectively weak, since the dipoles cannot follow the field.

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

$$f_{eq}(x) = \exp(\xi x)/Z(\xi). \tag{3.8}$$

The corresponding equilibrium magnetization is

$$F_{eq}(\xi) = L(\xi), \tag{3.9}$$

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

$$L(\xi) = \coth \xi - \frac{1}{\xi}. \tag{3.10}$$

In the effective field approximation [10, 24] it is assumed that the distribution has the equilibrium form

$$f_e(x, t) = \exp[\xi_e(t)x]/Z(\xi_e(t)) \tag{3.11}$$

at all times with field $\xi_e(t)$ determined from the magnetization $F(t)$ according to equation (3.9)

$$F(t) = L(\xi_e(t)). \tag{3.12}$$

The magnetization itself is assumed to follow from a macroscopic relaxation equation. The latter is derived as a moment equation of equation (2.5), on the assumption that the distribution has the form of equation (3.11). We denote the approximate magnetization by $F_M(t)$. It satisfies the macroscopic equation

$$\frac{dF_M}{dt} = -2D_R \left[F_M(t) - \frac{F_M(t)}{\xi_{eM}(t)} \xi \cos \omega t \right]. \tag{3.13}$$

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

As an example we consider $\xi = 20, \omega = 9.588D_R$. In figure 1 we plot the exact distribution function, as a function of $x = \cos \theta$ and t , as found from equations (2.7)–(2.10). In figure 2 we plot the corresponding magnetization $F(t)$, as well as the solution $F_M(t)$ of the macroscopic relaxation equation (3.13). This shows that the latter describes the behaviour of the magnetization quite well. The exact magnetization passes through zero at time $t_0 = 0.431T$, where $T = 2\pi/\omega$ is the period. The approximate magnetization $F_M(t)$ passes through zero at time $t_{0M} = 0.439T$. The exact magnetization is maximal at time $t_x = 0.167T$, whereas the approximate magnetization is maximal at time $t_{xM} = 0.166T$. The value at maximum is $F(t_x) = 0.894$, whereas $F_M(t_{xM}) = 0.901$. The difference is more pronounced when expressed in terms of the field. In figure 3 we plot the field $\xi_e(t)$ accompanying the exact solution $F(t)$ according to equation (3.12), as well as the field $\xi_{eM}(t)$ corresponding to the solution $F_M(t)$ of equation (3.13). At the maximum $\xi_e(t_x) = 9.452$, whereas $\xi_{eM}(t_{xM}) = 10.125$.

In figure 4 we plot the exact distribution $f(x, t_0)$ at time t_0 , as well as the flat distribution $f_e(x, t_0) = \frac{1}{2}$ found from $\xi_e(t_0) = 0$, and the distribution $f_{eM}(x, t_0)$ found from $\xi_{eM}(t_0)$. This shows that at time t_0 the approximation of equation (3.11) to the distribution function is quite poor, whether calculated from $\xi_e(t_0)$, or from $\xi_{eM}(t_0)$. The exact distribution is far from flat when the magnetization vanishes.

In figure 5 we plot the order parameter $S(t)$ as a function of time, again for $\xi = 20, \omega = 9.588D_R$. In principle the order parameter can take values between $-\frac{1}{2}$ and 1. In our example the order parameter turns negative when the magnetization passes through zero and tends to unity when the absolute value of the magnetization is maximal. We also plot the order parameter $S_M(t)$ that follows from the effective field approximation of Martsenyuk *et al* [10]. This approximate order parameter remains positive, exhibiting a defect of the approximation.

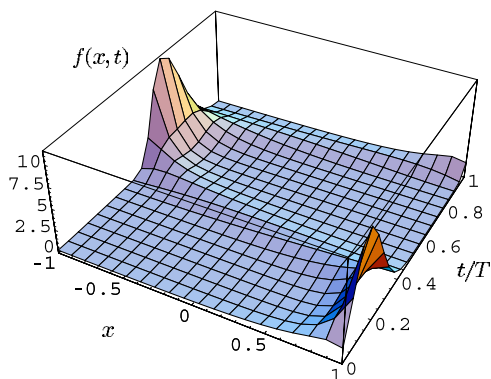


Figure 1. Plot of the distribution function $f(x, t)$ for field $\xi = 20$ and frequency $\omega = 9.588D_R$.

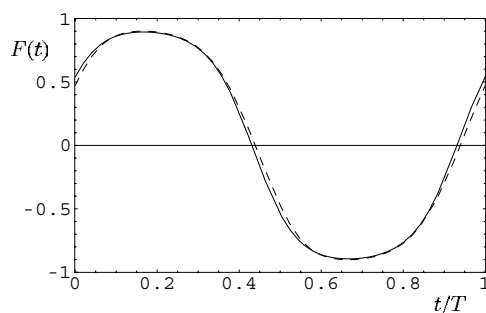


Figure 2. Plot of dimensionless magnetization $F(t)$ for field $\xi = 20$ and frequency $\omega = 9.588D_R$ (full curve), compared with the approximate value $F_M(t)$ calculated from the macroscopic relaxation equation (3.13).

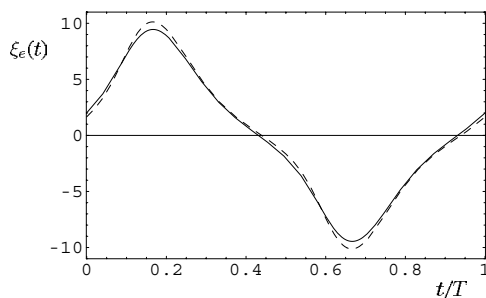


Figure 3. Plot of dimensionless field $\xi_e(t)$ for field $\xi = 20$ and frequency $\omega = 9.588D_R$ (full curve), compared with the approximate value $\xi_{eM}(t)$ calculated from the macroscopic relaxation equation (3.13).

4. First-harmonic response and absorption

A quantity of prime interest in the nonlinear response of the magnetization is the amplitude of the first harmonic, swinging in phase with the applied oscillating field. This is characterized

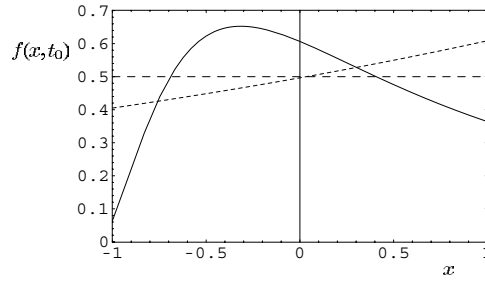


Figure 4. Plot of the distribution function $f(x, t_0)$ for field $\xi = 20$ and frequency $\omega = 9.588D_R$ at time t_0 defined by $F(t_0) = 0$ (full curve), compared with the flat distribution $f_e(x, t_0) = \frac{1}{2}$ (dashed curve), and the distribution $f_{eM}(x, t_0)$ corresponding to the effective field approximation (dotted curve).

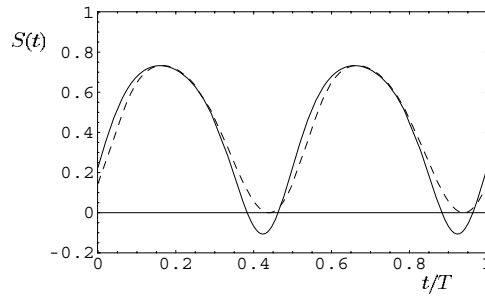


Figure 5. Plot of the order parameter $S(t)$ for field $\xi = 20$ and frequency $\omega = 9.588D_R$ (full curve), compared with $S_M(t)$, the order parameter found from the effective field approximation.

by the first-harmonic response, defined by

$$P(\xi, \omega) = \xi \omega \int_0^T F(t) \cos \omega t \, dt. \quad (4.1)$$

We note that $P(\xi, \omega)$ equals $-2\pi\beta$ times the time average of the mean potential energy of a dipole in the oscillating field. From equation (2.14) we find the exact value

$$P(\xi, \omega) = \frac{2\pi}{3} \xi A_{11}. \quad (4.2)$$

To first order in ξ the magnetization following from equation (3.4) is given by

$$F_w(t) = \frac{1}{3} \xi \cos \alpha \cos(\omega t - \alpha). \quad (4.3)$$

To this order we find from equation (4.1)

$$P_w(\xi, \omega) = \frac{\pi}{3} \xi^2 \cos^2 \alpha = \frac{\pi}{3} \xi^2 \frac{4}{4 + \omega^2 \tau_R^2}, \quad (4.4)$$

where $\tau_R = 1/D_R$ is a relaxation time.

In the zero-frequency limit one finds from equation (3.1)

$$F_{ad}(t) = L(\xi \cos \omega t). \quad (4.5)$$

Hence one finds for the first-harmonic response at zero frequency

$$P(\xi, 0) = \xi \int_0^{2\pi} L(\xi \cos \tau) \cos \tau \, d\tau. \quad (4.6)$$

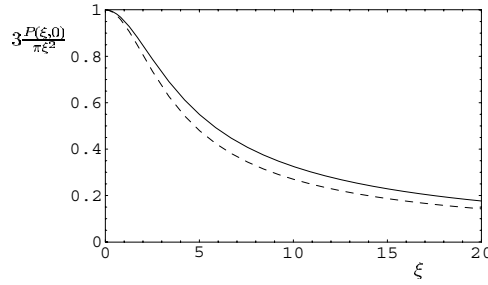


Figure 6. Plot of the function $3P(\xi, 0)/(\pi\xi^2)$ as a function of ξ (full curve), compared with Rosensweig's result $3L(\xi)/\xi$ (dashed curve).

For small ξ this reduces to $P_w(\xi, 0) = \pi\xi^2/3$. In figure 6 we plot $3P(\xi, 0)/(\pi\xi^2)$ as a function of ξ .

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

$$Q(\xi, \omega) = \xi \int_0^T \frac{dF}{dt} \cos \omega t dt. \quad (4.7)$$

It follows from equation (2.14) that the exact absorption is

$$Q(\xi, \omega) = \frac{2\pi}{3}\xi B_{11}. \quad (4.8)$$

To second order in ξ the absorption is

$$Q_w(\xi, \omega) = \frac{\pi}{3}\xi^2 \sin \alpha \cos \alpha = \frac{\pi}{3}\xi^2 \frac{2\omega\tau_R}{4 + \omega^2\tau_R^2}. \quad (4.9)$$

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

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 figure 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 a strong field. We also plot the corresponding quantities calculated from the macroscopic equation. The approximate theory performs quite well. At the maximum at $\omega_m = 9.588D_R$ the exact value is $Q(20, \omega_m) = 56.096$, whereas the approximate value is $Q_M(20, \omega_m) = 57.078$. At high frequency both curves tend to the expression for a weak field, equation (4.9). This expression has its maximum $Q_w(20, 2D_R) = 209.44$ at $\omega = 2D_R$.

It follows from the above example that at high field the frequency ω_m of maximum absorption is significantly larger than the Debye value $\omega_{mw} = 2D_R$. At the same time the absorption $Q_m = Q(\xi, \omega_m)$ at the maximum is strongly reduced from the value $Q_{mw} = Q_w(\xi, \omega_{mw}) = \pi\xi^2/6$ predicted by equation (4.9). In figure 8 we plot the ratios ω_{mw}/ω_m and Q_m/Q_{mw} as functions of field strength ξ . In the linear theory the location of the maximum is used to find the Debye relaxation time, and the value at the maximum is used to find the static susceptibility [25]. These characteristic quantities can be used to test the nonlinear theory experimentally.

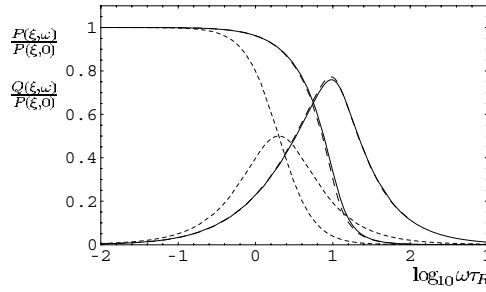


Figure 7. Plot of the reduced functions $P(\xi, \omega)/P(\xi, 0)$ and $Q(\xi, \omega)/P(\xi, 0)$ as functions of $\log_{10} \omega\tau_R$ for $\xi = 20$ (full curves), compared with the quantities $P_w(\xi, \omega)/P_w(\xi, 0)$ and $Q_w(\xi, \omega)/P_w(\xi, 0)$ valid in the weak field limit (short dashed 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 dashed curves).

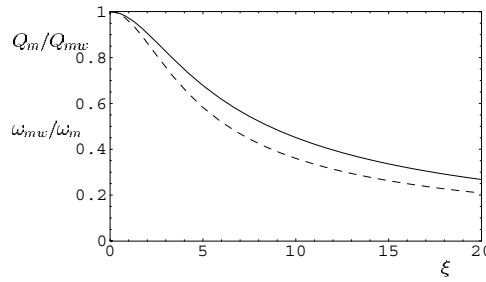


Figure 8. Plot of the ratios ω_{mw}/ω_m (dashed curve) and Q_m/Q_{mw} (full curve) as functions of field strength ξ .

The response of the system for a weak field is characterized by the frequency-dependent susceptibility

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \quad (4.10)$$

with real and imaginary parts

$$\chi'(\omega) = \frac{1}{3}nm^2\beta \frac{1}{1 + \omega^2\tau_D^2}, \quad \chi''(\omega) = \frac{1}{3}nm^2\beta \frac{\omega\tau_D}{1 + \omega^2\tau_D^2}. \quad (4.11)$$

The latter are proportional to the quantities $P_w(\xi, \omega)$ and $Q_w(\xi, \omega)$ defined in equations (4.4) and (4.9). The real and imaginary part are related by Kramers–Kronig relations, but this is not true of their nonlinear counterparts $P(\xi, \omega)$ and $Q(\xi, \omega)$. The breakdown of these relations can be shown explicitly from the response to third order in the field strength ξ . This corresponds to the cubic term in the susceptibility. Since the cubic term is given incorrectly by Raikher and Stepanov [3], and the expression derived by Coffey and Paranjape [2] is quoted incorrectly by Déjardin *et al* [7, 9], we give the result explicitly

$$P(\xi, \omega) + iQ(\xi, \omega) = \frac{\pi\xi^2}{3} \left[\frac{1}{1 - i\omega\tau_D} - \frac{\xi^2}{60} \frac{1}{1 + \omega^2\tau_D^2} \frac{1}{1 - i\omega\tau_D} \frac{9 - i\omega\tau_D}{3 - 2i\omega\tau_D} + O(\xi^4) \right]. \quad (4.12)$$

It is evident that the second term has a pole in the complex ω -plane at i/τ_D in conflict with the Kramers–Kronig relations. To elucidate the state of affairs we note the relation

$$P(\xi, \omega) + iQ(\xi, \omega) = \xi\omega \int_0^{2\pi/\omega} F(t)e^{i\omega t} dt \quad \text{for } \omega > 0. \quad (4.13)$$

Here $F(t)$ itself depends on ω , unlike the usual situation where $F(t)$ is an ω -independent response function, and the integral runs to infinity.

To conclude this section we note that the fundamental of the magnetization can be expressed as

$$F_1(t) = \frac{1}{\pi\xi} [P(\xi, \omega) \cos \omega t + Q(\xi, \omega) \sin \omega t]. \quad (4.14)$$

This can be rewritten as

$$F_1(t) = \eta(\xi, \omega) \cos(\omega t - \phi(\xi, \omega)) \quad (4.15)$$

with spectral amplification $\eta(\xi, \omega)$ given by

$$\eta(\xi, \omega) = \sqrt{P(\xi, \omega)^2 + Q(\xi, \omega)^2} / (\pi\xi) \quad (4.16)$$

and loss angle $\phi(\xi, \omega)$ by

$$\phi(\xi, \omega) = \arctan \frac{Q(\xi, \omega)}{P(\xi, \omega)}. \quad (4.17)$$

It may be most convenient to find $P(\xi, \omega)$, $Q(\xi, \omega)$ from experimentally determined values of $\eta(\xi, \omega)$ and $\phi(\xi, \omega)$.

5. Absorption and dissipation

In this section we discuss the relation between absorption, defined as work done on the system by the oscillating field during a period, and dissipation, defined as the entropy produced due to irreversible processes occurring in the system. In order to explore the relationship we must consider the free energy and entropy of non-equilibrium states. We can associate an entropy per particle with the non-equilibrium distribution $f(\theta, t)$ according to Boltzmann's expression

$$\mathcal{S}(t) = -k \int_0^\pi f(\theta, t) \ln f(\theta, t) \sin \theta \, d\theta, \quad (5.1)$$

where k is Boltzmann's constant. The corresponding free energy per particle is

$$\mathcal{F} = \mathcal{U} - T_0 \mathcal{S}, \quad (5.2)$$

where \mathcal{U} is the mean potential energy

$$\mathcal{U}(t) = \int_0^\pi \varepsilon(\theta, t) f(\theta, t) \sin \theta \, d\theta \quad (5.3)$$

and $T_0 = 1/k\beta$ is the temperature of the heat bath with which the particles interact stochastically. Thus the free energy is a functional $\mathcal{F}[f]$ of the distribution function. The rate of change of the free energy is

$$\frac{d\mathcal{F}}{dt} = \int_0^\pi [\varepsilon(\theta, t) + kT_0 \ln f] \frac{\partial f}{\partial t} \sin \theta \, d\theta + \int_0^\pi \frac{\partial \varepsilon}{\partial t} f \sin \theta \, d\theta. \quad (5.4)$$

Substituting equation (2.4) and performing an integration by parts we transform this to

$$\frac{d\mathcal{F}}{dt} = -kT_0 D_R \int_{-1}^1 (1-x^2) \left[\frac{\partial \ln f}{\partial x} - \xi \cos \omega t \right]^2 f(x, t) \, dx - mF(t) \frac{dH}{dt}. \quad (5.5)$$

Integrating this expression over a period we find for the periodic solution of equation (2.5) the relation

$$\mathcal{D}(\xi, \omega) = Q(\xi, \omega), \quad (5.6)$$

where $\mathcal{D}(\xi, \omega)$ is the dissipation defined by

$$\mathcal{D}(\xi, \omega) = D_R \int_{-1}^1 \int_0^T (1 - x^2) \left[\frac{\partial \ln f}{\partial x} - \xi \cos \omega t \right]^2 f(x, t) dx dt. \quad (5.7)$$

Clearly the integrand is positive in the whole xt -rectangle. Hence the dissipation is positive. The relation (5.6) shows that the dissipation is calculated conveniently from the absorption, i.e. from the work done on the system.

For a distribution of the exponential form of equation (3.11), a so-called e -distribution, the free energy becomes a functional $\mathcal{F}_e[F]$ of the magnetization F , or alternatively of the effective field ξ_e related to F by equation (3.12). By substitution of equation (3.11) into (5.1) one finds for the corresponding entropy

$$\mathcal{S}_e(F) = k \ln Z(\xi_e) - k\xi_e F. \quad (5.8)$$

Hence the free energy is

$$\beta \mathcal{F}_e(F, t) = (\xi_e - \xi \cos \omega t) F - \ln Z(\xi_e). \quad (5.9)$$

We see by use of the relation

$$F = \frac{\partial \ln Z(\xi_e)}{\partial \xi_e}, \quad (5.10)$$

equivalent to equation (3.12), that ξ_e is the thermodynamic force conjugate to F

$$\xi_e = -\frac{1}{k} \frac{\partial \mathcal{S}_e(F)}{\partial F}. \quad (5.11)$$

The entropy $\mathcal{S}_e(F)$ is an even function of the magnetization, $\mathcal{S}_e(-F) = \mathcal{S}_e(F)$, and $\mathcal{S}_e(0) = k \ln 2$. From equations (5.9) and (5.10) we find

$$\xi_e - \xi \cos \omega t = \frac{\partial \beta \mathcal{F}_e}{\partial F}. \quad (5.12)$$

If at time t the distribution has the exponential form assumed in equation (3.11), then the rate of change of the magnetization at that time is

$$\left. \frac{dF}{dt} \right|_e = \int_{-1}^1 x \frac{\partial f_e}{\partial t} dx. \quad (5.13)$$

Substituting from equation (2.5) one finds

$$\left. \frac{dF}{dt} \right|_e = D_R (\xi \cos \omega t - \xi_e) \langle \sin^2 \theta \rangle_{\xi_e}. \quad (5.14)$$

By use of equation (5.12) we can write

$$\left. \frac{dF}{dt} \right|_e = -\gamma(F) \beta \frac{\partial \mathcal{F}_e}{\partial F} \quad (5.15)$$

with the Onsager coefficient

$$\gamma(F) = D_R \langle \sin^2 \theta \rangle_{\xi_e(F)}. \quad (5.16)$$

One obtains the macroscopic relaxation equation (3.13) by postulating that

$$\frac{dF_M}{dt} = -\gamma(F_M) \beta \frac{\partial \mathcal{F}_e}{\partial F_M} \quad (5.17)$$

holds at all times. The rate coefficient can be expressed alternatively as

$$\gamma(F_M) = 2D_R \frac{L(\xi_{eM})}{\xi_{eM}}. \quad (5.18)$$

The coefficient is always positive, but vanishes in the limit $F_M \rightarrow \pm 1$. At $F_M = 0$ it takes the maximum value $\gamma(0) = \frac{2}{3}D_R$.

Multiplying equation (5.17) by $\xi \cos \omega t - \xi_{eM}(t)$ and integrating over a period we obtain by use of equation (5.12)

$$\int_0^T (\xi \cos \omega t - \xi_{eM}(t)) \frac{dF_M}{dt} dt = \int_0^T \gamma(F_M) \left(\beta \frac{\partial \mathcal{F}_e}{\partial F_M} \right)^2 dt. \quad (5.19)$$

The left-hand side of this equation can be simplified to $Q_M(\xi, \omega)$ by use of equation (5.11), so that the equation can be expressed as

$$Q_M(\xi, \omega) = \mathcal{D}_M(\xi, \omega) \quad (5.20)$$

with the macroscopic dissipation

$$\mathcal{D}_M(\xi, \omega) = \int_0^T \gamma(F_M) \left(\beta \frac{\partial \mathcal{F}_e}{\partial F_M} \right)^2 dt. \quad (5.21)$$

The dissipation can be calculated from the absorption by use of equation (5.20). It is evident that $\mathcal{D}_M(\xi, \omega)$ provides a macroscopic approximation to the actual dissipation $\mathcal{D}(\xi, \omega)$, given by equation (5.7).

6. The Shliomis relaxation equation

In the preceding sections we have compared the first-harmonic response and absorption calculated from the Smoluchowski rotational diffusion equation with that found from the approximate macroscopic equation proposed by Martsenyuk *et al* [10]. The macroscopic equation leads to quite good agreement with the results found from the exact solution of the Smoluchowski equation. It should be stressed that the exact calculation is actually simpler to perform than the one based on the approximate equation.

It is also worthwhile to make a comparison with a second macroscopic equation, that proposed by Shliomis [11]. In our notation the Shliomis equation reads for the situation studied here

$$\frac{dF_S}{dt} = -2D_R[F_S(t) - L(\xi \cos \omega t)]. \quad (6.1)$$

Rosensweig [12] has calculated the first-harmonic response and absorption on the basis of the Shliomis equation, but his calculation involved an approximation.

The absorption calculated from equation (6.1) according to the definition equation (4.7) is given by

$$Q_S(\xi, \omega) = -2D_R \xi \int_0^T [F_S(t) - L(\xi \cos \omega t)] \cos \omega t dt. \quad (6.2)$$

By comparison with equation (4.1) we find the relation with the first-harmonic response

$$P_S(\xi, \omega) + \frac{1}{2}\omega\tau_R Q_S(\xi, \omega) = P(\xi, 0), \quad (6.3)$$

with $P(\xi, 0)$ given by equation (4.6). In particular at zero frequency

$$P_S(\xi, 0) = P(\xi, 0). \quad (6.4)$$

Rosensweig [12] finds instead for the right-hand side the value $\pi \xi L(\xi)$. We compare both functions by considering their series expansion in powers of ξ^2 . The function $\pi \xi L(\xi)$ has the expansion

$$\pi \xi L(\xi) = \pi \sum_{n=1}^{\infty} \frac{2^{2n} B_{2n}}{(2n)!} \xi^{2n}, \quad (6.5)$$

where $\{B_n\}$ are the Bernoulli numbers. The function $P(\xi, 0)$ has the expansion

$$P(\xi, 0) = 2\pi \sum_{n=1}^{\infty} \frac{B_{2n}}{(n!)^2} \xi^{2n}. \tag{6.6}$$

This shows that the two expansions agree only in the first term. In figure 6 we compare the functions $3P(\xi, 0)/\pi\xi^2$ and $3L(\xi)/\xi$. Both functions equal unity at $\xi = 0$.

The function $L(\xi \cos \omega t)$ occurring in equation (6.1) can be expanded in harmonics as

$$L(\xi \cos \omega t) = \sum_{n=0}^{\infty} p_n(\xi) \cos(2n + 1)\omega t \tag{6.7}$$

with first coefficient

$$p_0(\xi) = \frac{P(\xi, 0)}{\pi\xi}. \tag{6.8}$$

The periodic solution of equation (6.1) can be expressed as

$$F_S(t) = \sum_{n=0}^{\infty} a_n \cos(2n + 1)\omega t + \sum_{n=0}^{\infty} b_n \sin(2n + 1)\omega t. \tag{6.9}$$

Substituting into equation (6.1), one finds that the coefficients $\{a_n, b_n\}$ are given by

$$a_n(\xi, \omega) = \frac{1}{1 + (2n + 1)^2\omega^2\tau_D^2} p_n(\xi), \quad b_n(\xi, \omega) = \frac{(2n + 1)\omega\tau_D}{1 + (2n + 1)^2\omega^2\tau_D^2} p_n(\xi). \tag{6.10}$$

Rosensweig missed the higher harmonics. From equation (6.10) one finds

$$P_S(\xi, \omega) = \frac{1}{1 + \omega^2\tau_D^2} P(\xi, 0), \quad Q_S(\xi, \omega) = \frac{\omega\tau_D}{1 + \omega^2\tau_D^2} P(\xi, 0). \tag{6.11}$$

Equation (6.3) is clearly satisfied. The reduced functions $P_S(\xi, \omega)/P(\xi, 0)$ and $Q_S(\xi, \omega)/P(\xi, 0)$ are independent of ξ , and identical with

$$\frac{\chi'(\omega)}{\chi'(0)} = \frac{1}{1 + \omega^2\tau_D^2}, \quad \frac{\chi''(\omega)}{\chi''(0)} = \frac{\omega\tau_D}{1 + \omega^2\tau_D^2}. \tag{6.12}$$

The frequency dependence is the same as that found by Rosensweig. The resonance in the reduced functions is not shifted from the weak-field case. We have shown above that the Smoluchowski equation and the macroscopic equation of Martsenyuk *et al* [10] predict a strong shift with increasing field.

At low and high frequencies the Shliomis relaxation equation yields results for the magnetization in agreement with those found from the Smoluchowski equation. At intermediate frequencies there are appreciable deviations. As argued elsewhere [26], the Smoluchowski equation is reliable only in the dilute regime. For dense suspensions the microscopic description is difficult, and it becomes worthwhile to explore the consequences of various macroscopic relaxation equations.

7. Interacting dipoles in a 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 that 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 behaviour of the system is described by the single-particle distribution function. We consider a spherical sample placed in a uniform applied oscillating field $\mathbf{H}_0(t) = H_0 \mathbf{e}_z \cos \omega t$. The field induces a magnetization $\mathbf{M}(t)$ and a Maxwell field $\mathbf{H}(t)$, which are uniform throughout the sample. It follows from Maxwell's equations of magnetostatics that the Maxwell field inside the sphere is given by

$$\mathbf{H}(t) = H_0 \mathbf{e}_z \cos \omega t - \frac{4\pi}{3} \mathbf{M}(t) \mathbf{e}_z, \quad (7.1)$$

where the last term is the demagnetizing field, in Gaussian units. The distribution function will have cylindrical symmetry. Quite generally it can be assumed to satisfy the equation [27, 28]

$$\frac{\partial f}{\partial t} = D_R \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} + \xi_{loc}(t) \sin^2 \theta f \right) \right], \quad (7.2)$$

where $\xi_{loc}(t) = m H_{loc}(t) / k T_0$ is the acting field in dimensionless units. By our assumption of statistical independence of dipoles the local field $\mathbf{H}_{loc}(t)$ 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 $\mathbf{H}_L(t)$ given by

$$\mathbf{H}_L(t) = \mathbf{H}(t) + \frac{4\pi}{3} \mathbf{M}(t). \quad (7.3)$$

Substituting from equation (7.1) we see that for a spherical sample the Lorentz field $\mathbf{H}_L(t)$ is identical with the applied field $\mathbf{H}_0(t)$. Hence, with this approximation for the local field, equation (7.2) reduces to equation (2.4), and all our earlier results apply.

We note that upon decomposition into harmonics we can express equation (7.1) as

$$H_n = H_0 \delta_{n1} - \frac{4\pi}{3} M_n \quad (n \geq 1). \quad (7.4)$$

Defining the complex response function

$$X(H, \omega) = \frac{1}{\pi \xi} [P(\xi, \omega) + iQ(\xi, \omega)] \quad (7.5)$$

with $\xi = mH/kT$ as before, we find in the Lorentz local field approximation

$$M_1 = nm X \left(H_1 + \frac{4\pi}{3} M_1, \omega \right). \quad (7.6)$$

This is an implicit equation for M_1 in terms of H_1 , which has been called [29] the nonlinear Clausius–Mossotti relation. It is a nonlinear constitutive equation expressing the local magnetization at frequency ω in terms of the local Maxwell field at frequency ω . Note that the higher harmonics of the Maxwell field have no effect, since they cancel in the Lorentz field on account of equation (7.4).

Although we have derived equation (7.6) for a particular choice of geometry, the equation is expressed in terms of local quantities. It is therefore tempting to use it in combination with Maxwell's equations to predict the macroscopic response of a sample of any shape to a uniform applied oscillating field. In the first instance the calculation involves only the behaviour of the first harmonic. As a result one finds the fundamental of the magnetization and of the magnetic field at any point in space. However, the local distribution function also generates higher harmonics of the magnetization, as shown in equation (2.14), and therefore via Maxwell's equations higher harmonics of the field. For spherical geometry these have no effect, because of equations (7.3) and (7.4), but for different geometries they must in principle be taken into account. For a sharp resonance the higher harmonics can reasonably be neglected [29], but

in the present situation more care is needed. A general study of the effect of many-particle interactions on the nonlinear response has been presented by Palenberg and Felderhof [30] in the framework of a cluster expansion.

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 field with $\cos \omega t$ dependence the behaviour of the magnetization will depend on the shape of the sample. Only for a spherical sample do we have a prediction of the time dependence of the magnetization. The latter 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 function [31].

8. Discussion

We have studied the nonlinear response of a dipolar system to a strong oscillating field, both on the basis of the microscopic rotational diffusion equation, and on the basis of the Shliomis macroscopic relaxation equation. The predictions of the two equations differ markedly. We have also compared these predictions with the response calculated from the macroscopic relaxation equation of Martsenyuk *et al.*, derived from the rotational diffusion equation on the basis of an effective field approximation. We found that the approximation performs quite well in its prediction for the behaviour of the magnetization, even though the assumed form of the distribution function at times differs strongly from the exact value. On the other hand, its use in the present context is rather superfluous, since the calculation on the basis of the rotational diffusion equation, once the coupled set of equations (2.8) and (2.10) has been derived, is actually simpler than the solution of the approximate equation.

The nonlinear response calculated from the rotational diffusion equation shows quite interesting features. Firstly, the absorption resonance is considerably shifted and broadened in comparison with the linear response. This feature may be relevant in technical applications. Secondly, it is found that the real and imaginary part of the complex nonlinear response do not satisfy Kramers–Kronig relations. Thus in experimental investigations both parts must be determined separately.

The theory can be extended in several directions. First of all, it would be desirable to perform a similar calculation for a rotating field [32] and for an oscillating field with elliptic polarization. Secondly it would be desirable to extend the calculation to interacting dipoles in cylindrical geometry with an oscillating field directed along the axis of the cylinder. This is of relevance for the calculation of the so-called negative viscosity effect [33–35].

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