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Mean field theory of the nonlinear response of an interacting dipolar system with rotational diffusion to an oscillating field

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Abstract

A mean field theory of dipolar relaxation in a system of interacting dipoles is developed on the basis of a local field picture. The distribution of orientations of a selected dipole is assumed to satisfy a rotational diffusion equation of Smoluchowski type with time-dependent potential determined self-consistently from the mean dipole moment. The response to an oscillating Maxwell field acting in a volume element is studied for arbitrary amplitude and frequency of the field. For weak field the theory is similar to that developed by Debye, who used the Lorentz local field factor, and derived an expression for the frequency-dependent susceptibility of Clausius–Mossotti form. In the present theory the local field factor is found from the static linear response in thermal equilibrium. The same local field factor is used for strong field. Then the mean dipole moment oscillates anharmonically, and the maximum absorption shifts to higher frequency.

1. Introduction

The theory of dipolar relaxation in polar media has a long and distinguished history [1–8]. The theory applies to both electric and magnetic dipoles, and therefore finds application in dielectrics, as well as in ferrofluids and ferrosolids.

In early work Debye [1, 9] assumed that a selected dipole performs rotational Brownian motion in the applied field. For weak field and for a dilute system, where dipoles are independent, this leads to the celebrated Debye formula for the dynamic susceptibility with a single relaxation time calculated from the Stokes–Einstein formula for rotational friction.

For dense systems Debye took account of dipolar interactions by means of a Lorentz local field [1, 9, 10]. This led to an expression for the frequency-dependent susceptibility of Clausius–Mossotti type.

Onsager [11] modified the theory of static linear response by developing a cavity model from which it was evident that a selected dipole is subject to a reaction field, besides the Lorentz local field. This leads to Onsager’s expression for the static susceptibility. The expression was extended to include frequency dependence by Cole [12]. The Onsager–Cole expression was modified by Fatuzzo and Mason [13], who took account of dielectric friction exerted by the surrounding medium on the selected dipole. Their expression was rederived by Nee and Zwanzig [14] by a different method. The coupling of dielectric friction to hydrodynamic flow was taken into account by Felderhof [15, 16].

A more microscopic theory of the time-dependent response of dipolar liquids was developed by Chandra and Bagchi [7, 17]. The theory is based on a self-consistent Smoluchowski equation incorporating the equilibrium structure via the direct correlation function. We use a similar equation, but restrict attention to the long-wavelength limit, where less microscopic structural information is required. In our approach it suffices to specify the local field factor. Our expression for the linear susceptibility is essentially identical to that of Chandra and Bagchi [17]. The susceptibility takes the Debye form with an increased relaxation time.

In recent computer simulations of a dipolar hard-sphere fluid Wang *et al* [18] made a careful study of the equilibrium polarization or magnetization as a function of density and field. It turns out that the static susceptibility is described poorly by Onsager’s cavity model. We show in section 2 that the local field picture with a suitable local field factor describes the thermal equilibrium data quite well. The same local field factor is then used in the theory of dipolar relaxation.

We develop the theory of both linear and nonlinear response to an oscillating Maxwell field on the basis of a rotational diffusion equation of Smoluchowski type with time-dependent potential determined self-consistently from the mean dipole moment and with a local field factor taken from the equilibrium linear response. The theory is a natural extension of our earlier work for the dilute case [19]. For simplicity we assume cylindrical geometry with field applied parallel to the symmetry axis, but discuss in section 6 how the theory can be extended to different geometry. In principle the theory allows one to study the local nonlinear response to a Maxwell field of arbitrary periodic time variation. In the following we assume that the Maxwell field varies harmonically.

2. Dipoles in steady field

We consider a suspension of spherical particles with dipole moment $\boldsymbol{\mu} = m\boldsymbol{u}$, where \boldsymbol{u} is a unit vector, immersed in a fluid of small molecules in thermal equilibrium at temperature T_0 . We assume that the suspended particles interact as hard spheres besides having the long-range dipolar interaction. For definiteness we consider magnetic dipoles, but our considerations apply equally well in the electrical case. Conventionally the magnetic equation of state is expressed in terms of the dimensionless parameters [6]

$$\chi_0 = \frac{nm^2}{3kT_0}, \quad y = \frac{4\pi nm^2}{9kT_0} = \frac{4\pi}{3}\chi_0, \quad (1)$$

where n is the number density, and k is Boltzmann’s constant. In the following we use Gaussian units. For dipolar hard spheres of radius a the strength of the dipolar interaction is characterized

by the parameter

$$\lambda = \frac{m^2}{8kT_0a^3}. \quad (2)$$

For volume fraction $\phi = (4\pi/3)na^3$ we have the relation $\chi_0 = (2/\pi)\lambda\phi$.

For dipolar hard spheres the first three terms of the density expansion of the static susceptibility are known, and given by [20–22]

$$\chi = \chi_0 + \frac{4\pi}{3}\chi_0^2 + \frac{\pi^2}{9}\chi_0^3 + O(\chi_0^4). \quad (3)$$

To this order the susceptibility depends on density only via the product $\lambda\phi$, but at higher density one must expect χ to depend separately on λ and ϕ . Wang *et al* [18] have found by computer simulation that up to volume fraction $\phi = 0.2356$ the susceptibility is described quite well by just the first three terms of the expansion in equation (3).

In the following we use a local field picture in the study of the dynamical response. In this picture the average field acting on a selected dipole in a volume element with local Maxwell field \mathbf{H} and magnetization \mathbf{M} is given by

$$\mathbf{H}_{loc} = \mathbf{H} + \gamma\mathbf{M} \quad (4)$$

with local field factor γ . In thermal equilibrium the probability of directions of the selected dipole is given by the Boltzmann factor $\exp[\beta m\mathbf{u}\cdot\mathbf{H}_{loc}]$, with $\beta = 1/kT_0$. Hence one finds that the dimensionless magnetization F_{eq} , defined by $\mathbf{M}_{eq} = nm\mathbf{F}_{eq}$, is given by the self-consistent equation

$$F_{eq} = L(\xi + 3\gamma\chi_0F_{eq}), \quad (5)$$

where $\xi = mH/kT_0$ is the dimensionless field, and $L(\xi)$ is the Langevin function

$$L(\xi) = \coth \xi - \frac{1}{\xi}. \quad (6)$$

Expanding equation (5) to linear terms one finds for the susceptibility

$$\chi = \frac{\chi_0}{1 - \gamma\chi_0}. \quad (7)$$

We see by comparison with equation (3) that the first three terms of the expansion are reproduced if we assume the local field factor to be given by

$$\gamma = \frac{4\pi}{3 + \frac{15\pi}{4}\chi_0}. \quad (8)$$

Debye [9] used instead the Lorentz local field factor $\gamma_L = 4\pi/3$. Equation (7) with (8) may be regarded as a Padé approximant to the susceptibility. At $\chi_0 = 0.45$, corresponding to volume fraction $\phi = 0.2356$ at $\lambda = 3$, the expression yields $\chi = 1.412$, as compared with $\chi = 1.398$ from the first three terms in equation (3). The computer simulation of Wang *et al* [18] yields $\chi = 1.419$. For a dipolar system of spherical particles with different short-range interaction, the second numerical factor in the denominator of equation (8) will be slightly different.

It is of interest to compare equations (7) and (8) with Onsager's expression [3, 11] for the permeability $\mu = 1 + 4\pi\chi$:

$$\frac{(\mu - 1)(2\mu + 1)}{\mu} = 12\pi\chi_0 \quad (\text{Onsager}). \quad (9)$$

This corresponds to a local field factor

$$\gamma_O = \frac{4\pi}{3 + 8\pi\chi} \quad (10)$$

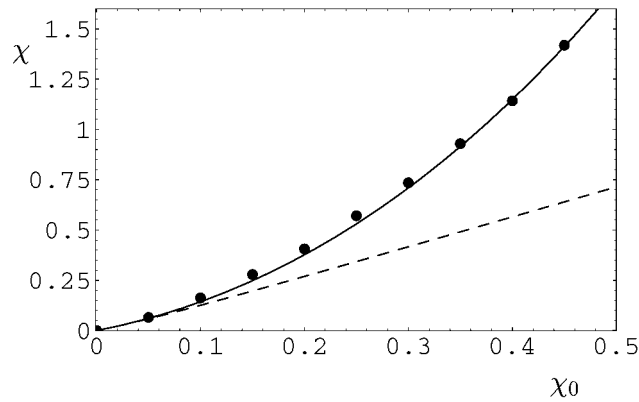


Figure 1. A plot of the susceptibility χ as a function of χ_0 , as given by equations (7) and (8) (solid curve), compared with Onsager expression (9) (dashed curve), and with the simulation results of Wang *et al* [18] for interaction strength $\lambda = 3$ (dots).

depending self-consistently on the susceptibility. In figure 1 we plot the susceptibility χ as a function of χ_0 , as given by equations (8) and (10) respectively, and compare with the computer simulation data of Wang *et al* for the (nearly) hard-sphere system with interaction strength $\lambda = 3$. It is evident that Onsager's approximation performs quite poorly. The exact permeability may be expressed as

$$\frac{(\mu - 1)(2\mu + 1)}{\mu} = 12\pi g_K \chi_0 \quad (11)$$

with Kirkwood factor [23] g_K . Our approximation equation (8) corresponds to a Kirkwood factor

$$g_K = \frac{(16 + 15y)(16 + 31y + 30y^2)}{(16 - y)(16 + 47y + 45y^2)}. \quad (12)$$

This takes the value $g_K = 1$ at $\chi_0 = 0$, and the value $g_K = 2.147$ at $\chi_0 = 0.45$, showing that the Kirkwood factor varies appreciably over the range considered. In the following we use the local field factor γ given by equation (8).

It will be useful to have a notation for the equilibrium magnetization given by the solution of equation (5) with local field factor γ . We use the abbreviation

$$C = \gamma \chi_0, \quad (13)$$

and define the function $F_{eq}(\xi; C)$ as the solution of equation (5). As an example we plot in figure 2 the function $F_{eq}(\xi; C)$ as a function of ξ for $C = 0.681191$, corresponding to $\chi_0 = 0.45$ for the local field factor given by equation (8). In the following we denote this particular value of C as C_0 . We compare with the Langevin function $L(\xi) = F_{eq}(\xi; 0)$. This shows that the equilibrium magnetization is affected appreciably by the local field effect.

3. Dipoles in oscillating field

Next we consider the dynamical response of the system to an oscillating field. We assume that the macroscopic sample has cylindrical symmetry with symmetry axis along the z -axis. Then the Maxwell magnetic field $\mathbf{H}(t)$ in the sample is identical to the applied field $\mathbf{H}_0(t) = H_0 \mathbf{e}_z \cos \omega t$. We shall study both the linear and the nonlinear response of the magnetization.

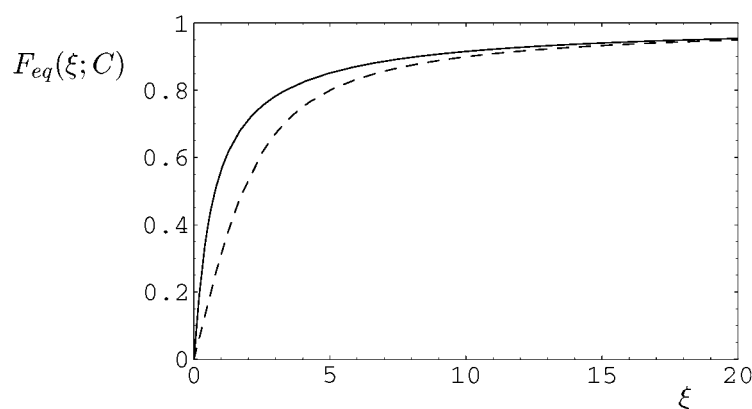


Figure 2. A plot of dimensionless equilibrium magnetization $F_{eq}(\xi; C)$ as a function of field ξ for $C = C_0 = 0.681\ 191$ (solid curve), compared with the Langevin function for $C = 0$ (dashed curve).

Earlier studies of the linear response have been based on extensions of the Onsager expression equation (9) to nonzero frequency. For example, the Onsager–Cole expression [12] for the dynamic permeability $\mu(\omega)$ reads

$$\frac{[\mu(\omega) - 1][2\mu(\omega) + 1]}{\mu(\omega)} = \frac{12\pi\chi_0}{1 - i\omega\tau_D} \quad (\text{Onsager–Cole}) \quad (14)$$

with Debye relaxation time τ_D . Fatuzzo and Mason [13] modified the expression equation (14) to take account of dielectric friction. Their result was rederived by Nee and Zwanzig [14] by use of a different method. Felderhof [15, 16] calculated the dielectric friction correction by taking account of the coupling to hydrodynamic flow. As we have shown above, the Onsager approximation gives a poor account of the thermal equilibrium susceptibility. On the other hand, the local field picture with local field factor given by equation (8) describes the equilibrium magnetization quite well. In the following we therefore study the dynamical response on the basis of the local field picture, with the local field factor given by equation (8). It seems reasonable to assume that the microscopic configuration in the oscillating field is not much different from that in equilibrium in zero field.

In the local field picture [1, 7, 9, 17] the distribution function of orientations $f(\mathbf{u}, t)$ is assumed to satisfy the nonlinear Smoluchowski equation

$$\frac{\partial f}{\partial t} = D_R \mathbf{L} \cdot [\mathbf{L}f + \beta(\mathbf{L}\varepsilon_{loc})f], \quad (15)$$

where D_R is the rotational diffusion coefficient, and \mathbf{L} is the rotation operator

$$\mathbf{L} = \mathbf{u} \times \frac{\partial}{\partial \mathbf{u}}. \quad (16)$$

The Debye relaxation time in equation (14) is $\tau_D = 1/(2D_R)$. The potential energy of a dipole in the local field $\mathbf{H}_{loc}(t)$ is

$$\varepsilon_{loc}(\mathbf{u}, t) = -m\mathbf{u} \cdot \mathbf{H}_{loc}(t). \quad (17)$$

It is convenient to normalize to

$$\int f(\mathbf{u}, t) d\mathbf{u} = 2\pi. \quad (18)$$

The local field is given by equation (4) with magnetization

$$\mathbf{M}(t) = \frac{nm}{2\pi} \int \mathbf{u} f(\mathbf{u}, t) d\mathbf{u}. \quad (19)$$

The distribution function will have cylindrical symmetry, so equation (15) can be simplified to

$$\frac{\partial f}{\partial t} = D_R \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} + \xi_{loc}(t) \sin^2 \theta f \right) \right], \quad (20)$$

where $\xi_{loc}(t) = mH_{loc}(t)/kT_0$ is the acting field in dimensionless units.

It is clear that in a steady field \mathbf{H} the time-independent solution of equation (15) is a Boltzmann distribution with the local field. This leads to the self-consistent equation (5) for the equilibrium magnetization.

Next we consider the linear response for small oscillatory field $\xi(t) = \xi \cos \omega t$ with $\xi = mH_0/k_B T_0$. In dimensionless units the local field is $\xi_{loc}(t) = \xi(t) + 3CF(t)$. To lowest order in ξ the distribution is isotropic, $f_0(\mathbf{u}) = 1/2$. To first order in ξ one finds by linearization of equation (20)

$$f(\mathbf{u}, t) = \frac{1}{2} + \frac{\xi \cos \alpha}{2 - 2C} \cos(\omega t - \alpha) \cos \theta, \quad (21)$$

with lag angle

$$\alpha(\omega) = \arctan \frac{\omega \tau_R}{2 - 2C}, \quad (22)$$

where τ_R is the relaxation time $\tau_R = 1/D_R$. Hence one finds for the magnetization in weak field

$$F_w(t) = \frac{1}{3} \xi \frac{\cos \alpha}{1 - C} \cos(\omega t - \alpha). \quad (23)$$

In general, the first-harmonic response is defined by

$$P(\xi, \omega) = \xi \omega \int_0^T F(t) \cos \omega t dt, \quad (24)$$

where $T = 2\pi/\omega$ is the period. The dimensionless absorption is

$$Q(\xi, \omega) = \xi \int_0^T \frac{dF}{dt} \cos \omega t dt. \quad (25)$$

To lowest order in ξ the first-harmonic response is

$$P_w(\xi, \omega) = \frac{4\pi}{3} \xi^2 \frac{1 - C}{(2 - 2C)^2 + \omega^2 \tau_R^2}. \quad (26)$$

The absorption is to lowest order in ξ

$$Q_w(\xi, \omega) = \frac{\pi}{3} \xi^2 \frac{2\omega \tau_R}{(2 - 2C)^2 + \omega^2 \tau_R^2}. \quad (27)$$

The frequency-dependent susceptibility is

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \quad (28)$$

with real and imaginary parts

$$\chi'(\omega) = \frac{1}{3} nm^2 \beta \frac{1 - C}{(1 - C)^2 + \omega^2 \tau_D^2}, \quad \chi''(\omega) = \frac{1}{3} nm^2 \beta \frac{\omega \tau_D}{(1 - C)^2 + \omega^2 \tau_D^2}. \quad (29)$$

Hence the response is Lorentzian with relaxation time

$$\tau = \frac{\tau_D}{1 - C}. \quad (30)$$

This shows that the dipolar interaction causes both the amplitude and the relaxation time to increase. The result was found already by Debye [9], who assumed $\gamma = 4\pi/3$, and is closely related to that found by Chandra and Bagchi [17]. The linear response is appreciably simpler than that predicted by the Onsager–Cole equation (14).

The magnetization can be calculated to terms cubic in the applied field. We quote the result for harmonic response and absorption:

$$P(\xi, \omega) + iQ(\xi, \omega) = \frac{\pi\xi^2}{3} \left[\frac{1}{1 - C - i\omega\tau_D} - \frac{\xi^2}{60} \frac{1}{(1 - C)^2 + \omega^2\tau_D^2} \frac{(1 - i\omega\tau_D)(9 - i\omega\tau_D)}{(1 - C - i\omega\tau_D)^2(3 - 2i\omega\tau_D)} + O(\xi^4) \right]. \quad (31)$$

This generalizes the result of Coffey and Paranjape [24] derived for the dilute case with $C = 0$.

4. Nonlinear response and macroscopic relaxation equation

In order to find the nonlinear response of the system to an oscillatory field $\xi(t) = \xi \cos \omega t$ of arbitrary amplitude ξ we must solve the nonlinear equation (20). In terms of the variable $x = \cos \theta$ the equation becomes

$$\frac{\partial f}{\partial t} = D_R \frac{\partial}{\partial x} \left[(1 - x^2) \frac{\partial f}{\partial x} - (\xi \cos \omega t + 3CF(t))(1 - x^2)f \right], \quad (32)$$

with magnetization $F(t)$ determined self-consistently from

$$F(t) = \int_{-1}^1 xf(x, t) dx. \quad (33)$$

We must find the solution that is periodic in time with period $T = 2\pi/\omega$. Therefore we expand in Legendre polynomials and harmonics:

$$f(x, t) = \sum_{\ell=0}^{\infty} \sum_{m=-\infty}^{\infty} f_{\ell m} P_{\ell}(x) \exp[-im\omega t]. \quad (34)$$

Substitution into equation (32) yields a set of equations for the amplitudes $f_{\ell m}$ for $\ell \geq 1$:

$$im\omega f_{\ell m} = \ell(\ell + 1)f_{\ell m} - \frac{\ell(\ell + 1)}{2\ell - 1} \sum_{n=-\infty}^{\infty} \eta_n f_{\ell-1, m-n} + \frac{\ell(\ell + 1)}{2\ell + 3} \sum_{n=-\infty}^{\infty} \eta_n f_{\ell+1, m-n} \quad (35)$$

with coefficients

$$\eta_n = \frac{1}{2}\xi[\delta_{n,1} + \delta_{n,-1}] + 2Cf_{1n}. \quad (36)$$

The equation for $\ell = 1$ in equation (35) contains the inhomogeneous term

$$f_{00} = \frac{1}{2}. \quad (37)$$

The equations have a symmetry which implies

$$f_{\ell m} = 0 \quad \text{for } \ell + m \text{ odd.} \quad (38)$$

In particular, the magnetization is composed of harmonics of frequency $\omega, 3\omega, 5\omega, \dots$. Equations (35) can be solved by truncation and iteration starting from $\eta_n^{(0)} = \frac{1}{2}\xi[\delta_{n,1} + \delta_{n,-1}]$. The procedure converges rapidly. Substituting the amplitudes $f_{\ell m}$ into equation (34) one obtains the distribution function $f(x, t)$. Alternatively one can expand the function $f(x, t)$ in Legendre polynomials $\{P_{\ell}(x)\}$ with time-dependent coefficients $\{f_{\ell}(t)\}$, and find the periodic solution for the set of coupled differential equations by integration and iteration. This method works also very well, and is faster if the applied field is strong.

One recovers the equations for the dilute case by putting $C = 0$ in equation (36). We found in our earlier work [19] that for that case the magnetization $F(t)$ is well approximated by the periodic solution $F_M(t)$ of the macroscopic equation of Martsenyuk *et al* [25]. It is clear from the structure of equations (34) and (35) that one expects a similar state of affairs here, provided the macroscopic equation is modified for the local field effect in the form

$$\frac{dF_M}{dt} = -2D_R \left[F_M(t) - \frac{F_M(t)}{\xi_{eM}(t)} (\xi \cos \omega t + 3C F_M(t)) \right], \quad (39)$$

where the effective field $\xi_{eM}(t)$ is related to the magnetization $F_M(t)$ by

$$F_M(t) = L(\xi_{eM}(t)). \quad (40)$$

It is clearly easier to solve the single macroscopic equation (39) than the set of equations (35). We do in fact find that equation (39) yields a good approximation to the magnetization, even though the distribution function $f(u, t)$ may be rather different from the corresponding quasi-equilibrium distribution of Boltzmann form with potential energy equation (17). Actually it is more convenient to solve the differential equation for the effective field $\xi_{eM}(t)$, and then find the magnetization $F_M(t)$ from equation (40). It is easily checked that for small field the solution of the linearized macroscopic equation is identical with the function $F_w(t)$ given by equation (23). We denote the values of the first-harmonic response and absorption calculated from the macroscopic approximation $F_M(t)$ by $P_M(\xi, \omega)$ and $Q_M(\xi, \omega)$.

In the zero-frequency limit the distribution function to a good approximation takes the quasi-equilibrium form. Hence in this limit the magnetization is given by

$$F_{ad}(t) = F_{eq}(\xi \cos \omega t; C). \quad (41)$$

This yields for the first-harmonic response at zero frequency

$$P(\xi, 0) = \xi \int_0^{2\pi} F_{eq}(\xi \cos \tau; C) \cos \tau \, d\tau. \quad (42)$$

For small ξ this reduces to $P_w(\xi, 0) = \pi \xi^2 / (3 - 3C)$. In figure 3 we plot $3P(\xi, 0) / (\pi \xi^2)$ as a function of ξ . The plot shows that for large ξ the local field effect on the value of $P(\xi, 0)$ is small. However, even for large ξ the effect of the local field on the absorption is appreciable. As an example we consider $\xi = 10$ and $\omega \tau_R = 0.5$. For these values of ξ and ω and for $C = 0$ we find $P(10, 0.5D_R) = 33.348$, whereas $P(10, 0.5D_R) = 34.133$ for $C = C_0$. On the other hand, we find for the absorption for $C = 0$ the value $Q(10, 0.5D_R) = 5.396$, whereas $Q(10, 0.5D_R) = 7.683$ for $C = C_0$, i.e. more than 42% higher than for $C = 0$. We also compare these values with those found from the macroscopic equation. For $C = 0$ we find $P_M(10, 0.5D_R) = 33.378$ and $Q_M(10, 0.5D_R) = 5.322$. For $C = C_0$ we find $P_M(10, 0.5D_R) = 34.159$ and $Q_M(10, 0.5D_R) = 7.622$. This shows that the macroscopic approximation is reasonably accurate.

The increased absorption with increasing C is also evident from a parametric plot of the magnetization $F(t)$ against the field $\xi \cos \omega t$. The plot for one period shows a hysteresis loop. In figure 4 we show the parametric plots for $\xi = 10$, $\omega \tau_R = 0.5$ for $C = 0$ and C_0 respectively. The second hysteresis loop is wider, corresponding to increased absorption.

It is also of interest to have a measure for the deviation from simple harmonic behaviour. It is evident from equation (21) that for weak field only the first harmonic contributes to the magnetization, albeit with a phase lag. More generally we define the first-harmonic fraction as the ratio

$$\Phi_1 = |f_{11}|^2 / \sum_{n=1}^{\infty} |f_{1n}|^2. \quad (43)$$

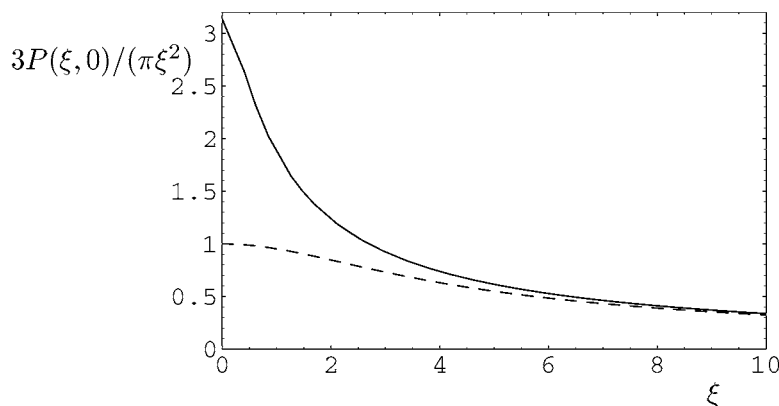


Figure 3. A plot of the function $P(\xi, 0)$ as given by equation (42) as a function of field ξ for $C = C_0$ (solid curve) and for $C = 0$ (dashed curve).

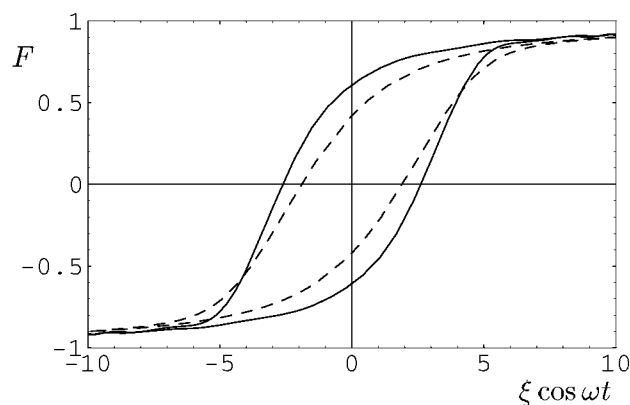


Figure 4. A parametric plot of magnetization $F(t)$ and field $\xi \cos \omega t$ for $\xi = 10$, $\omega \tau_R = 0.5$ for $C = C_0$ (solid curve) and for $C = 0$ (dashed curve).

For $\xi = 10$, $\omega \tau_R = 0.5$, one finds $\Phi_1 = 0.946$ for $C = 0$, and $\Phi_1 = 0.924$ for $C = C_0$. The corresponding values for the solution of the macroscopic equation are $\Phi_{1M} = 0.945$ for $C = 0$, and $\Phi_{1M} = 0.924$ for $C = C_0$. Even though the values of Φ_1 are not much less than unity, the hysteresis loop differs markedly from an ellipse. In order to get the accuracy quoted we need to include harmonics up to order 21. In figure 5 we show for fixed field $\xi = 10$ that the hysteresis loop becomes more and more elliptical as the frequency increases. At high frequency the solution tends to that for the weak-field limit, since the magnetization cannot follow the field.

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 $\omega_{mw} = (2 - 2C)/\tau_R$, corresponding to relaxation time $\tau_D/(1 - C)$. In figure 6 we plot the reduced first-harmonic response $P(\xi, \omega)/P(\xi, 0)$ as a function of $\log_{10} \omega \tau_R$ for $\xi = 10$ and $C = C_0$, 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

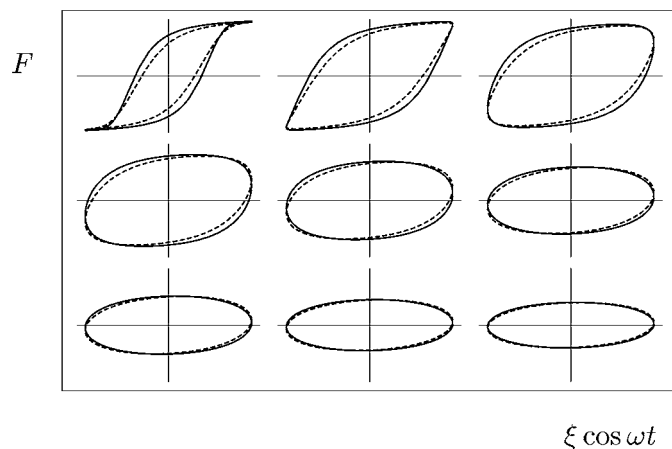


Figure 5. Parametric plots of magnetization $F(t)$ and field $\xi \cos \omega t$ for $\xi = 10$ for $C = C_0$ and frequencies $\omega \tau_R = 1, 3, 5, \dots, 17$ (solid curves), and corresponding plots for $C = 0$ (dashed curves).

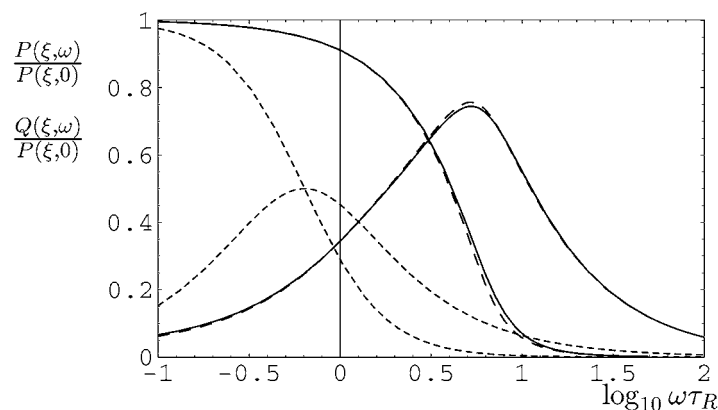


Figure 6. A plot of the reduced functions $P(\xi, \omega)/P(\xi, 0)$ and $Q(\xi, \omega)/P(\xi, 0)$ as functions of $\log_{10} \omega \tau_R$ for $\xi = 10$ (solid curves) and $C = C_0$, compared with the quantities $P_w(\xi, \omega)/P_w(\xi, 0)$ and $Q_w(\xi, \omega)/P_w(\xi, 0)$ valid in the weak-field 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).

approximate theory performs quite well. At the maximum at $\omega_m = 5.243 D_R$ the exact value is $Q(10, \omega_m) = 26.358$, whereas the approximate value is $Q_M(10, \omega_m) = 26.791$. At high frequency both curves tend to the expression for weak field, equation (27). This expression has its maximum $Q_w(10, (2 - 2C)D_R) = 164.236$ at $\omega_{mw} = (2 - 2C)D_R$. At the maximum $P(10, \omega_m) = 12.617$, whereas the approximate value is $P_M(10, \omega_m) = 11.778$. The value at zero frequency is $P(10, 0) = 35.401$.

5. Free energy, 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 production 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. It is of interest to see how our earlier discussion is affected by the local field effect.

We can associate an entropy per particle with the non-equilibrium distribution $f(\theta, t)$ according to Boltzmann's expression

$$\mathcal{S}(t) = -k \int_0^\pi f(\theta, t) \ln f(\theta, t) \sin \theta \, d\theta. \quad (44)$$

The corresponding free energy per particle is

$$\mathcal{F} = \mathcal{U} - T_0 \mathcal{S}, \quad (45)$$

where \mathcal{U} is the mean potential energy

$$\mathcal{U}(t) = \int_0^\pi \varepsilon(\theta, t) f(\theta, t) \sin \theta \, d\theta - \frac{3}{2} C k T_0 F^2(t), \quad (46)$$

with $\varepsilon(\theta, t) = -mH(t) \cos \theta$. Thus the free energy is a functional $\mathcal{F}[f]$ of the distribution function. Note the factor $\frac{1}{2}$ in the last term of equation (46) in comparison with the local field appearing in equation (32). The rate of change of the free energy is

$$\frac{d\mathcal{F}}{dt} = \int_0^\pi [\varepsilon(\theta, t) + kT_0 \ln f] \frac{\partial f}{\partial t} \sin \theta \, d\theta + \int_0^\pi \frac{\partial \varepsilon}{\partial t} f \sin \theta \, d\theta - 3CkT_0 F \frac{dF}{dt}. \quad (47)$$

Substituting equation (32) and performing an integration by parts we transform this to

$$\frac{d\mathcal{F}}{dt} = -kT_0 D_R \int_{-1}^1 (1-x^2) \left[\frac{\partial \ln f}{\partial x} - \xi \cos \omega t - 3CF \right]^2 f(x, t) \, dx - mF(t) \frac{dH}{dt}. \quad (48)$$

Integrating this expression over a period we find for the periodic solution of equation (32) the relation

$$\mathcal{D}(\xi, \omega) = \mathcal{Q}(\xi, \omega), \quad (49)$$

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

$$\mathcal{D}(\xi, \omega) = D_R \int_{-1}^1 \int_0^T (1-x^2) \left[\frac{\partial \ln f}{\partial x} - \xi \cos \omega t - 3CF \right]^2 f(x, t) \, dx \, dt. \quad (50)$$

Clearly the integrand is positive in the whole xt -rectangle. Hence the dissipation is positive. The relation (49) shows that the dissipation is calculated conveniently from the absorption, i.e. from the work done on the system.

For distributions of the exponential form

$$f_e(x, t) = \exp[\xi_e(t)x] / Z(\xi_e(t)), \quad (51)$$

so-called e-distributions, the free energy becomes a function $\mathcal{F}_e(F)$ of the magnetization F , or alternatively of the effective field ξ_e related to F by $F = L(\xi_e)$. By substitution of equation (51) into (44) one finds for the corresponding entropy

$$\mathcal{S}_e(F) = k \ln Z(\xi_e) - k\xi_e F. \quad (52)$$

Hence the free energy is

$$\beta \mathcal{F}_e(F, t) = (\xi_e - \xi \cos \omega t) F - \ln Z(\xi_e) - \frac{3}{2} C F^2. \quad (53)$$

We see by use of the relation

$$F = \frac{\partial \ln Z(\xi_e)}{\partial \xi_e} \quad (54)$$

that ξ_e is the thermodynamic force conjugate to F :

$$\xi_e = -\frac{1}{k} \frac{\partial \mathcal{S}_e(F)}{\partial F}. \quad (55)$$

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 (53) and (54) we find

$$\xi_e - \xi \cos \omega t - 3CF = \frac{\partial \beta \mathcal{F}_e}{\partial F}. \quad (56)$$

If at time t the distribution has the exponential form assumed in equation (51), then the rate of change of the magnetization at that time is

$$\left. \frac{dF}{dt} \right|_e = \int_{-1}^1 x \frac{\partial f_e}{\partial t} dx. \quad (57)$$

Substituting from equation (32) one finds

$$\left. \frac{dF}{dt} \right|_e = D_R (\xi \cos \omega t + 3CF - \xi_e) \langle \sin^2 \theta \rangle_{\xi_e}. \quad (58)$$

By use of equation (56) we can write

$$\left. \frac{dF}{dt} \right|_e = -\Gamma(F) \beta \frac{\partial \mathcal{F}_e}{\partial F} \quad (59)$$

with Onsager coefficient [19]

$$\Gamma(F) = D_R \langle \sin^2 \theta \rangle_{\xi_e(F)}. \quad (60)$$

One obtains the macroscopic relaxation equation (39) by postulating that

$$\frac{dF_M}{dt} = -\Gamma(F_M) \beta \frac{\partial \mathcal{F}_e}{\partial F_M} \quad (61)$$

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

$$\Gamma(F_M) = 2D_R \frac{F_M}{\xi_{eM}}. \quad (62)$$

Multiplying equation (61) by $\xi \cos \omega t + 3CF_M(t) - \xi_{eM}(t)$ and integrating over a period, we obtain by use of equation (56)

$$\int_0^T (\xi \cos \omega t + 3CF_M(t) - \xi_{eM}(t)) \frac{dF_M}{dt} dt = \int_0^T \Gamma(F_M) \left(\beta \frac{\partial \mathcal{F}_e}{\partial F_M} \right)^2 dt. \quad (63)$$

The left-hand side of this equation can be simplified to $Q_M(\xi, \omega)$ by use of equation (55), so the equation can be expressed as

$$Q_M(\xi, \omega) = \mathcal{D}_M(\xi, \omega) \quad (64)$$

with the macroscopic dissipation

$$\mathcal{D}_M(\xi, \omega) = \int_0^T \Gamma(F_M) \left(\beta \frac{\partial \mathcal{F}_e}{\partial F_M} \right)^2 dt. \quad (65)$$

The dissipation can be calculated from the absorption by use of equation (64). It is evident that $\mathcal{D}_M(\xi, \omega)$ provides a macroscopic approximation to the actual dissipation $\mathcal{D}(\xi, \omega)$, given by equation (50).

6. Discussion

Up till now we have assumed that the macroscopic sample has cylindrical shape, though with a cross-section that is not necessarily circular. As a consequence, for applied field parallel to the symmetry axis, the Maxwell field in the sample is identical to that field. For different macroscopic geometry the Maxwell field differs from the applied field, since the induced magnetization itself generates a field in addition to the applied field. The situation is simple only for a uniform ferrofluid in ellipsoidal geometry with applied field parallel to one of the axes. In that case, for applied field $\mathbf{H}_0(t) = H_0 \mathbf{e}_z \cos \omega t$ the Maxwell field inside the sample is uniform and given by

$$\mathbf{H}(t) = H_0 \mathbf{e}_z \cos \omega t - \gamma_S \mathbf{M}(t) \mathbf{e}_z, \quad (66)$$

where the last term is the demagnetizing field with shape-dependent factor γ_S . As a consequence the local field in equation (4) becomes

$$\mathbf{H}_{loc} = H_0 \mathbf{e}_z \cos \omega t + (\gamma - \gamma_S) \mathbf{M}(t) \mathbf{e}_z. \quad (67)$$

Hence all our preceding considerations apply with the replacement of the coefficient C by $\Delta_S = (\gamma - \gamma_S) \chi_0$. The periodic response of the system clearly depends on the sample shape via the coefficient γ_S . The Maxwell field in general will have a shape-dependent contribution of higher harmonics. Only for weak applied field is the response purely harmonic, and can one define a susceptibility $\chi(\omega)$ independent of sample shape, and given by equation (29). It is easy to show explicitly that in the linear regime the shape-dependent coefficient γ_S does not occur in the linear relation between \mathbf{M} and \mathbf{H} . More generally, it is clear that equations (4), (19), and (20) provide a mechanism by which any periodic function $\mathbf{H}(t)$ yields a periodic magnetization $\mathbf{M}(t)$ in the same direction. Thus there is a nonlinear mapping $\mathbf{M}(t) = \mathbf{X}[\mathbf{H}(t)]$ dependent on the local field factor γ , but not on the shape-dependent factor γ_S . In combination with equation (66) this provides an algorithm for finding the magnetization $\mathbf{M}(t)$ and the field $\mathbf{H}(t)$ by iteration. Clearly both the magnetization and the field depend on γ_S , even though the nonlinear mapping \mathbf{X} does not.

In summary, we have shown that the linear and nonlinear responses of a system of interacting dipoles to an applied oscillating field can be calculated from a nonlinear rotational diffusion equation with local field effect. The local response depends on the shape of the macroscopic sample according to Maxwell theory. We have derived explicit results for cylindrical and ellipsoidal geometry with applied field parallel to an axis of symmetry. The choice of cylindrical geometry yields direct insight into the local nonlinear constitutive equation.

In the linear regime the frequency-dependent susceptibility $\chi(\omega)$ is given by the simple expression (29). This extends the expressions (7) and (8) for the static response to nonzero frequency. The expression for the static response agrees much better with computer simulation data of Wang *et al* [18] for a system of hard spheres with dipolar interaction than Onsager's equation (9).

Admittedly, the local field picture represents a simplified model of the actual situation. Nonetheless it would be desirable to confront its predictions with experiment and computer simulation. The local field picture provides a benchmark to be compared with more sophisticated theories. Onsager's cavity model with its improvements provides suggestions for further exploration. A theory involving a typical pair of particles with interactions and correlations, as well as dielectric friction of the pair with its environment, including hydrodynamic effects, would necessarily be more involved.

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