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LECTURE NOTES 8

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Rotational Diffusion in Dispersive Media

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Preface

This book contains material from 10 lectures and a seminar given at the Centre of Excellence for Advanced Materials and Structures (AMAS) in the Institute of Fundamental Technological Research, Polish Academy of Sciences (IFTR PAS), Warsaw in May-June 2003. I want to express my thanks here to some of the many people who made my stay pleasant, stimulating and memorable. I thank Prof. Zenon Mróz for his invitation to visit AMAS and present a series of lectures. I thank Miss Izabela Śleczkowska for help with travel, accommodation and computer systems and Mr. Tomasz Zieliński for assistance in preparing these notes for publication. I thank Prof. Tomasz Kowalewski for explaining the interesting work of his group. Above all I thank Prof. Bogdan Cichocki of the Institute of Theoretical Physics of the University of Warsaw and Dr. Maria Ekiel-Jeżewska of the Department of Mechanics and Physics of Fluids in IFTR for continuous and overwhelming hospitality and for scientific collaboration of the highest quality.

Chapter 1

Introduction

Diffusion is a process of the widest occurrence, important as a transport mechanism in physics, chemistry, biology and engineering. It is seen in all phases of matter, solid, liquid and gaseous and it rests on a common set of theoretical ideas which give coherence to an enormous range of phenomena. Our theoretical understanding of diffusion originates in the work of Einstein [1], Smoluchowski [2, 3] and Langevin [4]. The initial description by Einstein referred to translational diffusion but as early as 1913 Debye [5, 6] extended the ideas to the rotational motion of polar molecules in order to understand the dielectric properties of polar liquids. Although we are much more familiar with translational diffusion, both translational and rotational diffusion are present in liquids and gases and the use of experimental techniques like depolarized light scattering, fluorescence depolarization, nuclear magnetic resonance, and more recently, photo-bleaching/fluorescence recovery as well as phosphorescence anisotropy has made it possible to observe rotational diffusion directly and in detail. For ferrofluids and suspensions of rigid rod polymers, rotational diffusion underlies and explains much of the macroscopic dynamical behaviour. For dense glassy colloid suspensions and for porous media filled with liquid, rotational diffusion is a useful probe of the local microstructure. In these lectures I shall introduce some of these ideas and applications but always starting from quite elementary situations. I will derive and explain the ideas explicitly in simple model cases, giving references to the literature for more technical aspects.

In Chapter 2 I introduce the ideas of diffusional dynamics in the context of translational diffusion. Using a simple Langevin description to get an idea of the time and length scales involved, we see how, on an appropriately long time scale, a Smoluchowski equation description can be set up to describe mesoparticle dynamics. Taking advantage of the simplicity of translational diffusion, a number of formal properties of Smoluchowski dynamics are illustrated. In Chapter 3 I consider Debye's original problem [5] of 1913, a sphere constrained to rotate about a fixed axis, in order to introduce the concept of rotational diffusion. I sketch briefly the two simple problems of response and relaxation which Debye posed and solved in that paper to set the background for later extensions of these two archetypal problems. In Chapters 4 and 5 I extend the description to full three-dimensional rotations as Debye did in 1929 [6]. In Chapter 6 a brief discussion of non-spherically symmetric particles is used to point out an area where difficult problems remain. In Chapter 7 I introduce the interaction of permanent and induced dipole moments with an external field with a description of the polarization and birefringence phenomena that follow from that interaction. In Chapter 8, the relaxation problem of Debye is extended to sudden changes of field which do not involve turning off the field completely. It is shown here how the time dependence of polarization and birefringence is controlled by the eigenspectrum of the adjoint Smoluchowski operator. In Chapter 9, Debye's problem of response to a sinusoidal field is extended to study the linear response in the presence of a static non-vanishing background field. For strong harmonic fields I show in Chapter 10 how one can study the non-linear response and how the Smoluchowski equation description can be approximated by an effective field description. In Chapter 11 the full generalized Smoluchowski equation for a many-body suspension of particles with rotational degrees of freedom is introduced and in Chapter 12 I outline how depolarized light scattering measurements can be used to extract information about both translational and rotational dynamics in the presence of many-body hydrodynamic interactions. In a final afterword I sketch some outstanding problems of current interest and give further reading suggestions to extend the content of the lectures and to point the way to physical applications for which there was no room in the lecture course.

Chapter 2

The physical assumptions underlying diffusion

Let us start by recalling the physical picture that underlies Einstein's discussion of the Brownian motion of a mesoscale sized particle suspended in a liquid of much smaller molecules. The mesoparticle is a particle of linear scale L where $5\,\mathrm{nm} \leq L \leq 1\,\mu\mathrm{m}$ and it is suspended in a molecular fluid of small, roughly spherical molecules of size $\ell_{\mathrm{molecule}} \approx 0.3\,\mathrm{nm}$. Such a large particle is subject to incessant collisions with the fluid molecules, each collision lasting of the order of 10^{-12} sec. In each single collision the momentum of the mesoparticle is scarcely changed. However, what we observe on a much longer time scale of times greater than about 10^{-6} sec is an erratic trajectory of the particle in configuration space. Thus the time scale of observation is much longer than the time scale of the microscopic dynamics (individual collisions). This separation of time scales is necessary to get a simple theoretical picture and it will be a feature of all the examples I shall discuss below.

The microscopic dynamics is given by Newton's equations for all the particles both large and small, or, alternatively, by the Liouville equation in the phase space of the mesoparticles and suspending molecules. However, we need a simplified description on the long time scale which incorporates the underlying physical picture of many extremely rapid collisions leading to slow erratic movement in configuration. We can incorporate both elements in a phenomenological way by using the Langevin description [4, 7, 8]. For simplicity we look at a one-dimensional system. Let $x(t)$ be the position of the mesoparticle at time t. Then, we simplify its equation of motion by writing

$$\begin{aligned} m\ddot{x} &= \textit{Force due to all other fluid particles} \\ &= \textit{Average Force} + \textit{Fluctuating Force}\,. \end{aligned}$$

The average force on a moving particle is a drag force which we represent by $-\zeta\dot{x}$ with friction constant ζ, and we can approximate ζ by its Stokes Law value (for a spherical particle)

$$\zeta = 6\pi\eta a\,,$$

where η is the shear viscosity of the suspending fluid and a is the radius of the particle.

We represent the fluctuating force by a stochastic force called the Langevin force $L(t)$. The force $L(t)$ is regarded as a stochastic process defined only by its statistical properties. These statistical properties relate to an ensemble of mesoparticles each one of which is a realization of a diffusion process. Statistical averages are interpreted as averages over this ensemble of systems. To specify $L(t)$ uniquely we must specify all its time correlation functions [7]. Specifically, $L(t)$ has zero mean

$$\langle L(t)\rangle = 0\,, \tag{2.1}$$

delta function 2-point correlations

$$\langle L(t)L(t')\rangle = \Gamma\delta(t-t')\,, \tag{2.2}$$

and factorization of higher order correlations

$$\begin{aligned} \langle L(t_1)L(t_2)L(t_3)L(t_4)\rangle &= \langle L(t_1)L(t_2)\rangle\langle L(t_3)L(t_4)\rangle \\ &+ \langle L(t_1)L(t_3)\rangle\langle L(t_2)L(t_4)\rangle + \langle L(t_1)L(t_4)\rangle\langle L(t_2)L(t_3)\rangle\,, \end{aligned} \tag{2.3}$$

with analogous factorization for general $2n$-point correlations and vanishing of all odd order correlations. With these properties we say that $L(t)$ is an example of Gaussian white noise [7].

The mesoparticle equation of motion now becomes

$$m\ddot{x} = -\zeta\dot{x} + L(t)\,, \tag{2.4}$$

which makes $x(t)$ itself a stochastic process (linear functional of $L(t)$) whose stochastic properties follow from those of $L(t)$. To see this explicitly, we can integrate the Langevin equation in the following form

$$\frac{d}{dt}\left(e^{\zeta t/m} m\dot{x}\right) = e^{\zeta t/m} L(t)\,,$$
$$\dot{x}(t) = v_0 e^{-\zeta t/m} + \frac{1}{m} e^{-\zeta t/m} \int_0^t e^{\zeta t_1/m} L(t_1)dt_1\,, \tag{2.5}$$

where v_0 is the initial velocity $\dot{x}(0)$. If we average (2.5) over the ensemble we get for the mean velocity

$$\langle \dot{x}(t) \rangle = v_0 e^{-\zeta t/m}\,, \tag{2.6}$$

which vanishes as $t \to \infty$ with a decay time $\tau_p = m/\zeta$ which is a characteristic momentum decay time. We can next look at the mean of the squared velocity using the delta correlation (2.2)

$$\langle \dot{x}^2(t) \rangle = v_0^2 e^{-2\zeta t/m}$$
$$+ \frac{1}{m^2} e^{-2\zeta t/m} \int_0^t e^{\zeta t_1/m} dt_1 \int_0^t e^{\zeta t_2/m} \langle L(t_1)L(t_2)\rangle dt_2\,, \tag{2.7}$$
$$\langle \dot{x}^2(t) \rangle = v_0^2 e^{-2\zeta t/m} + \frac{\Gamma}{2m\zeta}\left(1 - e^{-2\zeta t/m}\right).$$

As $t \to \infty$, this gives $\langle \dot{x}^2(t) \rangle \to \frac{\Gamma}{2m\zeta}$, but from equilibrium statistical mechanics this limit should be $\langle \frac{1}{2} m\dot{x}^2 \rangle_{\rm eq} = \frac{1}{2} k_B T$ giving

$$\Gamma = 2k_B T\zeta\,, \tag{2.8}$$

which is an example of the fluctuation-dissipation theorem.

We can integrate once more to obtain the configuration $x(t)$.

$$x(t) - x(0) = \int_0^t \dot{x}(t)dt$$
$$= v_0 \int_0^t e^{-\zeta t_1/m} dt_1 + \frac{1}{m} \int_0^t e^{-\zeta t_1/m} dt_1 \int_0^{t_1} e^{\zeta t_2/m} L(t_2) dt_2\,,$$
$$x(t) - x(0) = \frac{m v_0}{\zeta}\left(1 - e^{-\zeta t/m}\right) + \frac{1}{\zeta} \int_0^t \left(1 - e^{\zeta (t_1 - t)/m}\right) L(t_1) dt_1\,.$$

Next we can calculate the mean squared displacement

$$
\begin{aligned}
\langle (x(t)-x(0))^2\rangle &= \left(\frac{mv_0}{\zeta}\right)^2 \left(1-e^{-\zeta t/m}\right)^2 \\
&\quad + \frac{\Gamma}{\zeta^2}\int_0^t \left(1-e^{\zeta(t_1-t)/m}\right)^2 dt_1\,, \\
\langle (x(t)-x(0))^2\rangle &= \left(\frac{m}{\zeta}\right)^2 \left(v_0^2-\frac{k_BT}{m}\right)\left(1-e^{-\zeta t/m}\right)^2 \\
&\quad + \frac{2k_BT}{\zeta}\left[t-\frac{m}{\zeta}\left(1-e^{-\zeta t/m}\right)\right].
\end{aligned}
\tag{2.9}
$$

In doing the integrals here we have used (2.2) and then the fluctuation-dissipation relation (2.8). In the limit of large t we get

$$
\begin{aligned}
\langle (x(t)-x(0))^2\rangle_{t\to\infty} &\approx \frac{2k_BT}{\zeta}t + \left(\frac{m}{\zeta}\right)^2\left(v_0^2-\frac{3k_BT}{m}\right) \\
&= \frac{2k_BT}{\zeta}t + \tau_p^2\left(v_0^2-\frac{3k_BT}{m}\right),
\end{aligned}
$$

where τ_p is the damping time of the momentum. Thus on a long time scale we have the diffusive result

$$\langle (x(t)-x(0))^2\rangle_{t\to\infty} \approx 2Dt\,,$$

where the diffusion coefficient is given by the Einstein relation

$$D=\frac{k_BT}{\zeta}. \tag{2.10}$$

It is useful to estimate the magnitude of some of the quantities introduced above. For that purpose let us treat the mesoparticle as a hard sphere of radius a, mass density ρ, in a fluid of shear viscosity η. Then, from $m=\frac{4}{3}\pi a^3\rho$ and $\zeta = 6\pi\eta a$ we find

$$\tau_p=\frac{m}{\zeta}=\frac{2\rho a^2}{9\eta}, \tag{2.11}$$

which for values $a = 100\,\mathrm{nm}$, $\rho = 10^3\ \mathrm{kg\,m^{-3}}$, and $\eta = 0.01$ poise, gives $\tau_p \approx 2\times 10^{-9}$ sec. For the diffusion coefficient D we find $D = k_BT/\zeta \approx 2.2\times 10^{-12}\ \mathrm{m^2\,sec^{-1}}$. We can ask for the time τ_c required to move a distance equal to the particle radius

$$\langle \Delta x^2\rangle = 2D\tau_c = a^2\,,$$

giving

$$\tau_c = \frac{3\pi\eta a^3}{k_B T}\,. \tag{2.12}$$

For the particle above with radius $a = 100\,\text{nm}$, we find $\tau_c = 2.3 \times 10^{-3}\,\text{sec}$ while for a radius of one micron $\tau_c = 2.3\,\text{sec}$. The point to remember here is that $\tau_c \gg \tau_p$, the momentum of the particle has relaxed long before we could observe any appreciable change of configuration. Thus the slow time scale on which diffusion is manifest is truly macroscopic as opposed to the microscopic time scales of the momentum dynamics.

We note that if on this slow time scale we neglect momentum change in the Langevin equation (neglect particle inertia), we have the simpler equation $0 = -\zeta\dot{x} + L(t)$ or

$$\dot{x} = \frac{1}{\zeta}L(t)\,. \tag{2.13}$$

Exercise 2.1: *Integrate this simplified equation and show that*

$$\langle (x(t) - x(0))^2 \rangle = \frac{\Gamma}{\zeta^2}t\,. \tag{2.14}$$

There are gross over-simplifications above but the qualitative picture is extremely useful in identifying important timescales in the problem. If we want a simplified description of our system on the slow time scale $t \gg \tau_p$, in which only configuration $x(t)$ plays a role, we use a Smoluchowski description [3, 7, 8, 9]. In this picture we consider an ensemble of N mesoparticles with a probability density $P(x,t)$ of finding a particle at position x at time t. The number density $n(x,t)$ of particles at x at time t is $n(x,t) = NP(x,t)$. The probability density is normalized and obeys a conservation equation,

$$\int P(x,t)\,dx = 1\,, \tag{2.15}$$

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial j(x,t)}{\partial x}\,. \tag{2.16}$$

The flux or current density is related to $P(x,t)$ by Fick's Law

$$j(x,t) = -D\frac{\partial P(x,t)}{\partial x}\,, \tag{2.17}$$

where we introduce the macroscopic diffusion constant D. From (2.16) and (2.17) we get

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} = \mathcal{D}P(x,t)\,, \tag{2.18}$$

which is the diffusion equation or the Smoluchowski equation, with Smoluchowski operator

$$\mathcal{D} = D\frac{\partial^2}{\partial x^2} \,. \tag{2.19}$$

We can select the sub-ensemble of particles that were at position x_0 at time $t = 0$ and we introduce a special solution $P(x, t|x_0)$, the probability density of finding a particle at position x at time t, given that it was at x_0 at time $t = 0$. This special solution of the Smoluchowski equation has as initial condition

$$P(x, 0|x_0) = \delta(x - x_0) \,. \tag{2.20}$$

Explicitly it is

$$P(x, t|x_0) = e^{\mathcal{D}t}\,\delta(x - x_0) = \frac{1}{\sqrt{4\pi Dt}}\exp\frac{-(x - x_0)^2}{4Dt} \,. \tag{2.21}$$

Exercise 2.2: *Using*

$$\delta(x - x_0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik(x-x_0)}\,dk \,,$$

derive (2.21) by applying the operator $\exp(\mathcal{D}t)$ *and doing the integration over* k.

It follows from (2.21) that the mean squared displacement in time t is given by

$$\langle (x(t) - x(0))^2 \rangle = \int_{-\infty}^{\infty} (x - x_0)^2 P(x, t|x_0)\,dx = 2Dt \,, \tag{2.22}$$

recovering the same result as we had from the Langevin equation on the long time scale $t \gg \tau_p$.

Next, suppose that the particle is subject to an external force arising from a potential $V(x)$, $F(x) = -\partial V/\partial x$. The Langevin equation is modified to

$$m\ddot{x} = -\zeta\dot{x} + F(x) + L(t) \,,$$

where we assume that $L(t)$ has the same statistical properties as in the absence of $F(x)$. Note that, apart from harmonic potentials, the Langevin equation is no longer linear. In the light of the time scale discussion above, we again neglect the inertial term to get the first order equation

$$\dot{x} = \frac{1}{\zeta}F(x) + \frac{1}{\zeta}L(t) = \mu F(x) + \mu L(t)\,, \tag{2.23}$$

where we have introduced the mobility, $\mu = 1/\zeta$. If we average this equation

$$\langle \dot{x} \rangle = \mu \langle F(x) \rangle\,,$$

and assume that $F(x)$ varies slowly in space, $\langle F(x) \rangle \approx F(\langle x \rangle)$, we see that the external force produces a steady drift at a velocity determined by the mobility,

$$\langle \dot{x} \rangle = \mu F(\langle x \rangle)\,. \tag{2.24}$$

In the Smoluchowski description we argue that the presence of the force $F(x)$ generates an advective current j_{Ad} associated with the force which is in addition to the Brownian current j_B arising from Fick's Law,

$$\begin{aligned} j = j_B + j_{Ad} &= -D\frac{\partial P}{\partial x} + \langle \dot{x} \rangle P\,, \\ j(x,t) &= -D\frac{\partial P(x,t)}{\partial x} + \mu F(x) P(x,t) \\ &= -D\frac{\partial P(x,t)}{\partial x} - \mu \frac{\partial V(x)}{\partial x} P(x,t)\,, \end{aligned} \tag{2.25}$$

leading to a Smoluchowski equation [3]

$$\frac{\partial P}{\partial t} = -\frac{\partial j}{\partial x} = D\frac{\partial^2 P}{\partial x^2} + \mu \frac{\partial}{\partial x}\left(\left(\frac{\partial V}{\partial x}\right) P\right). \tag{2.26}$$

For free diffusion ($F = 0$) there is no steady solution, but in a potential $V(x)$ there can be such an equilibrium solution characterized by $\partial P_{\mathrm{eq}}/\partial t = 0$, $j_{\mathrm{eq}} = 0$,

$$j_{\mathrm{eq}} = -D\frac{\partial P_{\mathrm{eq}}}{\partial x} - \mu \frac{\partial V}{\partial x} P_{\mathrm{eq}} = 0\,.$$

Integrating to find P_{eq} gives

$$P_{\mathrm{eq}}(x) = \frac{1}{Z} \exp -\frac{\mu}{D} V(x)\,, \tag{2.27}$$

with normalizing constant Z. However, from equilibrium statistical mechanics we know that P_{eq} has Boltzmann form,

$$P_{\mathrm{eq}}(x) = \frac{1}{Z} \exp -\frac{V(x)}{k_B T}\,, \tag{2.28}$$

giving $\mu/D = 1/k_BT$ or $D = k_BT\mu = k_BT/\zeta$ which is the Einstein relation (2.10) again. Using this result we re-express the current as

$$j = -D\frac{\partial P}{\partial x} - D\frac{\partial \beta V}{\partial x}P\,, \tag{2.29}$$

where $\beta = 1/k_BT$, and the diffusion equation as

$$\frac{\partial P}{\partial t} = D\left[\frac{\partial^2 P}{\partial x^2} + \frac{\partial}{\partial x}\left(\left(\frac{\partial \beta V}{\partial x}\right)P\right)\right] = \mathcal{D}P\,, \tag{2.30}$$

with Smoluchowski operator

$$\mathcal{D} = D\frac{\partial}{\partial x}e^{-\beta V}\frac{\partial}{\partial x}e^{\beta V}\,. \tag{2.31}$$

In conjunction with the Smoluchowski operator we can introduce a scalar product between real functions of configuration $u(x)$, $v(x)$,

$$(u,v) = \int_{-\infty}^{\infty} u(x)v(x)\,dx\,. \tag{2.32}$$

Associated with this scalar product is a Green identity obtained by integrating by parts

$$\begin{aligned}(u,\mathcal{D}v) &= D\int u(x)\frac{\partial}{\partial x}e^{-\beta V}\frac{\partial}{\partial x}e^{\beta V}v(x)dx\,,\\ &= D\int\left(e^{\beta V}\frac{\partial}{\partial x}e^{-\beta V}\frac{\partial u}{\partial x}\right)v(x)dx = (\mathcal{L}u,v)\,,\end{aligned} \tag{2.33}$$

where we assume appropriate boundary conditions so that all surface terms vanish. The operator

$$\mathcal{L} = De^{\beta V}\frac{\partial}{\partial x}e^{-\beta V}\frac{\partial}{\partial x} = \mathcal{D}^\dagger \tag{2.34}$$

is called the adjoint Smoluchowski operator.

The operator $\mathcal{L}$ is of great usefulness in expressing time dependent averages. For example, given an observable $M(x)$, we can ask what is its conditional average at time t given that the particle started at x_0 at time $t = 0$

$$\begin{aligned}\langle M(x(t))\rangle_{x_0} &= \int M(x)P(x,t|x_0)dx = \int M(x)e^{\mathcal{D}t}\delta(x-x_0)dx\\ &= \int\left(e^{\mathcal{L}t}M(x)\right)\delta(x-x_0)dx = e^{\mathcal{L}t}M(x)|_{x=x_0}\,.\end{aligned} \tag{2.35}$$

Here we have integrated by parts repeatedly as in (2.33) to replace the operator $\mathcal{D}$ by the adjoint operator $\mathcal{L}$. For infinitesimal time $t = dt$, we expand $\exp \mathcal{L}dt = 1 + dt\mathcal{L} + \mathcal{O}(dt^2)$ to calculate

$$\langle M(x(t))\rangle_{x_0} = M(x_0) + dt\mathcal{L}M(x)|_{x=x_0} + \dots \,. \tag{2.36}$$

Thus, for $M(x) = x$,

$$\begin{aligned}
\langle x(dt)\rangle_{x_0} &= x_0 + dtDe^{\beta V}\frac{\partial}{\partial x}e^{-\beta V}\frac{\partial x}{\partial x}|_{x=x_0} + \dots \\
&= x_0 - dtD\frac{\partial\,\beta V(x)}{\partial x}|_{x=x_0} + \dots \\
&= x_0 + dt\beta DF(x_0) + \dots\,,
\end{aligned}$$

or

$$\langle x(dt) - x(0)\rangle_{x_0} = dt\,\mu F(x_0) + \dots\,, \tag{2.37}$$

where we recognize the drift velocity expression from (2.24).

Exercise 2.3: *Show that*

$$\langle (x(dt) - x(0))^2\rangle_{x_0} = 2Ddt + \mathcal{O}(dt^2)\,. \tag{2.38}$$

Exercise 2.4: *Show that for even integer values n*

$$\langle (x(dt) - x(0))^n\rangle_{x_0} = \mathcal{O}(dt^{n/2})\,. \tag{2.39}$$

If, instead of these conditional averages, we are interested in equilibrium time correlation functions we proceed somewhat differently. If $A(x)$ and $B(x)$ are two observables, then we can express the time correlation function $C_{AB}(t)$ as follows where angled brackets denote equilibrium averages

$$\begin{aligned}
C_{AB}(t) = \langle A(x(0))B(x(t))\rangle &= \int dx_0 dx P_{\text{eq}}(x_0)P(x,t|x_0)A(x_0)B(x) \\
&= \int dx_0 dx P_{\text{eq}}(x_0)B(x)\left(e^{\mathcal{D}t}\delta(x-x_0)\right)A(x_0) \\
&= \int dx_0 dx P_{\text{eq}}(x_0)\left(e^{\mathcal{L}t}B(x)\right)A(x_0)\delta(x-x_0) \\
&= \int dx P_{\text{eq}}(x)A(x)e^{\mathcal{L}t}B(x) = \langle Ae^{\mathcal{L}t}B\rangle\,.
\end{aligned} \tag{2.40}$$

The Laplace transform of time correlation functions is also of interest. It can be expressed as

$$\begin{aligned}\hat{C}_{AB}(s) &= \int_0^\infty e^{-st} C_{AB}(t)dt = \int dx P_{\text{eq}}(x)A(x)\int_0^\infty dt\, e^{-(s-\mathcal{L})t}B(x) \\ &= \langle A(s-\mathcal{L})^{-1}B\rangle\,.\end{aligned} \tag{2.41}$$

Equivalently we can use a Fourier-Laplace transform, $s \to -i\omega$,

$$\hat{C}_{AB}(\omega) = \int_0^\infty e^{i\omega t} C_{AB}(t)dt = -\langle A(i\omega + \mathcal{L})^{-1}B\rangle\,. \tag{2.42}$$

We can say something about the detailed time dependence of $C_{AB}(t)$ from the eigenvalue spectrum of the operator $\mathcal{L}$. Consider the eigenvalue problem

$$\mathcal{L}\phi_i = -D\lambda_i\phi_i\,, \tag{2.43}$$

which, from the form of $\mathcal{L}$ given in (2.34), has the special eigenvalue $\lambda_0 = 0$ corresponding to the eigenfunction $\phi_0(x) = 1$. From the form of the operators $\mathcal{D}$, $\mathcal{L}$ given in (2.31) and (2.34) there follows the identity

$$\mathcal{D}P_{\text{eq}}(x)f(x) = P_{\text{eq}}(x)\mathcal{L}f(x)\,, \tag{2.44}$$

for any function of configuration $f(x)$, so that if we define functions $\psi_i(x) = P_{\text{eq}}(x)\phi_i(x)$, we find another eigenvalue problem with the same spectrum,

$$\mathcal{D}\psi_i = -D\lambda_i\psi_i\,. \tag{2.45}$$

The special eigenfunction corresponding to the zero eigenvalue $\lambda_0 = 0$ is simply the equilibrium distribution, $\psi_0(x) = P_{\text{eq}}(x)\phi_0(x) = P_{\text{eq}}(x)$. Using (2.33) it is easy to show that

$$(\lambda_i - \lambda_j)(\phi_i, \psi_j) = 0\,. \tag{2.46}$$

Thus we can choose the ϕ_i, ψ_j as a bi-orthonormal set

$$(\phi_i, \psi_j) = (\psi_j, \phi_i) = \delta_{ij}\,. \tag{2.47}$$

Moreover, from the expression (2.34) for $\mathcal{L}$ we deduce

$$\lambda_i = -\frac{1}{D}(\psi_i, \mathcal{L}\phi_i) = \int P_{\text{eq}}(x)\left(\frac{\partial\phi_i(x)}{\partial x}\right)^2 dx \geq 0\,. \tag{2.48}$$

We can use the eigensolutions to expand observables $A(x)$, $B(x)$ as

$$
\begin{aligned}
A(x) &= \sum_{i=0}^{\infty} a_i \phi_i(x)\,, \quad a_i = (\psi_i, A)\,, \\
B(x) &= \sum_{i=0}^{\infty} b_i \phi_i(x)\,, \quad b_i = (\psi_i, B)\,,
\end{aligned}
\tag{2.49}
$$

noting the special expansion coefficients associated with the zero eigenvalue, $a_0 = (\psi_0, A) = (P_{\text{eq}}, A) = \langle A \rangle$, $b_0 = \langle B \rangle$. Using these expansions in the time correlation function expression (2.40) gives

$$
C_{AB}(t) = \langle A \rangle \langle B \rangle + \sum_{i>0} a_i b_i e^{-D\lambda_i t}\,. \tag{2.50}
$$

Since $\lambda_i \geq 0$, we see that the time correlation functions are examples of relaxation processes, given as a sum of decaying exponential functions of time. We define normalized relaxation functions as follows

$$
\Gamma_{AB}(t) = \frac{C_{AB}(t) - C_{AB}(\infty)}{C_{AB}(0) - C_{AB}(\infty)} = \frac{C_{AB}(t) - \langle A \rangle \langle B \rangle}{\langle AB \rangle - \langle A \rangle \langle B \rangle}\,, \tag{2.51}
$$

with the properties $\Gamma_{AB}(0) = 1$ and $\Gamma_{AB}(t \to \infty) \to 0$.

There are two important correlation times we can define to characterize the relaxation. One is a short-time decay time τ_S defined by the initial slope of $\Gamma_{AB}(t)$,

$$
\tau_S^{-1} = -\dot{\Gamma}_{AB}(0) = -\frac{\dot{C}_{AB}(0)}{\langle AB \rangle - \langle A \rangle \langle B \rangle} = -\frac{\langle A \mathcal{L} B \rangle}{\langle AB \rangle - \langle A \rangle \langle B \rangle}\,. \tag{2.52}
$$

There is a long-time relaxation time τ_L defined by

$$
\tau_L = \int_0^{\infty} \Gamma_{AB}(t)\,dt\,. \tag{2.53}
$$

If we use the eigenfunction expansion (2.50) and define $\Delta A = A - \langle A \rangle$, $\Delta B = B - \langle B \rangle$, we can show that

$$
\tau_L = -\frac{\langle \Delta A\, \mathcal{L}^{-1} \Delta B \rangle}{\langle \Delta A\, \Delta B \rangle}\,. \tag{2.54}
$$

Exercise 2.5: *Show that*

$$
\tau_S^{-1} = -\frac{\langle \Delta A\, \mathcal{L}\, \Delta B \rangle}{\langle \Delta A\, \Delta B \rangle}\,. \tag{2.55}
$$

As a final observation in this section I note yet another way to write the current density in the Smoluchowski equation. We can re-write (2.29) as

$$j = -\mu\left(\frac{\partial k_B T \ln P}{\partial x} + \frac{\partial V}{\partial x}\right) P = \mu(F_B(x,t) + F(x))P(x,t)\,, \qquad (2.56)$$

where we have introduced a so-called Brownian force $F_B(x,t)$ which is expressible in terms of a Brownian potential V_B,

$$V_B(x,t) = k_B T \ln P(x,t)\,, \quad F_B = -\frac{\partial V_B}{\partial x}\,. \qquad (2.57)$$

Each force, F_B and F, can be thought of as giving rise via the mobility to an associated velocity $v_B = \mu F_B$, $v_{Ad} = \mu F$, in terms of which the current (2.56) takes the form

$$j = (v_B + v_{Ad})P = vP\,. \qquad (2.58)$$

The Smoluchowski equation then has the simple form of an equation of continuity,

$$\frac{\partial P}{\partial t} + \frac{\partial}{\partial x}(vP) = 0\,. \qquad (2.59)$$

Although we have spent this entire chapter discussing translational diffusion in one dimension, all of the results will be generalized in the following chapters to describe rotational diffusion. Each of the formal properties discussed above will have its analogue in the more complicated description of rotating particles.

Chapter 3

Debye's problem of a rigid rotator

3.1. Smoluchowski description of rotation

Consider next a spherical particle with a special direction picked out in it, say a net dipole moment $\boldsymbol{m}$ which we can write as $\boldsymbol{m} = m\boldsymbol{u}$ with $\boldsymbol{u}$ a unit vector. Suppose further that the particle is constrained to rotate only about a fixed axis through its centre which is perpendicular to $\boldsymbol{u}$ and that it is immersed in a molecular fluid. By choosing x and y axes in the plane in which $\boldsymbol{u}$ moves we can represent the configuration by a single angle φ.

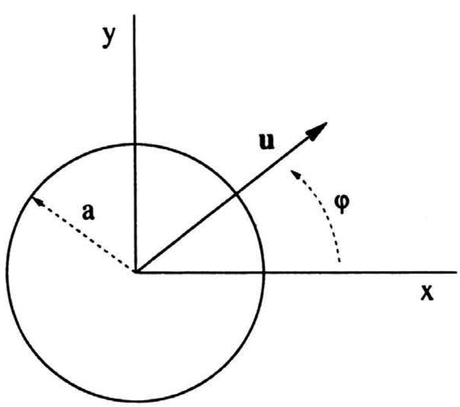

FIGURE 3.1.

Collisions with the fluid molecules will generate a fluctuating torque on the sphere, while on the other hand, if we try to rotate the sphere by an externally applied torque there will be a systematic drag resistance to rotation. Thus we could write a Langevin-like equation for the angular momentum L about the rotation axis (z-axis)

$$\dot{L} = I\ddot{\varphi} = -\zeta^{\mathrm{r}}\dot{\varphi} + T_B(t)\,, \tag{3.1}$$

where I is the moment of inertia about the rotation axis, ζ^{r} is a rotational friction coefficient and T_B is a fluctuating Brownian torque with statistical properties similar to those of the earlier Langevin force $L(t)$ given in (2.1), (2.2),

$$\langle T_B(t)\rangle = 0\,, \qquad \langle T_B(t)T_B(t')\rangle = \Gamma^{\mathrm{r}}\delta(t-t')\,. \tag{3.2}$$

We can average the equation to get

$$\frac{d\langle L\rangle}{dt} = -\zeta^{\mathrm{r}}\langle\dot{\varphi}\rangle = -\frac{\zeta^{\mathrm{r}}}{I}\langle L\rangle\,. \tag{3.3}$$

It follows that on average, the angular momentum will decay with a decay time $\tau_L = I/\zeta^{\mathrm{r}}$. For a sphere of uniform density ρ and radius a, $I = 2ma^2/5 = 8\pi\rho a^5/15$. The rotational drag is given by the Stokes friction for rotation, $\zeta^{\mathrm{r}} = 8\pi\eta a^3$, so we find

$$\tau_L = \frac{\rho a^2}{15\eta} = \frac{3}{10}\tau_p\,, \tag{3.4}$$

where τ_p is the momentum relaxation time given in (2.11). As in the earlier estimate, for a particle of size $a = 10^{-7}$ m, angular momentum will decay on a time scale of 10^{-9} sec. Thus, just as with translational motion, on time scales longer than about 10^{-6} sec we can ignore the inertial term to get a rotational Langevin equation of the form

$$\zeta^{\mathrm{r}}\dot{\varphi} = T_B(t)\,. \tag{3.5}$$

We integrate exactly as in the translational case to get

$$\langle\dot{\varphi}^2(t)\rangle = \langle\dot{\varphi}^2(0)\rangle e^{-2\zeta^{\mathrm{r}}t/I} + \frac{\Gamma^{\mathrm{r}}}{2I\zeta^{\mathrm{r}}}\left(1 - e^{-2\zeta^{\mathrm{r}}t/I}\right). \tag{3.6}$$

At long times, $t \to \infty$, we find that the mean squared angular velocity tends to a constant value

$$\lim_{t\to\infty}\langle\dot{\varphi}^2(t)\rangle = \frac{\Gamma^{\mathrm{r}}}{2I\zeta^{\mathrm{r}}} = \frac{k_BT}{I}\,,$$

where we used the equilibrium equipartition result $\langle \frac{1}{2} I \dot{\varphi}^2 \rangle_{\text{eq}} = \frac{1}{2} k_B T$. We find the fluctuation-dissipation result corresponding to (2.8)

$$\Gamma^{\text{r}} = 2\zeta^{\text{r}} k_B T \,. \tag{3.7}$$

For angular displacements we find on the slow time scale as in the translational case

$$\langle (\varphi(t) - \varphi(0))^2 \rangle = \frac{2k_B T}{\zeta^{\text{r}}} t = 2D^{\text{r}} t \,, \tag{3.8}$$

with rotational diffusion coefficient

$$D^{\text{r}} = \frac{k_B T}{\zeta^{\text{r}}} = k_B T \mu^{\text{r}} \,. \tag{3.9}$$

However, in interpreting (3.8) we must remember that physically the angles φ and $\varphi + 2\pi$ are identical so that the result is identical to that for translational diffusion only in a mathematical sense.

To write the corresponding Smoluchowski equation we introduce a probability density $P(\varphi, t)$ for finding the vector $\boldsymbol{u}$ at angle φ at time t. Again write a continuity equation

$$\frac{\partial P(\varphi, t)}{\partial t} = -\frac{\partial j(\varphi, t)}{\partial \varphi} \,, \tag{3.10}$$

with current

$$j(\varphi, t) = -D^{\text{r}} \frac{\partial P(\varphi, t)}{\partial \varphi} \,, \tag{3.11}$$

giving a rotational diffusion equation

$$\frac{\partial P(\varphi, t)}{\partial t} = D^{\text{r}} \frac{\partial^2 P(\varphi, t)}{\partial \varphi^2} = \mathcal{D}^{\text{r}} P(\varphi, t) \,. \tag{3.12}$$

As in (2.56) and (2.57) we can express the current in terms of an angular velocity arising from a Brownian torque T_B through a rotational mobility

$$j_B(\varphi, t) = \dot{\varphi}_B P(\varphi, t) \,, \tag{3.13}$$

where

$$\begin{gathered} \dot{\varphi}_B = \mu^{\text{r}} T_B \,, \qquad T_B = -\frac{\partial V_B}{\partial \varphi} \,, \\ V_B(\varphi, t) = k_B T \ln P(\varphi, t) \,. \end{gathered} \tag{3.14}$$

The only difference from translational diffusion (2.18) is that physically we have periodicity in φ, $P(\varphi + 2\pi, t) = P(\varphi, t)$, and the physical space is compact and finite rather than infinite. Once again we can ask for the conditional probability density, $P(\varphi, t|\varphi_0)$, of finding the vector $\boldsymbol{u}$ at angle φ at time t given that it was at φ_0 at time $t = 0$. We solve (3.12) with initial condition

$$P(\varphi, 0|\varphi_0) = \delta(\varphi - \varphi_0). \tag{3.15}$$

The solution is easily found using a Fourier series

$$\begin{aligned} P(\varphi, t|\varphi_0) &= \frac{1}{2\pi}\left[1 + 2\sum_{m=1}^{\infty} e^{-D^{\mathrm{r}} m^2 t} \cos m(\varphi - \varphi_0)\right] \\ &= \frac{1}{2\pi}\Theta_3(\frac{1}{2}(\varphi - \varphi_0), e^{-D^{\mathrm{r}} t}), \end{aligned} \tag{3.16}$$

where $\Theta_3(z, \tau)$ is the Jacobian theta function of the third kind. By using the result from Whittaker and Watson [10]

$$\Theta_3(z, \tau) = (-i\tau)^{-1/2} \exp\left(\frac{z^2}{i\pi\tau}\right) \Theta_3(\frac{z}{\tau}, -\frac{1}{\tau}), \tag{3.17}$$

we obtain $P(\varphi, t|\varphi_0)$ also as

$$P(\varphi, t|\varphi_0) = \frac{1}{\sqrt{4\pi D^{\mathrm{r}} t}} \sum_{n=-\infty}^{\infty} \exp\left[-\frac{(\varphi - \varphi_0 - 2n\pi)^2}{4D^{\mathrm{r}} t}\right]. \tag{3.18}$$

For short times and for values $\varphi \approx \varphi_0$, we have

$$P(\varphi, t|\varphi_0) \approx \frac{1}{\sqrt{4\pi D^{\mathrm{r}} t}} \exp\left[-\frac{(\varphi - \varphi_0)^2}{4D^{\mathrm{r}} t}\right] + \dots, \tag{3.19}$$

where the omitted terms are exponentially small. Thus at short times the conditional probability looks like translational diffusion but at long times the behaviour is quite different,

$$P(\varphi, t|\varphi_0) \approx \frac{1}{2\pi}, \quad t \to \infty. \tag{3.20}$$

Suppose now that there is an external torque due to an electric field $\boldsymbol{E}$ in the x-direction. There will be an external potential energy

$$V(\varphi) = -\boldsymbol{m} \cdot \boldsymbol{E} = -mE\cos\varphi, \tag{3.21}$$

corresponding to a torque

$$T_{\text{ext}} = -\frac{\partial V}{\partial \varphi} = -mE\sin\varphi = (\boldsymbol{m} \times \boldsymbol{E})_z\,. \tag{3.22}$$

The flux density in the Smoluchowski equation now has an extra contribution (compare (2.58))

$$j = (\dot{\varphi}_{\text{ext}} + \dot{\varphi}_B)P = \mu^{\text{r}}(T_{\text{ext}} + T_B)P\,, \tag{3.23}$$

giving the Smoluchowski equation for rotation in a field as

$$\frac{\partial P}{\partial t} = D^{\text{r}}\frac{\partial}{\partial \varphi}\left(\frac{\partial P}{\partial \varphi} + \frac{\partial \beta V}{\partial \varphi}P\right). \tag{3.24}$$

This looks very like translational diffusion, but with a subtle difference. Whereas $\partial/\partial x$ was the generator of infinitesimal translations along a line $\partial/\partial\varphi$ is the generator of infinitesimal rotations about the z-axis. If we introduce the notation $L_z = \partial/\partial\varphi$ we can write the Smoluchowski equation as

$$\frac{\partial P}{\partial t} = D^{\text{r}}L_z\left(L_zP + (L_z\beta V)P\right), \tag{3.25}$$

where we note also that the torque $T_{\text{ext}} = -L_zV$.

3.2. Interaction with weak external field

Debye introduced his model because he was interested in the possibility that molecules with permanent dipole moments could interact with time dependent electric fields to give information about molecular properties. He considered two problems of this nature:

1. the steady response of a dipole to a sinusoidally oscillating weak external field,
2. the relaxation of the average dipole moment if a weak constant electric field is suddenly switched off.

To outline his calculation we first express the potential energy (3.21) in terms of a dimensionless field $\xi(t) = mE(t)/k_BT$,

$$\beta V(\varphi, t) = -\beta mE(t)\cos\varphi = -\xi(t)\cos\varphi\,. \tag{3.26}$$

The Smoluchowski equation now looks like

$$\frac{\partial P}{\partial t} = D^{\text{r}}\frac{\partial}{\partial \varphi}\left(\frac{\partial P}{\partial \varphi} + \xi(t)\sin\varphi\,P\right). \tag{3.27}$$

For problem (1) Debye assumed a weak external field $E(t) = E_0 e^{-i\omega t}$, which, in dimensionless form, is $\xi(t) = \xi_0 e^{-i\omega t}$ with $\xi_0 = mE_0/k_B T \ll 1$. In this weak field limit we can solve for the first order linear response by expanding the distribution function in the small parameter ξ_0 as

$$P = P_0 + \xi_0 P_1 + \dots , \tag{3.28}$$

with the zero-field uniform distribution $P_0 = 1/2\pi$. The equation for P_1 is

$$\frac{\partial P_1}{\partial t} - D^{\mathrm{r}} \frac{\partial^2 P_1}{\partial \varphi^2} = D^{\mathrm{r}} \frac{1}{2\pi} \cos\varphi \, e^{-i\omega t} , \tag{3.29}$$

with solution

$$P_1(\varphi, t) = \frac{\cos\varphi}{2\pi(1 - i\omega\tau_{\mathrm{r}})} e^{-i\omega t} , \tag{3.30}$$

where a characteristic time appears, $\tau_{\mathrm{r}} = 1/D^{\mathrm{r}}$. For a dilute suspension of such particles with number density n, the polarization is calculated as

$$P_x = nm \int_0^{2\pi} \cos\varphi P(\varphi, t) d\varphi = \frac{nm^2}{2k_B T} \chi(\omega) \, E_0 e^{-i\omega t} , \tag{3.31}$$

where we have defined a complex susceptibility

$$\chi(\omega) = \frac{1}{1 - i\omega\tau_{\mathrm{r}}} = \chi'(\omega) + i\chi''(\omega) = \frac{1}{1 + \omega^2\tau_{\mathrm{r}}^2} + i \frac{\omega\tau_{\mathrm{r}}}{1 + \omega^2\tau_{\mathrm{r}}^2} . \tag{3.32}$$

This famous result of Debye was used by him to calculate the complex dielectric function of the suspension $\epsilon(\omega)$ and the corresponding frequency dependent complex index of refraction. Debye proposed this mechanism of rotational diffusion as an explanation of anomalous dispersion in certain liquids, the phenomenon that the real index of refraction and the absorption of the medium vary with frequency. In Figs. 3.2 and 3.3 we plot the real and imaginary parts of the susceptibility, $\chi'(\omega)$, $\chi''(\omega)$ against $\log_{10}(\omega\tau_{\mathrm{r}})$. They reveal a characteristic shape with the imaginary part $\chi''(\omega)$, which describes absorption of energy from the applied field, having a resonant maximum at the characteristic frequency $\omega_{\mathrm{r}} = 1/\tau_{\mathrm{r}} = D^{\mathrm{r}}$.

In Fig. 3.4 we plot χ'' against χ', the so-called Cole-Cole plot [11], showing a perfect semicircle, characteristic of the simple Debye formula for $\chi(\omega)$.

In the 1913 paper, Debye solved another problem as well. In the second calculation he assumed the dipole is in equilibrium in constant field $\xi(t) = \xi_0$

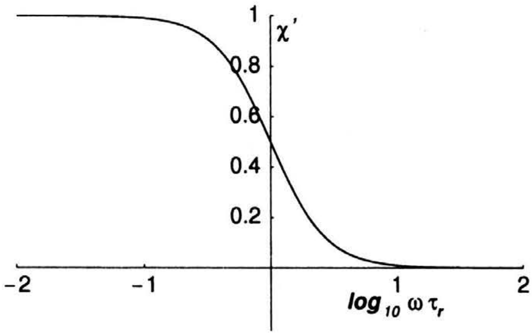

FIGURE 3.2.

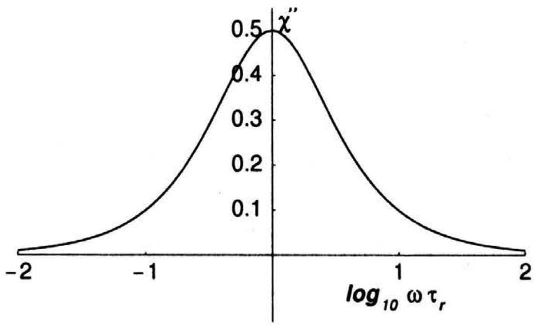

FIGURE 3.3.

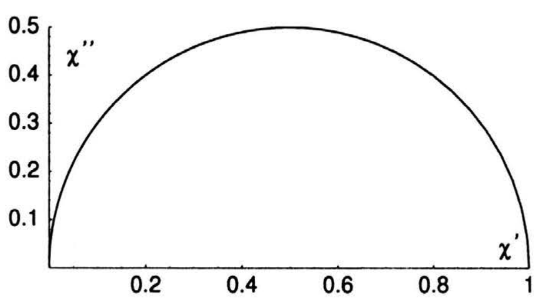

FIGURE 3.4.

for times $t \leq 0$ and then, at $t = 0$, the field is suddenly turned off for all subsequent times. Now the calculation involves free diffusion but with an initial value. For $t > 0$ the probability density $P(\varphi, t)$ satisfies

$$\frac{\partial P}{\partial t} = D^{\mathrm{r}} \frac{\partial^2 P}{\partial \varphi^2}, \tag{3.33}$$

but with initial value (weak field again)

$$P(\varphi, 0) = \frac{1}{2\pi}\left(1 + \xi_0 \cos\varphi\right). \tag{3.34}$$

It is trivial to check that the solution is

$$P(\varphi, 0) = \frac{1}{2\pi}\left(1 + \xi_0 e^{-t/\tau_{\mathrm{r}}} \cos\varphi\right). \tag{3.35}$$

Whereas the first problem was a linear response calculation, the second problem concerns a relaxation process in which there is pure single-exponential decay with the same characteristic time that appeared in the first problem. Although these calculations seem simple, they represent a significant first step in the understanding of polar liquids since Debye envisaged that the rotating particles were the molecules themselves and thus showed that measurements of anomalous dispersion could be used to infer molecular properties.

Chapter 4

The three dimensional rotator

We now generalize the problem to that of a sphere with permanent embedded dipole moment $\boldsymbol{m} = m\boldsymbol{u}$ which is free to rotate in three dimensions instead of being confined to rotate only about a fixed axis [6]. The configuration is specified by the unit vector $\boldsymbol{u}$ which can also be represented as a point on a sphere of unit radius.

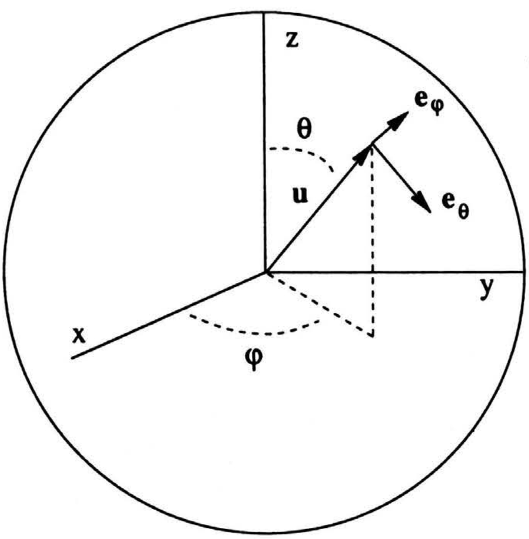

FIGURE 4.1.

The molecular collisions will drive the vector $\boldsymbol{u}$ stochastically over the surface of the sphere. We may use spherical polar coordinates θ, φ to describe the configuration space and we must consider a probability density $P(\boldsymbol{u},t) = P(\theta,\varphi,t)$ for finding the dipole moment to point in the direction θ, φ at time t. The normalization condition is

$$\int P(\boldsymbol{u},t)\,d\boldsymbol{u} = \int P(\theta,\varphi,t)\sin\theta\,d\theta d\varphi = 1\,. \tag{4.1}$$

The rotational diffusion problem can now be regarded as the diffusion of a point on a unit sphere. The Smoluchowski equation is again a continuity equation of the form

$$\frac{\partial P(\boldsymbol{u},t)}{\partial t} = -\operatorname{Div}\cdot\boldsymbol{j}_B(\boldsymbol{u},t)\,, \tag{4.2}$$

with Brownian current density

$$\boldsymbol{j}_B(\boldsymbol{u},t) = -D^{\mathrm{r}}\operatorname{Grad}P(\boldsymbol{u},t)\,, \tag{4.3}$$

where Div and Grad are defined on the surface of the unit sphere, a curved manifold. For infinitesimal displacement on the unit sphere $d\boldsymbol{u}$, the gradient operator is defined in terms of the infinitesimal change in a scalar function $f(\boldsymbol{u})$ by $df = \operatorname{Grad} f\cdot d\boldsymbol{u}$, where, in local coordinates, $d\boldsymbol{u} = d\theta\,\boldsymbol{e}_\theta + \sin\theta\,d\varphi\,\boldsymbol{e}_\varphi$ and $df = (\partial f/\partial\theta)\,d\theta + (\partial f/\partial\varphi)\,d\varphi$, giving

$$\begin{aligned}\operatorname{Grad} f(\boldsymbol{u}) = \frac{\partial f}{\partial \boldsymbol{u}} &= \boldsymbol{e}_\theta\frac{\partial f}{\partial\theta} + \frac{\boldsymbol{e}_\varphi}{\sin\theta}\frac{\partial f}{\partial\varphi}\,,\\ \frac{\partial}{\partial\boldsymbol{u}} &= \boldsymbol{e}_\theta\frac{\partial}{\partial\theta} + \frac{\boldsymbol{e}_\varphi}{\sin\theta}\frac{\partial}{\partial\varphi}\,.\end{aligned} \tag{4.4}$$

The divergence operator follows from Gauss' Theorem on the sphere

$$\int_A \operatorname{Div}\cdot\boldsymbol{j}\,\sin\theta\,d\theta d\varphi = \int_C \boldsymbol{j}\cdot\boldsymbol{n}ds = \textit{Flux out of Area } A\,, \tag{4.5}$$

where $\boldsymbol{n}$ is the outward pointing normal to the bounding curve C of the area A, and ds is infinitesimal arclength along the curve C. Applying this theorem to an infinitesimal area on the sphere bounded by the coordinate values θ, $\theta + d\theta$, φ, $\varphi + d\varphi$, we find

$$\operatorname{Div}\cdot\boldsymbol{j} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta j_\theta) + \frac{1}{\sin\theta}\frac{\partial j_\varphi}{\partial\varphi} = \frac{\partial}{\partial\boldsymbol{u}}\cdot\boldsymbol{j}\,. \tag{4.6}$$

The Laplacian follows from

$$\mathrm{Div}\cdot\mathrm{Grad}\,P = -D^{\mathrm{r}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 P}{\partial\varphi^2}\right]. \tag{4.7}$$

Exercise 4.1: *Using $\partial \boldsymbol{e}_\theta/\partial\varphi = \cos\theta\,\boldsymbol{e}_\varphi$, $\partial\boldsymbol{e}_\varphi/\partial\theta = 0$, verify that*

$$\mathrm{Div}\cdot\mathrm{Grad}\,P(\boldsymbol{u},t) = \frac{\partial}{\partial\boldsymbol{u}}\cdot\frac{\partial}{\partial\boldsymbol{u}}P(\boldsymbol{u},t). \tag{4.8}$$

Exercise 4.2: *For single valued scalar functions $A(\boldsymbol{u})$ and vector functions $\boldsymbol{B}(\boldsymbol{u})$ on the unit sphere, verify that*

$$\int A\frac{\partial}{\partial\boldsymbol{u}}\cdot\boldsymbol{B}d\boldsymbol{u} = -\int\frac{\partial A}{\partial\boldsymbol{u}}\cdot\boldsymbol{B}d\boldsymbol{u}, \tag{4.9}$$

where the integration is over the entire unit sphere.

Using these results the Smoluchowski equation becomes

$$\begin{aligned}\frac{\partial P}{\partial t} &= -\,\mathrm{Div}\cdot\boldsymbol{j}_B(\boldsymbol{u},t) = D^{\mathrm{r}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 P}{\partial\varphi^2}\right],\\ \frac{\partial P}{\partial t} &= D^{\mathrm{r}}\frac{\partial}{\partial\boldsymbol{u}}\cdot\frac{\partial}{\partial\boldsymbol{u}}P = \mathcal{D}P.\end{aligned} \tag{4.10}$$

Exercise 4.3: *Show that for free rotational diffusion*

$$\mathcal{L} = \mathcal{D}^\dagger = \mathcal{D}. \tag{4.11}$$

The initial value problem requires us to find the conditional probability density $P(\boldsymbol{u},t|\boldsymbol{u}_0)$ with initial condition

$$P(\boldsymbol{u},0|\boldsymbol{u}_0) = \delta(\boldsymbol{u}-\boldsymbol{u}_0), \tag{4.12}$$

which is given in operator form by

$$P(\boldsymbol{u},t|\boldsymbol{u}_0) = e^{\mathcal{D}t}\,\delta(\boldsymbol{u}-\boldsymbol{u}_0). \tag{4.13}$$

Just as for translational diffusion we can calculate expectation values of an observable $A(\boldsymbol{u})$,

$$\langle A(\boldsymbol{u}(t))\rangle_{\boldsymbol{u}_0} = \int A(\boldsymbol{u})P(\boldsymbol{u},t|\boldsymbol{u}_0)d\boldsymbol{u} = e^{\mathcal{L}t}A(\boldsymbol{u})|_{\boldsymbol{u}=\boldsymbol{u}_0}. \tag{4.14}$$

To apply this result to the observable $\boldsymbol{u}$ itself we need two preliminary results.

Exercise 4.4:

$$\frac{\partial}{\partial \boldsymbol{u}}\boldsymbol{u} = \boldsymbol{e}_\theta \boldsymbol{e}_\theta + \boldsymbol{e}_\varphi \boldsymbol{e}_\varphi = \boldsymbol{K} = \mathbf{1} - \boldsymbol{u}\boldsymbol{u}\,. \tag{4.15}$$

Exercise 4.5:

$$\frac{\partial}{\partial \boldsymbol{u}}\boldsymbol{K} = -\boldsymbol{K}\boldsymbol{u} - \boldsymbol{u}\boldsymbol{K}\,. \tag{4.16}$$

From these results we calculate

$$\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}}\boldsymbol{u} = -2\boldsymbol{u}\,, \tag{4.17}$$

or

$$\mathcal{L}\boldsymbol{u} = -2D^{\mathrm{r}}\boldsymbol{u}\,, \tag{4.18}$$

giving

$$e^{\mathcal{L}t}\boldsymbol{u} = e^{-2D^{\mathrm{r}}t}\boldsymbol{u}\,. \tag{4.19}$$

Thus we compute

$$\langle \boldsymbol{u}(t)\rangle_{\boldsymbol{u}_0} = e^{-2D^{\mathrm{r}}t}\boldsymbol{u}_0\,. \tag{4.20}$$

Remembering that $\boldsymbol{u}(t)$ is a unit vector we compute the mean squared displacement

$$\langle(\boldsymbol{u}(t) - \boldsymbol{u}(0))^2\rangle_{\boldsymbol{u}_0} = 2\left(1 - e^{-2D^{\mathrm{r}}t}\right), \tag{4.21}$$

where we simply expand the square and use (4.20). For short times, $t \approx dt$,

$$\langle(\boldsymbol{u}(dt) - \boldsymbol{u}(0))^2\rangle_{\boldsymbol{u}_0} \approx 4D^{\mathrm{r}}dt\,, \tag{4.22}$$

while at long times, $t \to \infty$,

$$\langle(\boldsymbol{u}(t) - \boldsymbol{u}(0))^2\rangle_{\boldsymbol{u}_0} \to 2\,. \tag{4.23}$$

Thus at short times the result is identical to translational diffusion in a two-dimensional flat space, while at longer times, the curvature and compactness of the sphere totally changes the limiting behaviour as compared with translational diffusion in a noncompact and infinite Euclidean space. We have examined the time dependence of only the simplest observables here which are linear or quadratic functions of $\boldsymbol{u}$. The results (4.15), (4.16) could also be used to consider observables which are general polynomial functions of $\boldsymbol{u}$. However, there is another formulation of the three dimensional problem which gives an alternative method which is important for problems where the dipole moment is subject to an external field.

Chapter 5

The dual formulation

In Chapter 4 rotational diffusion was presented in terms of the translational diffusion of a point on a sphere, but it is also possible to think of it as diffusion in a space of directions. To see how this other point of view is described mathematically we introduce the operator

$$\boldsymbol{L} = \boldsymbol{u} \times \frac{\partial}{\partial \boldsymbol{u}} = \boldsymbol{e}_\varphi \frac{\partial}{\partial \theta} - \frac{\boldsymbol{e}_\theta}{\sin\theta} \frac{\partial}{\partial \varphi}, \tag{5.1}$$

which also satisfies

$$\boldsymbol{u} \times \boldsymbol{L} = -\frac{\partial}{\partial \boldsymbol{u}}. \tag{5.2}$$

Thus the gradient operation can be written as

$$\mathrm{Grad}\, f(\boldsymbol{u}) = \frac{\partial f(\boldsymbol{u})}{\partial \boldsymbol{u}} = -\boldsymbol{u} \times \boldsymbol{L} f(\boldsymbol{u}), \tag{5.3}$$

and

$$df(\boldsymbol{u}) = \mathrm{Grad}\, f \cdot d\boldsymbol{u} = -(\boldsymbol{u} \times \boldsymbol{L} f) \cdot d\boldsymbol{u} = (\boldsymbol{u} \times d\boldsymbol{u}) \cdot \boldsymbol{L} f = d\boldsymbol{\omega} \cdot \boldsymbol{L} f, \tag{5.4}$$

where $d\boldsymbol{\omega} = \boldsymbol{u} \times d\boldsymbol{u}$ is an infinitesimal rotation and $\boldsymbol{L}$ is the generator of rotations in the space of unit directions $\boldsymbol{u}$. Note that $d\boldsymbol{u} = d\boldsymbol{\omega} \times \boldsymbol{u}$ as we expect for a rotation.

Exercise 5.1:

$$\mathrm{Div} \cdot \mathrm{Grad} = \frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} = \boldsymbol{L} \cdot \boldsymbol{L}. \tag{5.5}$$

Exercise 5.2:

$$\frac{\partial}{\partial \boldsymbol{u}} \cdot (\boldsymbol{A}(\boldsymbol{u}) \times f(\boldsymbol{u})\boldsymbol{u}) = \boldsymbol{L} \cdot (f(\boldsymbol{u})\boldsymbol{A}(\boldsymbol{u})), \tag{5.6}$$

where $\boldsymbol{A}(\boldsymbol{u})$ and $f(\boldsymbol{u})$ are respectively vector and scalar functions of orientation.

Suppose now that $\boldsymbol{u}$ has an additional rigid body angular velocity $\boldsymbol{\Omega}_{Ad}$ imposed on it by an external torque acting on the dipole moment. In addition to the Brownian current density $-D^{\mathrm{r}}\,\mathrm{Grad}\,P$ we have an advective current as well

$$\boldsymbol{j}_{Ad} = (\boldsymbol{\Omega}_{Ad} \times \boldsymbol{u})P, \tag{5.7}$$

with total current

$$\boldsymbol{j} = \boldsymbol{j}_B + \boldsymbol{j}_{Ad} = -D^{\mathrm{r}}\,\mathrm{Grad}\,P + (\boldsymbol{\Omega}_{Ad} \times \boldsymbol{u})P. \tag{5.8}$$

The Smoluchowski equation has the form

$$\frac{\partial P}{\partial t} = -\,\mathrm{Div}\cdot \boldsymbol{j} = D^{\mathrm{r}}\,\mathrm{Div}\cdot\mathrm{Grad}\,P - \mathrm{Div}\cdot((\boldsymbol{\Omega}_{Ad} \times \boldsymbol{u})P),$$

which by use of (5.6) can be put in the final form

$$\begin{aligned}\frac{\partial P}{\partial t} &= D^{\mathrm{r}}\,\boldsymbol{L}\cdot(\boldsymbol{L}P - \boldsymbol{\Omega}_{Ad}P) = -\boldsymbol{L}\cdot\boldsymbol{j}, \\ \boldsymbol{j} &= -D^{\mathrm{r}}\,\boldsymbol{L}P + \boldsymbol{\Omega}_{Ad}P.\end{aligned} \tag{5.9}$$

For a dipole $\boldsymbol{m}$ in an electric field $\boldsymbol{E}$, there is a torque arising from the potential $V(\boldsymbol{u}) = -\boldsymbol{m}\cdot\boldsymbol{E} = -m\boldsymbol{u}\cdot\boldsymbol{E}$ which can be expressed as

$$\boldsymbol{T} = \boldsymbol{m} \times \boldsymbol{E} = -\boldsymbol{L}V(\boldsymbol{u}). \tag{5.10}$$

By Stokes' Law for rotation a steady torque produces an angular velocity $\boldsymbol{\Omega}$ of the form

$$\boldsymbol{\Omega}_{Ad} = \frac{1}{\zeta^{\mathrm{r}}}\boldsymbol{T} = \mu^{\mathrm{r}}\boldsymbol{T}, \tag{5.11}$$

so that the current $\boldsymbol{j}$ can also be expressed as

$$\boldsymbol{j} = -D^{\mathrm{r}}\,\boldsymbol{L}P + \mu^{\mathrm{r}}\boldsymbol{T}P = (-D^{\mathrm{r}}\,\boldsymbol{L}\ln P - \mu^{\mathrm{r}}\boldsymbol{L}V)P.$$

In equilibrium the current must vanish which implies that $D^{\mathrm{r}}\ln P + \mu^{\mathrm{r}}V$ is constant. Thus we have for the equilibrium distribution

$$P_{\mathrm{eq}}(\boldsymbol{u}) = Ce^{-\mu^{\mathrm{r}}V(\boldsymbol{u})/D^{\mathrm{r}}}, \tag{5.12}$$

where C is a constant. By comparing with the Boltzmann form, $P_{\text{eq}} = Z^{-1}\exp -V(\boldsymbol{u})/k_BT$ we find again the Einstein-Debye relation

$$D^{\text{r}} = k_BT\mu^{\text{r}} = \frac{k_BT}{\zeta^{\text{r}}}. \tag{5.13}$$

In analogy to (2.57) we can introduce a Brownian potential V_B and its associated Brownian torque $\boldsymbol{T}_B$,

$$V_B(\boldsymbol{u},t) = k_BT\ln P(\boldsymbol{u},t), \qquad \boldsymbol{T}_B = -\boldsymbol{L}\,V_B. \tag{5.14}$$

Using the rotational mobility μ^{r} we have angular velocities $\boldsymbol{\Omega}_B = \mu^{\text{r}}\boldsymbol{T}_B$, $\boldsymbol{\Omega}_{Ad} = \mu^{\text{r}}\boldsymbol{T}$, in terms of which the current can be expressed analogously to (2.58)

$$\boldsymbol{j} = (\boldsymbol{\Omega}_B + \boldsymbol{\Omega}_{Ad})P = \boldsymbol{\Omega}P. \tag{5.15}$$

The rotational Smoluchowski equation again takes the form of an equation of continuity as in (2.59)

$$\frac{\partial P}{\partial t} + \boldsymbol{L}\cdot(\boldsymbol{\Omega}P) = 0. \tag{5.16}$$

We get a more explicit form by combining (5.9),(5.10) and (5.13) to give the Smoluchowski equation as

$$\begin{aligned}\frac{\partial P(\boldsymbol{u},t)}{\partial t} &= -\boldsymbol{L}\cdot\boldsymbol{j} = D^{\text{r}}\boldsymbol{L}\cdot(\boldsymbol{L}P + (\boldsymbol{L}(\beta V))P)\\ &= D^{\text{r}}\,\boldsymbol{L}\cdot e^{-\beta V}\boldsymbol{L}e^{\beta V}P = \mathcal{D}P.\end{aligned} \tag{5.17}$$

Alternatively, from (5.5) we can also write it as

$$\begin{aligned}\frac{\partial P(\boldsymbol{u},t)}{\partial t} &= -\frac{\partial}{\partial \boldsymbol{u}}\cdot\boldsymbol{j} = D^{\text{r}}\,\frac{\partial}{\partial \boldsymbol{u}}\cdot\left(\frac{\partial P}{\partial \boldsymbol{u}} + \left(\frac{\partial(\beta V)}{\partial \boldsymbol{u}}\right)P\right)\\ &= D^{\text{r}}\,\frac{\partial}{\partial \boldsymbol{u}}\cdot e^{-\beta V}\frac{\partial}{\partial \boldsymbol{u}}e^{\beta V}P = \mathcal{D}P.\end{aligned} \tag{5.18}$$

Exercise 5.3:

$$\begin{aligned}\mathcal{L} = \mathcal{D}^{\dagger} &= D^{\text{r}}\,e^{\beta V}\frac{\partial}{\partial \boldsymbol{u}}\cdot e^{-\beta V}\frac{\partial}{\partial \boldsymbol{u}}\\ &= D^{\text{r}}\,e^{\beta V}\boldsymbol{L}\cdot e^{-\beta V}\boldsymbol{L}.\end{aligned} \tag{5.19}$$

This dual formulation in terms of the rotation operator $\boldsymbol{L}$ is particularly useful since mathematically the operator $\boldsymbol{L}$ is related to the quantum mechanical angular momentum operator $\hat{\boldsymbol{L}}_{QM}$ by

$$\boldsymbol{L} = \frac{i}{\hbar}\hat{\boldsymbol{L}}_{QM}\,.$$

This correspondence allows us to use many mathematical results that have been worked out for the quantum mechanical theory of angular momentum. As an example of this, consider free diffusion again in the dual picture, where we must solve the free Smoluchowski equation

$$\frac{\partial P}{\partial t} = D^{\mathrm{r}}\boldsymbol{L}^2 P\,, \tag{5.20}$$

to find the conditional probability $P(\boldsymbol{u}, t|\boldsymbol{u}_0)$. We can use a spherical harmonic expansion [12] in the form

$$P(\boldsymbol{u}, t|\boldsymbol{u}_0) = \sum_{\ell m} a_{\ell m}(t) Y_{\ell m}(\boldsymbol{u})\,, \tag{5.21}$$

where

$$\boldsymbol{L}^2 Y_{\ell m}(\boldsymbol{u}) = -\ell(\ell+1) Y_{\ell m}(\boldsymbol{u})\,. \tag{5.22}$$

Putting the expansion into the Smoluchowski equation gives for the coefficient functions $a_{\ell m}(t)$ the differential equation $\dot{a}_{\ell m}(t) = -D^{\mathrm{r}}\ell(\ell+1)a_{\ell m}(t)$ with solution

$$a_{\ell m}(t) = e^{-D^{\mathrm{r}}\ell(\ell+1)t} a_{\ell m}(0)\,. \tag{5.23}$$

The initial condition gives

$$P(\boldsymbol{u}, 0|\boldsymbol{u}_0) = \delta(\boldsymbol{u} - \boldsymbol{u}_0) = \sum_{\ell m} a_{\ell m}(0) Y_{\ell m}(\boldsymbol{u})\,,$$

from which we identify $a_{\ell m}(0) = Y^*_{\ell m}(\boldsymbol{u}_0)$ and find

$$P(\boldsymbol{u}, t|\boldsymbol{u}_0) = \sum_{\ell m} e^{-D^{\mathrm{r}}\ell(\ell+1)t} Y^*_{\ell m}(\boldsymbol{u}_0) Y_{\ell m}(\boldsymbol{u})\,. \tag{5.24}$$

By the spherical harmonic addition theorem [12] we have

$$P_\ell(\boldsymbol{u}_0 \cdot \boldsymbol{u}) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{m=\ell} Y_{\ell m}(\boldsymbol{u}_0) Y^*_{\ell m}(\boldsymbol{u})\,, \tag{5.25}$$

where P_ℓ is the Legendre polynomial of order ℓ. Thus by combining (5.24) and (5.25) we can easily compute the conditional average

$$\begin{aligned}\langle P_\ell(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t))\rangle_{\boldsymbol{u}_0} &= \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{m=\ell} Y_{\ell m}(\boldsymbol{u}_0)\int P(\boldsymbol{u},t|\boldsymbol{u}_0)Y^*_{\ell m}(\boldsymbol{u})d\boldsymbol{u} \\ &= e^{-D^r\ell(\ell+1)t}P_\ell(\boldsymbol{u}_0\cdot\boldsymbol{u}_0) = e^{-D^r\ell(\ell+1)t},\end{aligned} \tag{5.26}$$

where we recall that $P_\ell(\boldsymbol{u}_0\cdot\boldsymbol{u}_0) = P_\ell(1) = 1$. As we shall see later, such averages enter the analysis of certain light scattering experiments.

Chapter 6

Asymmetric particles

The results so far refer to spherical mesoparticles whose rotational diffusion is described by a single scalar diffusion coefficient, $D^{\mathrm{r}} = k_B T/\zeta^{\mathrm{r}}$. In such a case applied torques and resultant angular velocities are collinear. However, for non-spherical particles, the relations become tensorial in nature and hence more complicated,

$$\boldsymbol{T} = \boldsymbol{\zeta}^{\mathrm{r}} \cdot \boldsymbol{\Omega}\,, \qquad \boldsymbol{\Omega} = (\boldsymbol{\zeta}^{\mathrm{r}})^{-1} \cdot \boldsymbol{T} = \boldsymbol{\mu}^{\mathrm{r}} \cdot \boldsymbol{T}\,, \tag{6.1}$$

with the friction and mobility given by symmetric second rank tensors [13]. Thus for prolate or oblate spheroids, in the body-fixed frame of reference with z-axis along the axis of rotational symmetry, the friction tensor is diagonal

$$\boldsymbol{\zeta}^{\mathrm{r}} = \begin{pmatrix} \zeta^{\mathrm{r}}_{\perp} & 0 & 0 \\ 0 & \zeta^{\mathrm{r}}_{\perp} & 0 \\ 0 & 0 & \zeta^{\mathrm{r}}_{\parallel} \end{pmatrix}. \tag{6.2}$$

However, in a general laboratory frame of reference $\boldsymbol{\zeta}^{\mathrm{r}}$ is not diagonal and its elements will change with time as the particle changes its orientation. To avoid this complication we may work in the body-fixed frame of reference where $\boldsymbol{\zeta}^{\mathrm{r}}$ and $\boldsymbol{\mu}^{\mathrm{r}}$ are diagonal and unchanging. In that frame the relation between current density and torque becomes

$$\begin{aligned} \boldsymbol{j} &= (\boldsymbol{\Omega}_B + \boldsymbol{\Omega}_{Ad})P = \boldsymbol{\mu}^{\mathrm{r}} \cdot (\boldsymbol{T}_B + \boldsymbol{T})P \\ &= -\boldsymbol{\mu}^{\mathrm{r}} \cdot (\boldsymbol{L}V_B + \boldsymbol{L}V)P = -\boldsymbol{D}^{\mathrm{r}} \cdot (\boldsymbol{L}P + \boldsymbol{L}(\beta V)P)\,, \end{aligned} \tag{6.3}$$

where we have a tensorial Einstein relation

$$\boldsymbol{D}^{\mathrm{r}} = k_B T \boldsymbol{\mu}^{\mathrm{r}} = k_B T \left(\boldsymbol{\zeta}^{\mathrm{r}}\right)^{-1} . \tag{6.4}$$

The Smoluchowski equation can be written in the body-fixed frame as

$$\frac{\partial P}{\partial t} = -\boldsymbol{L} \cdot \boldsymbol{j} = \boldsymbol{L} \cdot \boldsymbol{D}^{\mathrm{r}} \cdot (\boldsymbol{L}P + \boldsymbol{L}(\beta V)P) . \tag{6.5}$$

For a spheroid the orientation may still be described by a unit vector $\boldsymbol{u}$ fixed in the body and pointing along the symmetry axis. However, for the most general asymmetric body the configuration space is more complicated than the space of unit vectors in three dimensions. One may use Euler angles [14] or coordinates on a hypersphere in four dimensions [15, 16, 17]. If we solve the Smoluchowski equation in the body-fixed frame there is still the necessity to transform results back to the laboratory frame. For the analysis of light-scattering from such asymmetric particles Berne and Pecora [14] have given these transformation formulae in terms of an Euler angle description. The mathematical link with the theory of angular momentum in quantum mechanics which was mentioned in Chapter 5 is of particular use in this application.

Life may be yet more complicated. If the particle shape is suitably chosen (a propeller shape for example), then as it rotates at angular velocity $\boldsymbol{\Omega}$ it generates not only a torque but a force as well. Conversely, if it translates at velocity $\boldsymbol{U}$ it generates both a drag force and a torque. The relation of forces and torques to velocities and angular velocities must be written as

$$\begin{pmatrix} \boldsymbol{F} \\ \boldsymbol{T} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\zeta}^{\mathrm{tt}} & \boldsymbol{\zeta}^{\mathrm{tr}} \\ \boldsymbol{\zeta}^{\mathrm{rt}} & \boldsymbol{\zeta}^{\mathrm{rr}} \end{pmatrix} \begin{pmatrix} \boldsymbol{U} \\ \boldsymbol{\Omega} \end{pmatrix}, \tag{6.6}$$

or, for short,

$$\mathsf{F} = \zeta \cdot \mathsf{U} , \tag{6.7}$$

where ζ is a symmetric 6×6 matrix comprised of the 3×3 blocks $\boldsymbol{\zeta}^{\mathrm{tt}}$, $\boldsymbol{\zeta}^{\mathrm{tr}}$, $\boldsymbol{\zeta}^{\mathrm{rt}}$, $\boldsymbol{\zeta}^{\mathrm{rr}}$. In summary then, for asymmetric particles there may be translation-rotation coupling. The Smoluchowski equation becomes

$$\frac{\partial P}{\partial t} = \nabla \cdot \mathsf{D} \cdot (\nabla P + \nabla(\beta V)P) , \tag{6.8}$$

where

$$\nabla = (\frac{\partial}{\partial \boldsymbol{R}}, \boldsymbol{L}) , \qquad \mathsf{D} = k_B T \zeta^{-1} , \tag{6.9}$$

and the probability density $P(\boldsymbol{R}, \boldsymbol{\psi})$ is a function of both centre of mass position $\boldsymbol{R}$ and general orientation variables $\boldsymbol{\psi}$. These much more complicated problems are of current theoretical interest with the development of reproducible experimental systems of axisymmetric particles (rods and disks [18]) which may interact with external fields [19, 20], but we are unable to devote any more time to this topic in an introductory set of lectures such as this.

A final remark is in order here to conclude this description of single particle rotational diffusion. The use of a Smoluchowski equation description is based on the picture of a separation of time scales with strong over-damping due to rapid collisions of the surrounding small molecules with the mesoparticle. This picture fails for particles in a dilute gas or for small molecules in a fluid of other small molecules. In such a case one must also track the momentum relaxation as well as the configuration relaxation. To do this people have modified the simple Debye diffusional model in various ways or have turned to a full Langevin description or a Fokker–Planck equation describing a probability distribution of velocities and configurations. For further discussion of these extensions of the theory, see Berne and Pecora [14] or McConnell [8].

Chapter 7

Polar and polarizable particles

We now must consider more closely what properties of the mesoparticles make it possible to observe the effects of rotational diffusion. There are two distinct sorts of particle that lead to easily measured properties:

1. particles with a permanent and/or induced dipole moment,
2. particles with an internal crystal structure that gives them a non-isotropic dielectric tensor at optical frequencies.

For particles of type (1) we can measure the polarization/magnetization and the susceptibility in externally applied fields and we can observe both static and dynamic birefringence (Kerr effect [21, 22]). For particles of type (2) we can observe depolarized dynamic light scattering which gives direct information on rotational correlation functions [14].

In addition to these techniques, mesoparticles can now be labelled with dyes like eosin and rhodamine which exhibit fluorescence and phosphorescence [23]. The atomic transitions causing phosphorescence have relatively long life-times (up to 4 ms) and can be excited with polarized light pulses that create a subset of particles which will emit polarized light. The excitation probability is proportional to $|\boldsymbol{\mu}_A \cdot \boldsymbol{n}_i|^2$ and the emission probability is proportional to $|\boldsymbol{\mu}_E \cdot \boldsymbol{n}_i|^2$ where $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_E$ are transition dipole moments for absorption and emission respectively and $\boldsymbol{n}_i$ and $\boldsymbol{n}_f$ are initial and final polarization states. These dipole moments are fixed relative to the dye molecule and hence to the mesoparticle. Thus the orientation of $\boldsymbol{\mu}_E$ relative to $\boldsymbol{\mu}_A$ and $\boldsymbol{n}_f$ will change with time due to rotational motion of the particles. For rhodamine doped spheres it is possible to photo-bleach permanently a sub-population with an intense laser pulse polarized in a particular direction, thus creating in the remainder of the population an anisotropic distribution of unbleached particles. As these unbleached particles rotate, the fluorescence response to a weak laser probe beam reveals the rate of rotational diffusion within a wide range of times from milliseconds to seconds. For further explanation of these methods and for details of experimental results using them see [23].

Consider the simplest case first, a dilute suspension of particles which carry a permanent electric dipole moment $\boldsymbol{m} = m\boldsymbol{u}$, subject to an external electric field $\boldsymbol{E}(t)$, producing a potential energy

$$V(\boldsymbol{u}) = -\boldsymbol{m}\cdot\boldsymbol{E} = -m\boldsymbol{u}\cdot\boldsymbol{E} = -mE\cos\theta\,. \tag{7.1}$$

Note that although I use electrical language, by letting $\boldsymbol{m}$ be a magnetic dipole moment and replacing the electric field $\boldsymbol{E}$ by a magnetic field $\boldsymbol{H}$, we get an equivalent description of a suspension of magnetic particles, a ferrofluid. For suitably dilute suspensions we can ignore dipole-dipole interactions and hydrodynamic interactions (which I will mention later) so that the dynamical description reduces to the rotational dynamics of single particles. To make the discussion as simple as possible I assume that the particles are spherical in shape and characterized by a scalar rotational diffusion coefficient D^{r}.

The basic observable for such a system is the mean polarization $\langle\boldsymbol{P}\rangle$. If the particle suspension has number density n then

$$\langle\boldsymbol{P}(t)\rangle = \langle n\boldsymbol{m}(t)\rangle = nm\langle\boldsymbol{u}(t)\rangle = nm\boldsymbol{F}(t)\,, \tag{7.2}$$

with the dimensionless polarization $\boldsymbol{F}$ defined as

$$\boldsymbol{F}(t) = \langle\boldsymbol{u}(t)\rangle = \int \boldsymbol{u}\,P(\boldsymbol{u},t)\,d\boldsymbol{u}\,, \tag{7.3}$$

and $P(\boldsymbol{u},t)$ a solution of the Smoluchowski equation given earlier in (5.18)

$$\frac{\partial P}{\partial t} = D^{\mathrm{r}}\,\frac{\partial}{\partial \boldsymbol{u}}\cdot\left(\frac{\partial P}{\partial \boldsymbol{u}} + \left(\frac{\partial(\beta V)}{\partial \boldsymbol{u}}\right)P\right) = \mathcal{D}P\,. \tag{7.4}$$

For the rest of this chapter let us assume that the electric field is unchanging in time. We introduce spherical polar coordinates with polar axis along the direction of the external field $\boldsymbol{E}$.

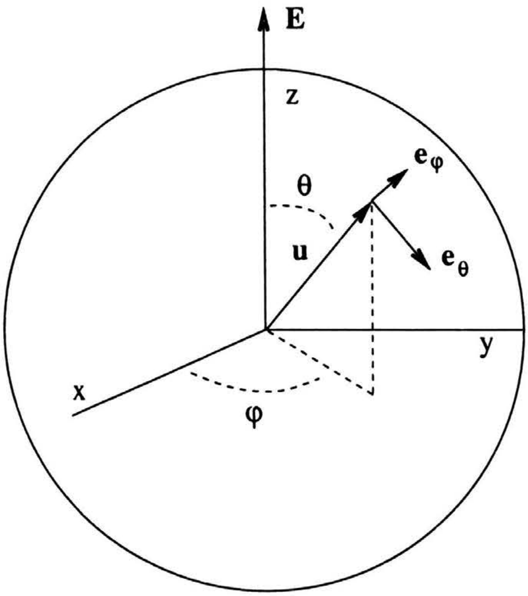

FIGURE 7.1.

Then, using (7.1) and (4.4) we calculate

$$\frac{\partial(\beta V)}{\partial \boldsymbol{u}} = \xi \sin\theta \boldsymbol{e}_\theta \,,$$

$$\frac{\partial(\beta V)}{\partial \boldsymbol{u}} \cdot \frac{\partial P}{\partial \boldsymbol{u}} = \xi \sin\theta \frac{\partial P}{\partial \theta} \,,$$

$$\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial(\beta V)}{\partial \boldsymbol{u}} = 2\xi \cos\theta \,,$$

where we introduce the dimensionless field strength

$$\xi = \beta m E \,. \tag{7.5}$$

In spherical polar coordinates the Smoluchowski equation (7.4) becomes

$$\frac{\partial P}{\partial t} = D^{\mathrm{r}} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial P}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 P}{\partial \varphi^2} + \xi \left(2\cos\theta P + \sin\theta \frac{\partial P}{\partial \theta} \right) \right) . \tag{7.6}$$

The equilibrium solution is

$$P_{\mathrm{eq}}(\boldsymbol{u}) = \frac{1}{Z(\xi)} e^{-\beta V} = \frac{1}{Z(\xi)} e^{\xi \cos\theta} \,, \tag{7.7}$$

with partition function

$$Z(\xi) = \int e^{\xi \cos\theta} d\boldsymbol{u} = \frac{4\pi \sinh \xi}{\xi} . \tag{7.8}$$

The equilibrium dimensionless polarization is

$$\boldsymbol{F}_{\text{eq}} = \langle \boldsymbol{u} \rangle_{\text{eq}} = \frac{1}{Z(\xi)} \int e^{\xi \cos\theta} \boldsymbol{u} \, d\boldsymbol{u} . \tag{7.9}$$

By symmetry the x and y components vanish and for the z component we have

$$F_{\text{eq}\, z} = \frac{1}{Z(\xi)} \int e^{\xi \cos\theta} \cos\theta \, d\boldsymbol{u} = \frac{\partial}{\partial \xi} \ln Z(\xi) = \coth \xi - \frac{1}{\xi} = L(\xi) , \tag{7.10}$$

where we introduce the Langevin function $L(\xi)$.

We can look at the form of the adjoint operator $\mathcal{L} = \mathcal{D}^{\dagger}$ in this case.

Exercise 7.1: *We had from (5.19)*

$$\mathcal{L} = D^{\text{r}} \, e^{\beta V} \frac{\partial}{\partial \boldsymbol{u}} \cdot e^{-\beta V} \frac{\partial}{\partial \boldsymbol{u}} = D^{\text{r}} \left(\frac{\partial}{\partial \boldsymbol{u}} - \frac{\partial (\beta V)}{\partial \boldsymbol{u}} \right) \cdot \frac{\partial}{\partial \boldsymbol{u}} .$$

Show that in spherical polar coordinates

$$\mathcal{L} = D^{\text{r}} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} - \xi \sin\theta \frac{\partial}{\partial\theta} \right) .$$

Exercise 7.2: *Show that if we define $f(\boldsymbol{u}, t)$ by $P(\boldsymbol{u}, t) = P_{\text{eq}}(\boldsymbol{u}) f(\boldsymbol{u}, t)$ then f obeys the differential equation*

$$\frac{\partial f}{\partial t} = \mathcal{L} f = D^{\text{r}} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 f}{\partial\varphi^2} - \xi \sin\theta \frac{\partial f}{\partial\theta} \right) . \tag{7.11}$$

Exercise 7.3: *For short times $t = dt$, given that $\boldsymbol{u} = \boldsymbol{u}_0$ at time $t = 0$, use the method of calculation outlined in Chapter 4 to show that, to first order in dt,*

$$\langle \boldsymbol{u}(dt) - \boldsymbol{u}_0 \rangle_{\boldsymbol{u}_0} = e^{\mathcal{L} dt} (\boldsymbol{u} - \boldsymbol{u}_0)|_{\boldsymbol{u}=\boldsymbol{u}_0} = -2 D^{\text{r}} dt \boldsymbol{u}_0 + D^{\text{r}} dt \beta \boldsymbol{T}_0 \times \boldsymbol{u}_0 ,$$

where the torque $\boldsymbol{T}_0$ is $\boldsymbol{T}_0 = m \boldsymbol{u}_0 \times \boldsymbol{E}$, and that for the mean squared displacement we have

$$\langle (\boldsymbol{u}(dt) - \boldsymbol{u}_0)^2 \rangle_{\boldsymbol{u}_0} = 4 D^{\text{r}} dt .$$

The existence of a dipole moment $\boldsymbol{m}$ may also be associated with a polarizability of the mesoparticles that can lead to interesting optical phenomena. For simplicity let us assume that our particles have an axisymmetric polarizability. In consequence, they will not scatter light isotropically and as they rotate the scattering pattern will change. To keep things simple I assume that the polarizability symmetry axis is aligned with the dipole moment axis $\boldsymbol{u}$. In the presence of an applied electric field $\boldsymbol{E}$ there will be an additional induced dipole moment

$$\boldsymbol{m}_E = \boldsymbol{\alpha} \cdot \boldsymbol{E}, \tag{7.12}$$

where the polarizability tensor $\boldsymbol{\alpha}$ is a symmetric second rank tensor which can be diagonalized in a set of principal axes as

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{pmatrix} \tag{7.13}$$

where $\alpha_\perp$, $\alpha_\parallel$ are polarizabilities perpendicular to and parallel to the optic axis defined by $\boldsymbol{u}$.

With our assumptions above, we see that the only vector quantity on which $\boldsymbol{\alpha}$ can depend is $\boldsymbol{u}$, so we can write

$$\boldsymbol{\alpha} = a\mathbf{1} + b\,\boldsymbol{u}\boldsymbol{u}. \tag{7.14}$$

Clearly $\boldsymbol{u}$ is one principal axis so

$$\boldsymbol{\alpha} \cdot \boldsymbol{u} = (a+b)\boldsymbol{u} = \alpha_\parallel \boldsymbol{u},$$

and from the trace of $\boldsymbol{\alpha}$,

$$Tr\boldsymbol{\alpha} = 3a + b = 2\alpha_\perp + \alpha_\parallel,$$

giving $a = \alpha_\perp$, $b = \alpha_\parallel - \alpha_\perp$ which can be summarized as

$$\boldsymbol{\alpha} = \frac{1}{3} Tr\boldsymbol{\alpha}\,\mathbf{1} + (\alpha_\parallel - \alpha_\perp)\boldsymbol{S} = \alpha_0 \mathbf{1} + b\,\boldsymbol{S}, \tag{7.15}$$

where $\alpha_0 = (2\alpha_\perp + \alpha_\parallel)/3$ and the traceless tensor $\boldsymbol{S}$ is defined by

$$\boldsymbol{S} = \boldsymbol{u}\boldsymbol{u} - \frac{1}{3}\mathbf{1}, \tag{7.16}$$

with $\mathbf{1}$ the unit tensor. Note that $\boldsymbol{S}$ is proportional to the nematic order parameter tensor for hard rod liquid crystals [24, 25].

In the presence of an external field $\boldsymbol{E}$ the interaction energy is altered from (7.1) to

$$V(\boldsymbol{u}) = -\boldsymbol{m}\cdot\boldsymbol{E} - \frac{1}{2}\boldsymbol{E}\cdot\boldsymbol{\alpha}\cdot\boldsymbol{E},$$

which, up to an orientation independent term, can be written as

$$\beta V(\boldsymbol{u}) = -\xi\cos\theta - \sigma\cos^2\theta\,, \tag{7.17}$$

where the dimensionless coefficient σ depends quadratically on the applied field, $\sigma = \beta(\alpha_{\parallel}-\alpha_{\perp})E^2/2$. In a static field the equilibrium distribution now is

$$\begin{aligned} P_{\text{eq}}(\boldsymbol{u}) &= \frac{1}{Z(\xi,\sigma)}e^{\xi\cos\theta+\sigma\cos^2\theta}, \\ Z(\xi,\sigma) &= \int e^{\xi\cos\theta+\sigma\cos^2\theta}d\boldsymbol{u}\,. \end{aligned} \tag{7.18}$$

The partition function can be explicitly evaluated as shown elsewhere [26, 27].

Already, for free rotational diffusion, we have seen in (5.26) of Chapter 5 that the characteristic time scale for the relaxation of an initial orientation $\boldsymbol{u}_0$ is proportional to $\tau_{\text{r}} = 1/D^{\text{r}}$. Using the same parameters as used to estimate τ_p just after (2.11), we calculate $\tau_{\text{r}} \approx 6.07\times10^{-3}$ sec. For external fields that vary on time scales greater than or equal to τ_{r} the mesoparticles can respond to the changing field, both absorbing and dissipating energy. However, for optical frequency fields there is no time for a dynamical response on the time scale of diffusion so that optical fields act simply as probes of the polarization properties but do not themselves affect the dynamics. At optical frequencies there is an optical polarizability $\boldsymbol{\alpha}^{\text{o}}$ where

$$\boldsymbol{\alpha}^{\text{o}} = \frac{1}{3}Tr\boldsymbol{\alpha}^{\text{o}}\mathbf{1} + (\alpha^{\text{o}}_{\parallel} - \alpha^{\text{o}}_{\perp})\boldsymbol{S}\,. \tag{7.19}$$

The induced polarization is

$$\boldsymbol{P}^{\text{o}} = n\langle\boldsymbol{m}^{\text{o}}\rangle = n\langle\boldsymbol{\alpha}^{\text{o}}\rangle\cdot\boldsymbol{E}^{\text{o}} = \boldsymbol{\chi}^{\text{o}}\cdot\boldsymbol{E}^{\text{o}}\,, \tag{7.20}$$

with optical susceptibility tensor given as

$$\boldsymbol{\chi}^{\text{o}} = n\langle\boldsymbol{\alpha}^{\text{o}}\rangle = \frac{n}{3}Tr\boldsymbol{\alpha}^{\text{o}}\mathbf{1} + n(\alpha^{\text{o}}_{\parallel} - \alpha^{\text{o}}_{\perp})\langle\boldsymbol{S}\rangle\,. \tag{7.21}$$

We calculate the optical frequency dielectric tensor as

$$\begin{aligned} \langle\boldsymbol{D}^{\text{o}}\rangle &= \boldsymbol{E}^{\text{o}} + 4\pi\langle\boldsymbol{P}^{\text{o}}\rangle = (\mathbf{1}+4\pi\boldsymbol{\chi}^{\text{o}})\cdot\boldsymbol{E}^{\text{o}} = \boldsymbol{\epsilon}^{\text{o}}\cdot\boldsymbol{E}^{\text{o}} \\ \boldsymbol{\epsilon}^{\text{o}} &= \mathbf{1}+4\pi\boldsymbol{\chi}^{\text{o}}\,. \end{aligned} \tag{7.22}$$

The averages above are with respect to the equilibrium distribution (7.18) for static external field $\boldsymbol{E}$.

Consider a coordinate system with the z-axis along the direction of the external field $\boldsymbol{E}$ and let an optical frequency electromagnetic wave be incident propagating in the direction of the positive y-axis with electric field $\boldsymbol{E}^{\mathrm{o}}$ lying in the x-z plane. In this coordinate system $\boldsymbol{\epsilon}^{\mathrm{o}}$ will be diagonal

$$\boldsymbol{\epsilon}^{\mathrm{o}} = \begin{pmatrix} \epsilon^{\mathrm{o}}_{xx} & 0 & 0 \\ 0 & \epsilon^{\mathrm{o}}_{yy} & 0 \\ 0 & 0 & \epsilon^{\mathrm{o}}_{zz} \end{pmatrix} = \begin{pmatrix} \epsilon^{\mathrm{o}}_{\perp} & 0 & 0 \\ 0 & \epsilon^{\mathrm{o}}_{\perp} & 0 \\ 0 & 0 & \epsilon^{\mathrm{o}}_{\parallel} \end{pmatrix},$$

and

$$\epsilon^{\mathrm{o}}_{xx} = \epsilon^{\mathrm{o}}_{\perp} = 1 + 4\pi\chi^{\mathrm{o}}_{xx} = n_x^2\,,$$
$$\epsilon^{\mathrm{o}}_{zz} = \epsilon^{\mathrm{o}}_{\parallel} = 1 + 4\pi\chi^{\mathrm{o}}_{zz} = n_z^2\,,$$

with n_x, n_z the refractive indices with respect to waves polarized in the x and z directions respectively. We calculate the difference of refractive indices

$$n_z^2 - n_x^2 = (n_z + n_x)(n_z - n_x) = 2\overline{n}\Delta n,$$
$$n_z^2 - n_x^2 = 4\pi(\chi^{\mathrm{o}}_{zz} - \chi^{\mathrm{o}}_{xx}) = 4\pi n(\alpha^{\mathrm{o}}_{\parallel} - \alpha^{\mathrm{o}}_{\perp})(\langle S_{zz}\rangle - \langle S_{xx}\rangle)\,,$$

so that we expect to see birefringence with

$$\Delta n = n_z - n_x = \frac{2\pi n}{\overline{n}}(\alpha^{\mathrm{o}}_{\parallel} - \alpha^{\mathrm{o}}_{\perp})(\langle S_{zz}\rangle - \langle S_{xx}\rangle)\,. \tag{7.23}$$

In the equations immediately above note that n denotes the number density of the suspension while $\overline{n} = (n_z + n_x)/2$ is the mean refractive index.

Given an external static field in the direction $\boldsymbol{e}$, $\boldsymbol{E} = E\boldsymbol{e}$, we calculate the mean value of $\boldsymbol{S}$ as

$$\langle \boldsymbol{S}\rangle = \int P_{\mathrm{eq}}(\boldsymbol{u})\boldsymbol{S}d\boldsymbol{u} = c\mathbf{1} + d\,\boldsymbol{e}\boldsymbol{e}\,,$$

since $\boldsymbol{e}$ is the only vector on which $\langle \boldsymbol{S}\rangle$ can depend. The tracelessness of $\boldsymbol{S}$ gives $c = -d/3$ so that

$$\langle \boldsymbol{S}\rangle = d(\boldsymbol{e}\boldsymbol{e} - \frac{1}{3}\mathbf{1}),$$

from which we calculate

$$\boldsymbol{e}\cdot\langle \boldsymbol{S}\rangle\cdot\boldsymbol{e} = \frac{2}{3}d = \int P_{\mathrm{eq}}(\boldsymbol{u})((\boldsymbol{e}\cdot\boldsymbol{u})^2 - \frac{1}{3})d\boldsymbol{u} = \frac{2}{3}\langle P_2(\cos\theta)\rangle\,,$$

with $P_2(\cos\theta)$ the Legendre polynomial of order 2. The mean value of $\boldsymbol{S}$ then has the form

$$\langle \boldsymbol{S} \rangle = \langle P_2(\cos\theta) \rangle (\boldsymbol{ee} - \frac{1}{3}\mathbf{1}).$$

If the external field $\boldsymbol{E}$ is aligned along the z-axis so that $\boldsymbol{e} = \boldsymbol{e}_z$, we find

$$\langle S_{zz} \rangle - \langle S_{xx} \rangle = \langle P_2(\cos\theta) \rangle \,,$$

so that the difference of refractive indices becomes

$$\Delta n = n_z - n_x = \frac{2\pi n}{\overline{n}} (\alpha_{\parallel}^{\mathrm{o}} - \alpha_{\perp}^{\mathrm{o}}) \langle P_2(\cos\theta) \rangle \,, \qquad (7.24)$$

which gives the magnitude of the static Kerr effect. If the external field $\boldsymbol{E}$ is slowly varying in time then $\langle \boldsymbol{S} \rangle$ will have a slow dynamics as well and the birefringence will be time-dependent (dynamic Kerr effect) [21, 22].

We conclude by noting that the polarization $F_{\mathrm{eq}\,z}$ in (7.10) can be written as $F_{\mathrm{eq}\,z} = \langle P_1(\cos\theta) \rangle$ while $\langle P_2(\cos\theta) \rangle$ appears just above in the expression for the birefringence. The quantities $\langle P_\ell(\cos\theta) \rangle$ for $\ell = 1, 2$ can be regarded as order parameters describing the effect of the static external field $\boldsymbol{E}$ in aligning the dipolar particles.

Chapter 8

Response to external fields: sudden change

Thus far we have considered single particle properties in a fixed external field. An important generalization is to consider time-dependent external fields which was the original problem that Debye [5, 6] wanted to solve. There are at least four interesting situations:

1. sudden change of external field followed by relaxation phenomena,
2. adiabatic change of external field,
3. linear response to an external sinusoidal field,
4. non-linear response to a sinusoidal field.

The first problem above has been treated by many authors, both in the context of dielectric particles [21] and of magnetic particles [28]. I will mainly follow some recent work which has introduced a new approach [26, 27, 29]. For simplicity, consider dipolar particles with moment $\boldsymbol{m} = m\boldsymbol{u}$ and no additional polarizability, in equilibrium in external field $\boldsymbol{E}_0 = E_0\boldsymbol{e}_z$ at time $t = 0$. At that instant, the external field suddenly changes magnitude, $\boldsymbol{E}_0 \rightarrow \boldsymbol{E}_1 = E_1\boldsymbol{e}_z$. For dilute suspensions we can again neglect interparticle interactions and describe the dynamics by the single particle probability $P(\boldsymbol{u}, t)$. For $t > 0$ $P(\boldsymbol{u}, t)$ satisfies

$$\frac{\partial P}{\partial t} = \mathcal{D}_1 P\,, \tag{8.1}$$

where $\mathcal{D}_1$ is the Smoluchowski operator in field $\boldsymbol{E}_1$. At time $t = 0$, however, we have the initial condition $P(\boldsymbol{u}, 0) = P_{\mathrm{eq}0}(\boldsymbol{u}) = Z^{-1}(\xi_0)\exp(\xi_0\cos\theta)$ as given in (7.7). As $t \to \infty$, we expect $P(\boldsymbol{u}, t)$ to relax to a new equilibrium $P_{\text{eq}1}(\boldsymbol{u}) = Z^{-1}(\xi_1)\exp(\xi_1 \cos\theta)$ and the associated single particle polarization,

$$F_z(t) = \int u_z P(\boldsymbol{u}, t) d\boldsymbol{u} = \int \cos\theta P(\boldsymbol{u}, t) d\boldsymbol{u} \tag{8.2}$$

relaxes as well from an initial value $F_z(0) = L(\xi_0)$ to final value $F_z(\infty) = L(\xi_1)$. We introduce an associated normalized relaxation function by

$$\Gamma_z(t) = \frac{F_z(t) - F_z(\infty)}{F_z(0) - F_z(\infty)} = \frac{F_z(t) - L(\xi_1)}{L(\xi_0) - L(\xi_1)}, \tag{8.3}$$

with $\Gamma_z(0) = 1$ and $\Gamma_z(\infty) = 0$.

To elucidate the structure of the relaxation we proceed formally to solve by an eigenfunction expansion analogous to that mentioned earlier in the discussion of time correlation functions in Chapter 2. In doing so it is convenient to work with eigenfunctions of the adjoint Smoluchowski operator $\mathcal{L}_1$. Thus we factor out the final equilibrium distribution function by writing

$$P(\boldsymbol{u}, t) = P_{\text{eq}1}(\boldsymbol{u}) f(\boldsymbol{u}, t), \tag{8.4}$$

where $f(\boldsymbol{u}, t)$ is a solution of

$$\frac{\partial f}{\partial t} = \mathcal{L}_1 f, \tag{8.5}$$

with initial condition $f(\boldsymbol{u}, t) = P_{\text{eq}0}(\boldsymbol{u})/P_{\text{eq}1}(\boldsymbol{u})$. Define eigenfunctions ϕ_i and dimensionless eigenvalues λ_i as earlier,

$$\mathcal{L}_1 \phi_i = -D^{\mathrm{r}} \lambda_i \phi_i, \tag{8.6}$$

together with the biorthonormal functions $\psi_i = P_{\text{eq}1}\phi_i$ which satisfy

$$\mathcal{D}_1 \psi_j = -D^{\mathrm{r}} \lambda_j \psi_j, \tag{8.7}$$

and

$$(\psi_j, \phi_i) = \int \psi_j(\boldsymbol{u}) \phi_i(\boldsymbol{u}) d\boldsymbol{u} = \delta_{ij}. \tag{8.8}$$

Expand the distribution function $f(\boldsymbol{u}, t)$

$$f(\boldsymbol{u}, t) = \sum_{i=0}^{\infty} f_i(t) \phi_i(\boldsymbol{u}), \tag{8.9}$$

and insert in (8.5) using biorthonormality to obtain

$$\dot{f}_i(t) = -D^{\mathrm{r}}\lambda_i f_i(t)\,, \quad f_i(t) = f_i(0)e^{-D^{\mathrm{r}}\lambda_i t}\,. \tag{8.10}$$

Normalization gives

$$\begin{aligned}\int P(\boldsymbol{u},t)d\boldsymbol{u} = \int P_{\mathrm{eq1}}(\boldsymbol{u})f(\boldsymbol{u},t)d\boldsymbol{u}\\ = \int \psi_0(\boldsymbol{u})f(\boldsymbol{u},t)d\boldsymbol{u} = f_0(t) = 1\,,\end{aligned} \tag{8.11}$$

and for the polarization $F_z(t)$ we have

$$\begin{aligned}F_z(t) &= \sum_{i=0}^{\infty} f_i(0)e^{-D^{\mathrm{r}}\lambda_i t}\int u_z P_{\mathrm{eq1}}(\boldsymbol{u})\phi_i(\boldsymbol{u})d\boldsymbol{u}\\ &= L(\xi_1) + \sum_{i=1}^{\infty} f_i(0)g_i e^{-D^{\mathrm{r}}\lambda_i t}\,,\end{aligned} \tag{8.12}$$

where $g_i = (u_z, \psi_i)$. The relaxation function becomes formally

$$\Gamma_z(t) = \sum_{i=1}^{\infty} \frac{f_i(0)g_i}{L(\xi_0) - L(\xi_1)} e^{-D^{\mathrm{r}}\lambda_i t} = \sum_{i=1}^{\infty} p_i\, e^{-\lambda_i t/\tau_{\mathrm{r}}}\,, \tag{8.13}$$

where the relaxation time scale is set by $\tau_{\mathrm{r}} = 1/D^{\mathrm{r}}$. The λ_i are dimensionless relaxation rates. The amplitudes p_i obey a sum rule

$$\sum_{i=1}^{\infty} p_i = 1\,, \tag{8.14}$$

and we can define a mean relaxation time τ_M as

$$\tau_M = \int_0^{\infty} \Gamma_z(t)dt = \tau_{\mathrm{r}} \sum_{i=1}^{\infty} p_i/\lambda_i\,. \tag{8.15}$$

There is also a short-time decay rate τ_0

$$\tau_0^{-1} = -\dot{\Gamma}(0) = \frac{1}{\tau_{\mathrm{r}}} \sum_{i=1}^{\infty} p_i\lambda_i\,, \tag{8.16}$$

which is given by the initial slope of the relaxation function. The Laplace transform of $\Gamma_z(t)$ is given by

$$\hat{\Gamma}_z(s) = D^{\mathrm{r}} \int_0^{\infty} e^{-st/\tau_{\mathrm{r}}}\Gamma_z(t)\,dt = \sum_{i=1}^{\infty} \frac{p_i}{s + \lambda_i}\,. \tag{8.17}$$

Thus the decay rates (eigenvalues) λ_i appear as simple poles of $\hat{\Gamma}(s)$ with the amplitudes p_i as the associated residues.

The eigenvalue problem is not so easy to solve, however, there is a much faster numerical approach to obtain the rates λ_i and amplitudes p_i [29]. In the problem above we have azimuthal symmetry so that in spherical polar coordinates with polar axis along $\boldsymbol{E}_1$ we have $f(\boldsymbol{u},t) = f(\cos\theta, t) = f(z,t)$ where $z = \cos\theta$, and we can expand $f(z,t)$ in Legendre polynomials,

$$f(z,t) = \sum_{\ell=0}^{\infty} f_\ell(t) P_\ell(z) . \tag{8.18}$$

Normalization gives

$$\sum_{\ell=0}^{\infty} f_\ell(t) \langle P_\ell(z) \rangle_{\text{eq1}} = 1 , \tag{8.19}$$

where

$$\langle P_\ell(z) \rangle_{\text{eq1}} = \frac{1}{Z(\xi_1)} \int e^{\xi_1 \cos\theta} P_\ell(\cos\theta) d\boldsymbol{u} = \frac{I_{\ell+1/2}(\xi_1)}{I_{1/2}(\xi_1)} = L_\ell(\xi_1) , \tag{8.20}$$

where the $I_{\ell+1/2}$ are Bessel functions of imaginary argument [30]. The functions $L_\ell(\xi_1)$ generalize the Langevin function [28], $L(\xi_1) = L_1(\xi_1)$. The initial conditions give

$$\begin{aligned} f_\ell(0) &= \frac{2\ell+1}{2} \int P_\ell(z) f(z,0)\, d\boldsymbol{u} \\ &= (2\ell+1) \frac{Z(\xi_1) Z(\xi_0 - \xi_1)}{4\pi Z(\xi_0)} L_\ell(\xi_0 - \xi_1) . \end{aligned} \tag{8.21}$$

The adjoint Smoluchowski equation (8.5) becomes a coupled set of ordinary differential equations for $\ell = 0, 1, 2, \ldots$

$$\begin{aligned} \frac{df_\ell(t)}{dt} = -D^{\mathrm{r}} \Bigg(& \ell(\ell+1) f_\ell(t) + \xi_1 \frac{\ell(\ell-1)}{2\ell-1} f_{\ell-1}(t) \\ & - \xi_1 \frac{(\ell+1)(\ell+2)}{2\ell+3} f_{\ell+1}(t) \Bigg) . \end{aligned} \tag{8.22}$$

For $\ell = 0$ we have $df_0(t)/dt = (2/3) D^{\mathrm{r}} \xi_1 f_1(t)$. Thus the equations for $\ell \geq 1$ can be solved for $f_1(t), f_2(t), \ldots$ and $f_0(t)$ then follows either from $f_1(t)$ or from the normalization condition (8.19). The polarization has the form

$$F_z(t) = L(\xi_1) + \sum_{\ell=1}^{\infty} f_\ell(t) \left(\frac{\ell+1}{2\ell+1} L_{\ell+1}(\xi_1) + \frac{\ell}{2\ell+1} L_{\ell-1}(\xi_1) - L(\xi_1) L_\ell(\xi_1) \right), \quad (8.23)$$

and the relaxation function is

$$\Gamma_z(t) = \frac{1}{L(\xi_0) - L(\xi_1)} \sum_{\ell=1}^{\infty} f_\ell(t) \left(\frac{\ell+1}{2\ell+1} L_{\ell+1}(\xi_1) + \frac{\ell}{2\ell+1} L_{\ell-1}(\xi_1) - L(\xi_1) L_\ell(\xi_1) \right), \quad (8.24)$$

which we write in shorthand notation as

$$\Gamma_z(t) = \mathsf{c}_z \cdot \mathsf{f}(t), \quad (8.25)$$

where $\mathsf{c}_z = (c_1, c_2, \ldots)$ and $\mathsf{f}(t) = (f_1(t), f_2(t), \ldots)$ are infinite dimensional vectors with components of c_z defined as

$$c_\ell = \frac{1}{L(\xi_0) - L(\xi_1)} \left(\frac{\ell+1}{2\ell+1} L_{\ell+1}(\xi_1) + \frac{\ell}{2\ell+1} L_{\ell-1}(\xi_1) - L(\xi_1) L_\ell(\xi_1) \right). \quad (8.26)$$

To calculate $f_\ell(t)$ we Laplace transform (8.22) to get

$$(s + \ell(\ell+1))\, \hat{f}_\ell(s) + \xi_1 \frac{\ell(\ell-1)}{2\ell-1} \hat{f}_{\ell-1}(s) - \xi_1 \frac{(\ell+1)(\ell+2)}{2\ell+3} \hat{f}_{\ell+1}(s) = f_\ell(0), \quad (8.27)$$

which we abbreviate as

$$(s\,\mathsf{I} + \mathsf{M}(\xi_1)) \cdot \hat{\mathsf{f}} = \mathsf{f}(0), \quad (8.28)$$

where I is the unit operator and $\mathsf{M}(\xi_1)$ is an infinite dimensional tridiagonal matrix.

The tridiagonal nature of M makes possible a formal exact solution of (8.27) in terms of infinite continued fractions [31]. However, for numerical work these fractions must be truncated at finite order. We have shown that for numerical work it is easier to proceed in a different way [29]. If we truncate the infinite system (8.27) at order $\ell = \ell_{\max} = N$, we then have a finite dimensional matrix equation (8.28) which we can solve directly as

$$\hat{\mathsf{r}}_{zN}(s) = \mathsf{c}_{zN} \cdot (s\,\mathsf{I}_N + \mathsf{M}_N(\xi_1))^{-1} \cdot \mathsf{f}_N(0) = \frac{A_N(s)}{B_N(s)}, \tag{8.29}$$

with $A_N(s)$, $B_N(s)$ polynomials in s of order $N-1$ and N respectively with $B_N(s) = \mathrm{Det}(s\,\mathsf{I}_N + \mathsf{M}_N(\xi_1))$. The decay rates (eigenvalues) are now given approximately as the zeroes of $B_N(s)$, $\mathrm{Det}(s\,\mathsf{I}_N + \mathsf{M}_N(\xi_1)) = 0$, at $s = -\lambda_{1N}, -\lambda_{2N}, \ldots, -\lambda_{NN}$. The amplitudes p_{jN} are given as the residues of $A_N(s)/B_N(s)$ at the zeroes $-\lambda_{jN}$ of the denominator. The roots of $B_N(s) = 0$ are found easily by use of *Mathematica 4.0* and the residues p_{jN} are evaluated by numerical contour integration of $\hat{\mathsf{r}}_{zN}(s)$ on a small circle enclosing each root. This procedure is fast and rapidly convergent, even for large values of ξ_0, ξ_1. We found in practice that the truncation was convergent if we truncated the matrices at order $N \approx 2\max(\xi_0, |\xi_1|)$. Note that from the values of λ_{jN}, p_{jN} we get $\Gamma_z(t)$ directly in the time domain via Equation (8.13). Our calculations [29] show an interesting structure in the eigenspectrum $\lambda_j(\xi_1)$ as ξ_1 varies, with a double degeneracy developing at large $|\xi_1|$. This may be seen in Fig. 8.1 where we plot the lowest six eigenvalues $\lambda_j(\xi_1)$, for $j = 1$ (bottom curve) to $j = 6$ (top curve), as functions of ξ_1 in the range $0 \le \xi_1 \le 15$. At $\xi_1 = 0$ the eigenspectrum is just the one met already in Chapter 5 for free diffusion, $\lambda_j^{\mathrm{Free}} = j(j+1)$.

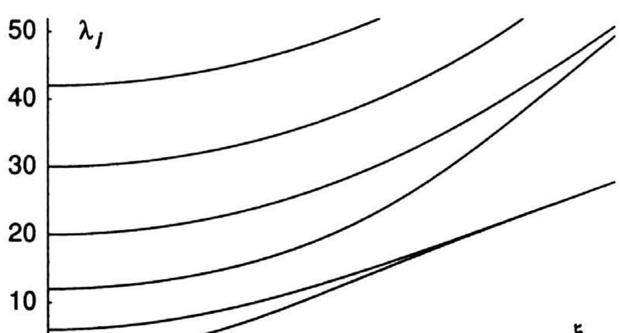

FIGURE 8.1.

The amplitudes $p_j(\xi_0, \xi_1)$ also vary markedly as ξ_0 and ξ_1 vary, being sometimes all positive but (for field reversal) also taking alternate positive and negative values. We illustrate this in Fig. 8.2 where we take the initial field strength to be $\xi_0 = 15$ and we study field reversal with final field $-15 \leq \xi_1 \leq 0$. For strong fields the amplitudes p_j become large in magnitude so we have plotted the quantity $\mu_j(15, \xi_1) = \log_{10}[1 - (-1)^j p_j(15, \xi_1)]$ against ξ_1, in the range $-15 \leq \xi_1 \leq 0$, for $j = 1$ (top curve) to $j = 9$ (bottom curve).

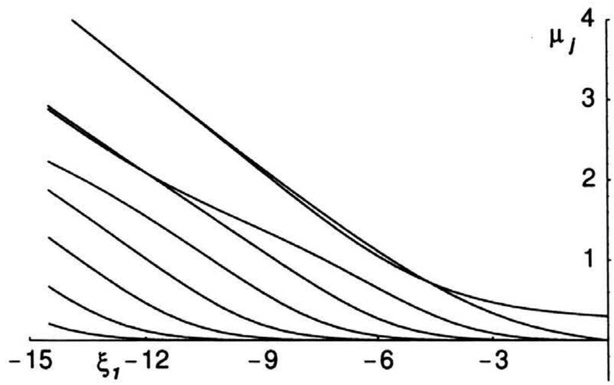

FIGURE 8.2.

This method for sudden field changes can be extended in two ways. Firstly, we can include polarizability which gives a more complicated external potential, $\beta V(\boldsymbol{u}) = -\xi_1 \cos\theta - \sigma_1 \cos^2\theta$ as defined in (7.17). We have found [26] that the nature of the eigenspectrum is altered with the lowest non-zero eigenvalue tending to zero as $\xi_1 \to \infty$. Moreover, we can calculate the relaxation function observed in the dynamic Kerr effect. We define the time dependent quantity

$$F_2(t) = \int P_2(\cos\theta) P(\boldsymbol{u}, t) d\boldsymbol{u}\,, \tag{8.30}$$

which generalizes the order parameter occurring in the static Kerr effect (7.24). Its normalized relaxation function is defined as

$$\Gamma_2(t) = \frac{F_2(t) - F_{2eq1}}{F_{2eq0} - F_{2eq1}}\,, \tag{8.31}$$

which has a representation like (8.13),

$$\Gamma_2(t) = \sum_{j=1}^{\infty} p_{2j}\, e^{-\lambda_j t/\tau_r}. \tag{8.32}$$

Full details of this calculation may be found in the literature [26].

A second generalization is to consider a sudden change of both direction and magnitude [27].

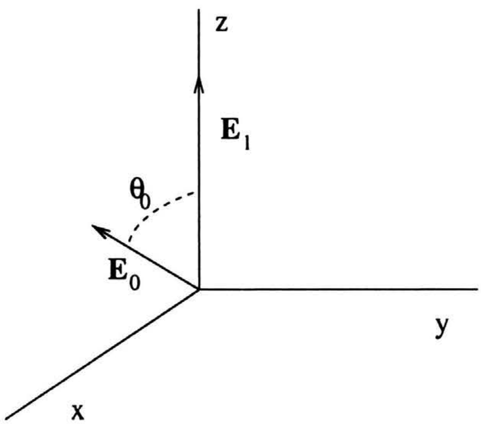

FIGURE 8.3.

In this more general problem the equation of motion (8.5) has azimuthal symmetry about the direction of the final field $\boldsymbol{E}_1$ but the initial conditions do not have this symmetry. Thus we must use more general spherical harmonics to describe the relaxation,

$$f(\boldsymbol{u},t) = f(\theta,\varphi,t) = \sum_{\ell m} B_{\ell m}(t) P_\ell^m(\cos\theta) e^{im\varphi} . \tag{8.33}$$

The calculation proceeds in the same spirit as the simpler one sketched above but with an extended eigenvalue spectrum $\lambda_{\ell m}(\xi_1)$ and with a more complicated set of observables. In addition to $F_z(t)$ and $\Gamma_z(t)$ there is now a transverse polarization component $F_x(t)$ and its relaxation function $\Gamma_x(t)$. We calculate $F_z(t)$ from the $B_{\ell 0}(t)$ while $F_x(t)$ requires the coefficients $B_{\ell 1}(t)$. In addition we must calculate the full order parameter tensor $\boldsymbol{S}(t)$ for the dynamic Kerr effect which, for the axis choice above, takes the form

$$\begin{aligned} \boldsymbol{S}(t) &= \int (\boldsymbol{u}\boldsymbol{u} - \frac{1}{3}\mathbf{1}) P(\boldsymbol{u},t) d\boldsymbol{u} , \\ &= \begin{pmatrix} S_{xx}(t) & 0 & S_{xz}(t) \\ 0 & S_{yy}(t) & 0 \\ S_{zx}(t) & 0 & S_{zz}(t) \end{pmatrix} , \end{aligned} \tag{8.34}$$

which has three independent components (traceless and symmetric). Here $S_{zz}(t)$ involves $B_{\ell 0}(t)$, $S_{xz}(t)$ requires $B_{\ell 1}(t)$ and $S_{xx}(t)$, $S_{yy}(t)$ involve the $B_{\ell 0}(t)$ and $B_{\ell 2}(t)$. For more information see [27].

In this chapter the Debye relaxation calculation in Sec. 3.2 of Chapter 3 has been generalized to changes of both field magnitude and direction. Now the final field values can be non-zero and the method of calculation works equally well for both weak and strong fields. The new feature we meet in comparison with the Debye result (3.35) is that the entire eigenspectrum of the Smoluchowski operators $\mathcal{D}$, $\mathcal{L}$ comes into play. At long times the relaxation is dominated by the smallest non-zero eigenvalue but at short and intermediate times several eigenvalues must be kept to obtain an accurate description.

Chapter 9

Linear response to sinusoidal field

Instead of considering relaxation effects after a sudden field change we can also calculate the response of the suspension of particles to external sinusoidal time-dependent fields with or without a DC background field. The solution to this problem enables us to obtain the frequency dependent dielectric function for the suspension. We may study this situation for weak sinusoidal fields in linear response which was Debye's original problem [5] or for strong perturbing fields which produce a non-linear response. I recently studied [32] the linear response to a weak oscillating field for polarizable particles with a permanent dipole moment $\boldsymbol{m}$ subject to a steady background field $\boldsymbol{E}_0 = E_0\boldsymbol{e}_z$. In this problem we assume that up to time $t = 0$ the system is in equilibrium in field $\boldsymbol{E}_0$ with single particle potential energy

$$\beta V(\boldsymbol{u}) = -\xi_0 \cos\theta - \sigma_0 \cos^2\theta\,, \tag{9.1}$$

where $\xi_0 = \beta m E_0$, $\sigma_0 = \beta(\alpha_\parallel - \alpha_\perp)E_0^2/2$ and θ is the polar angle of $\boldsymbol{u}$ with respect to $\boldsymbol{e}_z$. Suddenly, at $t = 0$, we switch on an additional probe field $\boldsymbol{E}_1 e^{-i\omega t}$ with $E_1 \ll E_0$ and we ask for both the transient and steady linear response of the order parameter $F_z(t)$ introduced in (8.2). This calculation reduces to Debye's original problem [5] if there is no background field, $\boldsymbol{E}_0 = 0$, and $\beta m E_1 \ll 1$. In linear response we can consider separately the longitudinal and transverse cases where $\boldsymbol{E}_1$ is parallel to or normal to $\boldsymbol{E}_0$. I have studied both [32] but for simplicity I will sketch the longitudinal case where $\boldsymbol{E}_1 = E_\parallel \boldsymbol{e}_z$ with $E_1 \ll E_0$.

In the potential energy function (9.1), for times $t > 0$, $\boldsymbol{E}_0$ is replaced by $\boldsymbol{E}_0 + \boldsymbol{E}_1 e^{-i\omega t}$ and we linearize the potential energy as

$$V(\boldsymbol{u}, t) = V_0(\boldsymbol{u}) + V_1(\boldsymbol{u}, t) + \dots , \tag{9.2}$$

where V_1 is linear in $E_{\|}$. Correspondingly we expand the one-particle distribution function

$$P(\boldsymbol{u}, t) = P_{\text{eq}0}(\boldsymbol{u}) + P_1(\boldsymbol{u}, t) + \dots , \tag{9.3}$$

where $P_{\text{eq}0}(\boldsymbol{u}) = Z^{-1}(\xi_0, \sigma_0) \exp(\xi_0 \cos\theta + \sigma_0 \cos^2\theta)$, to get the first order Smoluchowski equation which is satisfied by $P_1(\boldsymbol{u}, t)$,

$$\frac{\partial P_1(\boldsymbol{u}, t)}{\partial \boldsymbol{u}} = \mathcal{D}_0 P_1(\boldsymbol{u}, t) + D^{\text{r}} \frac{\partial}{\partial \boldsymbol{u}} \cdot \left(\beta \frac{\partial V_1(\boldsymbol{u}, t)}{\partial \boldsymbol{u}} P_{\text{eq}0}(\boldsymbol{u}) \right) . \tag{9.4}$$

Here, $\mathcal{D}_0$ is the Smoluchowski operator for the unperturbed system, the initial condition is $P_1(\boldsymbol{u}, 0) = 0$ and the normalization condition on $P(\boldsymbol{u}, t)$ gives, for $t > 0$,

$$\int P_1(\boldsymbol{u}, t) d\boldsymbol{u} = 0 . \tag{9.5}$$

Exercise 9.1: *Show that*

$$\beta V_1(\boldsymbol{u}, t) = -\left(1 + \frac{2\sigma_0}{\xi_0} \cos\theta \right) \cos\theta \, \xi_{\|} e^{-i\omega t} , \tag{9.6}$$

with $\xi_{\|} = \beta m E_{\|}$ *and* $\xi_{\|} \ll \xi_0$.

The inhomogeneous term in the Smoluchowski equation (9.4) becomes

$$D^{\text{r}} \frac{\partial}{\partial \boldsymbol{u}} \cdot \left(\beta \frac{\partial V_1(\boldsymbol{u}, t)}{\partial \boldsymbol{u}} P_{\text{eq}0}(\boldsymbol{u}) \right) = D^{\text{r}} P_{\text{eq}0}(\boldsymbol{u}) g_{\|}(\boldsymbol{u}) \xi_{\|} e^{-i\omega t} , \tag{9.7}$$

where

$$g_{\|}(\boldsymbol{u}) = \sum_{\ell=0}^{4} g_{\ell\|} P_\ell(\cos\theta) , \tag{9.8}$$

with

$$\begin{aligned} g_{0\|} &= -\frac{2}{3}\xi_0 - \frac{16}{15}\frac{\sigma_0^2}{\xi_0} , \qquad g_{1\|} = 2 - \frac{12}{5}\sigma_0 , \\ g_{2\|} &= \frac{2}{3}\xi_0 + 8\frac{\sigma_0}{\xi_0} - \frac{16}{21}\frac{\sigma_0^2}{\xi_0} , \qquad g_{3\|} = \frac{12}{5}\sigma_0 , \qquad g_{4\|} = \frac{64}{35}\frac{\sigma_0^2}{\xi_0} . \end{aligned} \tag{9.9}$$

The subsequent calculation simplifies by factoring out the equilibrium distribution function $P_{\mathrm{eq}0}(\boldsymbol{u})$,

$$P_1(\boldsymbol{u},t) = P_{\mathrm{eq}0}(\boldsymbol{u})\xi_\| f_\|(\boldsymbol{u},t)\,, \tag{9.10}$$

where

$$\frac{\partial f_\|(\boldsymbol{u},t)}{\partial t} = \mathcal{L}_0\, f_\|(\boldsymbol{u},t) + D^{\mathrm{r}}\, g_\|(\boldsymbol{u})\, e^{-i\omega t}\,, \tag{9.11}$$

with the adjoint Smoluchowski operator $\mathcal{L}_0$.

Exercise 9.2: *Show that*

$$\mathcal{L}_0 = D^{\mathrm{r}}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} -(\xi_0\sin\theta + 2\sigma_0\cos\theta\sin\theta)\frac{\partial}{\partial\theta}\right). \tag{9.12}$$

The solution technique is similar to that used in the relaxation problem in Chapter 8. We expand $f_\|$ in Legendre polynomials

$$f_\|(\boldsymbol{u},t) = \sum_{\ell=0}^{\infty} B_{\ell 0}(t) P_\ell(\cos\theta)\,, \tag{9.13}$$

giving coupled first order ordinary inhomogeneous differential equations

$$\begin{aligned}\frac{dB_{\ell 0}}{dt} = -D^{\mathrm{r}}\Bigg(&\ell(\ell+1)B_{\ell 0} + \xi_0\frac{(\ell-1)\ell}{(2\ell-1)}B_{\ell-10} - \xi_0\frac{(\ell+1)(\ell+2)}{(2\ell+3)}B_{\ell+10}\\ &+2\sigma_0\frac{(\ell-2)(\ell-1)\ell}{(2\ell-3)(2\ell-1)}B_{\ell-20} - 2\sigma_0\frac{\ell(\ell+1)}{(2\ell-1)(2\ell+3)}B_{\ell 0}\\ &-2\sigma_0\frac{(\ell+1)(\ell+2)(\ell+3)}{(2\ell+3)(2\ell+5)}B_{\ell+20}\Bigg) + D^{\mathrm{r}}\, g_{\ell\|}\, e^{-i\omega t},\end{aligned} \tag{9.14}$$

The $B_{\ell 0}(t)$ for $\ell \geq 1$ are independent of $B_{00}(t)$ which is given in terms of the $B_{\ell 0}$, $\ell \neq 0$, by putting $\ell = 0$ in (9.14). The normalization condition gives a sum rule

$$\sum_{\ell=0}^{\infty} B_{\ell 0}(t) M_\ell(\xi_0,\sigma_0) = 0\,, \tag{9.15}$$

where $M_\ell(\xi_0,\sigma_0) = \langle P_\ell(\cos\theta)\rangle_{\mathrm{eq}0}$. The functions M_ℓ and the partition function are expressible as

$$Z(\xi_0,\sigma_0) = 2\pi N_0(\xi_0,\sigma_0)\,, \quad M_\ell(\xi_0,\sigma_0) = N_\ell(\xi_0,\sigma_0)/N_0(\xi_0,\sigma_0)\,, \tag{9.16}$$

with the $N_\ell(\xi_0,\sigma_0)$ defined by

$$e^{\xi_0 x+\sigma_0 x^2} = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2} N_\ell(\xi_0,\sigma_0) P_\ell(x)\,. \tag{9.17}$$

An explicit expression for $N_\ell(\xi_0,\sigma_0)$ may be found elsewhere [27]. From (9.3), (9.10) and (9.13) we calculate the polarization order parameter $F_z(t)$ defined in (8.2) as

$$\begin{aligned} F_z(t) &= \int u_z P(\boldsymbol{u},t) d\boldsymbol{u} = \int \cos\theta P(\boldsymbol{u},t) d\boldsymbol{u} \\ &= M_1(\xi_0,\sigma_0) + \xi_\| \sum_{\ell=0}^{\infty} W_\ell(\xi_0,\sigma_0) B_{\ell 0}(t)\,, \end{aligned} \tag{9.18}$$

where the weights $W_\ell(\xi_0,\sigma_0)$ are

$$W_\ell(\xi_0,\sigma_0) = \frac{1}{2\ell+1}(\ell M_{\ell-1}(\xi_0,\sigma_0) + (\ell+1)M_{\ell+1}(\xi_0,\sigma_0))\,. \tag{9.19}$$

The system (9.14) is solved by Laplace transform, setting

$$\hat{B}_{\ell 0}(s) = D^{\mathrm{r}} \int_0^\infty e^{-st/\tau_{\mathrm{r}}} b_{\ell 0}(t) dt = \frac{\hat{C}_{\ell 0}(s)}{s + i\omega\tau_{\mathrm{r}}} \tag{9.20}$$

where we have explicitly displayed the steady state pole in $\hat{B}_{\ell 0}(s)$ at $s = -i\omega\tau_{\mathrm{r}}$. The $\hat{C}_{\ell 0}(s)$ obey the inhomogeneous algebraic system

$$\begin{aligned} &\left(s + \ell(\ell+1) - 2\sigma_0 \frac{\ell(\ell+1)}{(2\ell-1)(2\ell+3)}\right) \hat{C}_{\ell 0} + \xi_0 \frac{(\ell-1)\ell}{(2\ell-1)} \hat{C}_{\ell-10} \\ &\qquad - \xi_0 \frac{(\ell+1)(\ell+2)}{(2\ell+3)} \hat{C}_{\ell+10} + 2\sigma_0 \frac{(\ell-2)(\ell-1)\ell}{(2\ell-3)(2\ell-1)} \hat{C}_{\ell-20} \\ &\qquad\qquad - 2\sigma_0 \frac{(\ell+1)(\ell+2)(\ell+3)}{(2\ell+3)(2\ell+5)} \hat{C}_{\ell+20} = g_{\ell\|}\,, \end{aligned} \tag{9.21}$$

which is again of the form (8.28)

$$(s\,\mathsf{I} + \mathsf{M}(\xi_0,\sigma_0)) \cdot \hat{\mathsf{C}}(s) = \mathbf{g}_\|\,. \tag{9.22}$$

As before, the solution to this inhomogeneous equation gives $\hat{C}_{\ell 0}(s)$ as a function with simple poles at $s_j = -\lambda_{0j}(\xi_0,\sigma_0)$ with residues $d_{\ell 0j}$. Again by truncation at order $\ell = \ell_{\max} = N$ we find the λ_{0j} approximately as roots of $\mathrm{Det}(s\,\mathsf{I}_N + \mathsf{M}_N(\xi_0,\sigma_0)) = 0$ and the $d_{\ell 0j}$ are calculated by contour integration on a small circle encircling the roots.

Back transforming gives $F_z(t)$ explicitly in the time regime as

$$F_z(t) = M_1(\xi_0, \sigma_0) + \xi_\| M_1(\xi_0, \sigma_0) B_{00}(t) \\ + \xi_\| \sum_{j=1}^{\infty} P_{0j}(\omega) \exp[-\lambda_{0j} t/\tau_\mathrm{r}] + \xi_\| Q_0(\omega) \exp[-i\omega t] \,, \quad (9.23)$$

where

$$\begin{aligned} Q_0(\omega) &= \sum_{\ell=1}^{\infty} W_\ell(\xi_0, \sigma_0)\, \hat{C}_{\ell 0}(-i\omega\tau_\mathrm{r}), \\ P_{0j}(\omega) &= -\frac{D_{0j}(\xi_0, \sigma_0)}{\lambda_{0j} - i\omega\tau_\mathrm{r}}\,, \\ D_{0j}(\xi_0, \sigma_0) &= \sum_{\ell=1}^{\infty} W_\ell(\xi_0, \sigma_0)\, d_{\ell 0 j}(\xi_0, \sigma_0)\,. \end{aligned} \quad (9.24)$$

The $\ell = 0$ solution is

$$B_{00}(t) = \frac{2}{15} \sum_{j=1}^{\infty} \frac{5\,\xi_0\, d_{10j} + 6\,\sigma_0\, d_{20j}}{\lambda_{0j}(\lambda_{0j} - i\omega\tau_\mathrm{r})} \exp[-\lambda_{0j} t/\tau_\mathrm{r}] \\ - \frac{1}{i\omega\tau_\mathrm{r}} \left[\frac{2\xi_0}{3} (\hat{C}_{10}(-i\omega\tau_\mathrm{r}) - 1) + \frac{4\sigma_0}{5} \left(\hat{C}_{20}(-i\omega\tau_\mathrm{r}) - \frac{4\sigma_0}{3\xi_0} \right) \right] \exp[-i\omega t]\,. \quad (9.25)$$

We can subtract off the constant background contribution to $F_z(t)$ and thus identify a transient and a steady state response as

$$\Delta F_z(t) = F_z(t) - M_1(\xi_0, \sigma_0) = \xi_\| (T_z(t) + S_z(t))\,, \quad (9.26)$$

with

$$T_z(t) = \frac{2M_1(\xi_0, \sigma_0)}{15} \sum_{j=1}^{\infty} \frac{5\,\xi_0\, d_{10j} + 6\,\sigma_0\, d_{20j}}{\lambda_{0j}(\lambda_{0j} - i\omega\tau_\mathrm{r})} \exp[-\lambda_{0j} t/\tau_\mathrm{r}] \\ - \sum_{j=1}^{\infty} \frac{D_{0j}}{\lambda_{0j} - i\omega\tau_\mathrm{r}} \exp[-\lambda_{0j} t/\tau_\mathrm{r}]\,. \quad (9.27)$$

From $S_z(t)$, the steady state part of $\Delta F_z(t)$, we define a complex susceptibility associated with the order parameter $F_z(t)$,

$$S_z(t) = \frac{1}{3} \chi_\|(\omega) e^{-i\omega t}. \quad (9.28)$$

Note that $\chi_{\|}(\omega)$ is not the complete physical susceptibility because it refers only to the contribution of the permanent dipole moments to the polarization of the suspension. There will be another contribution as well from the induced polarization which will involve the time-dependent Kerr effect order parameter

$$F_2(t) = \int P_2(\cos\theta)\, P(\boldsymbol{u}, t)\, d\boldsymbol{u}\,. \tag{9.29}$$

For simplicity we do not consider $F_2(t)$ further although it could be calculated by the same technique as used for $F_z(t)$.

From (9.23) and (9.25) we can read off $\chi_{\|}(\omega)$, but we can obtain a more useful expression by recalling that the initial condition at $t = 0$ implies $\Delta F_z(0) = 0$, which gives $S_z(0) = \frac{1}{3}\chi_{\|}(\omega) = -T_z(0)$. Thus we can finally express the susceptibility as

$$\chi_{\|}(\omega) = -\frac{2M_1(\xi_0,\sigma_0)}{5}\sum_{j=1}^{\infty}\frac{5\,\xi_0\,d_{10j} + 6\,\sigma_0\,d_{20j}}{\lambda_{0j}(\lambda_{0j} - i\omega\tau_{\mathrm{r}})} + 3\sum_{j=1}^{\infty}\frac{D_{0j}}{\lambda_{0j} - i\omega\tau_{\mathrm{r}}}\,. \tag{9.30}$$

The contribution to the measurable polarization is the real part of the complex function $F_z(t)$,

$$Re\,\Delta F_z(t) = \xi_{\|}\left(Re\,T_z(t) + \frac{1}{3}Re(\chi_{\|}(\omega)e^{-i\omega t})\right). \tag{9.31}$$

From the real part of the transient term, $T_z'(t) = Re\,T_z(t)$, we can define a relaxation function

$$\Gamma_z(t) = T_z'(t)/T_z'(0)\,, \tag{9.32}$$

with mean relaxation time

$$\tau_{zM} = \int_0^{\infty}\Gamma_z(t)dt\,. \tag{9.33}$$

From (9.27) we get explicitly

$$\tau_{zM}(\omega)/\tau_{\mathrm{r}} = \left[\frac{2M_1(\xi_0,\sigma_0)}{15}\sum_{j=1}^{\infty}\frac{5\,\xi_0\,d_{10j} + 6\,\sigma_0\,d_{20j}}{\lambda_{0j}(\lambda_{0j}^2 + \omega^2\tau_{\mathrm{r}}^2)} - \sum_{j=1}^{\infty}\frac{D_{0j}}{\lambda_{0j}^2 + \omega^2\tau_{\mathrm{r}}^2}\right]$$
$$\times\left[\frac{2M_1(\xi_0,\sigma_0)}{15}\sum_{j=1}^{\infty}\frac{5\,\xi_0\,d_{10j} + 6\,\sigma_0\,d_{20j}}{\lambda_{0j}^2 + \omega^2\tau_{\mathrm{r}}^2} - \sum_{j=1}^{\infty}\frac{\lambda_{0j}D_{0j}}{\lambda_{0j}^2 + \omega^2\tau_{\mathrm{r}}^2}\right]^{-1}. \tag{9.34}$$

Thus both the susceptibility and transient relaxation time are determined entirely by the eigenspectrum λ_{0j} (poles of $\hat{C}_{\ell 0}(s)$) and the associated residues $d_{\ell 0j}$.

Debye's problem [6] corresponds to $\boldsymbol{E}_0 = 0$ in our present formalism. In that limit the coupled equations (9.21) reduce simply to

$$(s + \ell(\ell+1))\hat{C}_{\ell 0}(s) = 2\,\delta_{\ell 1}\,, \tag{9.35}$$

which gives $\hat{C}_{\ell 0}(s) = 0$ for $\ell \neq 1$ and

$$\hat{C}_{10}(s) = \frac{2}{s+2}\,. \tag{9.36}$$

Thus there is just a single pole at $s = -\lambda_{01} = -2$, with residue $d_{101} = 2$. In this limit, $\boldsymbol{E}_0 \to 0$, one has $M_\ell(\xi_0, \sigma_0) \to 0$ for $\ell \neq 0$ and $M_0(\xi_0, \sigma_0) \to 1$, so that

$$\begin{aligned} \chi_\parallel(\omega) &\to \frac{3D_{01}}{\lambda_{01} - i\omega\tau_{\mathrm{r}}} = \frac{d_{101}}{\lambda_{01} - i\omega\tau_{\mathrm{r}}}\,, \\ \chi_\parallel^D(\omega) &= \frac{2}{2 - i\omega\tau_{\mathrm{r}}} = \frac{1}{1 - i\omega\tau_D}\,, \end{aligned} \tag{9.37}$$

where the Debye relaxation time τ_D is given in terms of τ_{r} as $\tau_D = \tau_{\mathrm{r}}/2 = 1/2D^{\mathrm{r}}$.

If we split the susceptibility into reactive (real) and dissipative (imaginary) parts,

$$\chi_\parallel(\omega) = \chi_\parallel'(\omega) + i\chi_\parallel''(\omega)\,, \tag{9.38}$$

we have simple resonance forms in the Debye limit,

$$\chi_\parallel'^D(\omega) = \frac{1}{1 + \omega^2\tau_D^2}\,, \qquad \chi_\parallel''^D(\omega) = \frac{\omega\tau_D}{1 + \omega^2\tau_D^2}\,. \tag{9.39}$$

As we have seen already in Chapter 3 these have a characteristic shape when plotted as functions of ω or in the form of Cole-Cole [11] plots of $\chi_\parallel''(\omega)$ against $\chi_\parallel'(\omega)$. From the result (9.30) we can study these functions for a range of non-zero values of ξ_0, σ_0. We have calculated $\chi_\parallel(\omega)$ for selected values of ξ_0 and of the ratio $r_0 = \sigma_0/\xi_0^2 = (\alpha_\parallel - \alpha_\perp)/2\beta m^2$. These plots show significant differences from the Debye limiting results [32]. To illustrate this we show in Fig. 9.1 the dissipative part of the susceptibility $\chi_\parallel''(\omega)$ plotted against $\log_{10}(\omega\tau_D)$.

In this plot the solid curves from the top down correspond to pure dipoles with $\xi_0 = 0$ (the Debye susceptibility), $\xi_0 = 3, 6, 9$ respectively while the two

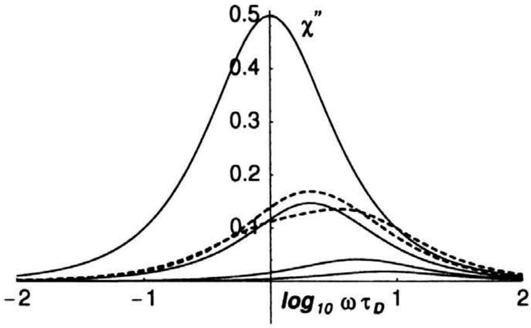

FIGURE 9.1.

dashed curves describe dipoles with additional polarizability, $\xi_0 = 3$, $r_0 = 0.1$ (top curve), $\xi_0 = 3$, $r_0 = 0.3$ (lower curve). The effect of the background field is to reduce the height of the resonance peak in $\chi''_{\|}(\omega)$ while moving it to higher frequency. In Fig. 9.2 we show Cole-Cole plots of $\chi''_{\|}(\omega)$ against $\chi'_{\|}(\omega)$. Here again the solid curves from the top down correspond to pure dipoles with $\xi_0 = 0$ (the Debye susceptibility), $\xi_0 = 3, 6$ respectively while the two dotted curves describe dipoles with additional polarizability, $\xi_0 = 3$, $r_0 = 0.1$ (top curve), $\xi_0 = 3$, $r_0 = 0.3$ (lower curve).

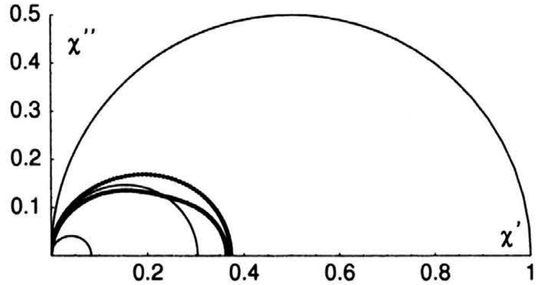

FIGURE 9.2.

The transient term $T_z(t)$ defined in (9.27) also simplifies greatly in the Debye limit,

$$T_z(t) \to T_z^D(t) = -\frac{3}{1 - i\omega\tau_D} e^{-t/\tau_D} , \qquad \Gamma_z(t) = e^{-t/\tau_D} , \tag{9.40}$$

with mean relaxation time $\tau_{zM} = \tau_D$. Away from the Debye limit we can use (9.34) to calculate $\tau_{zM}(\omega)/\tau_r$ for various values of ξ_0 and r_0 [32]. We finally note that everything given here for the case of a longitudinal AC field can be calculated similarly for transverse fields [32].

In conclusion then we have shown that the linear response of the suspension to weak sinusoidal fields is described in terms of the eigenspectrum λ_{0j} of the Smoluchowski equation and an associated set of weights $d_{\ell 0j}$ just as was the relaxation after sudden change of external field described in Chapter 8. If we desire to go beyond a linear response calculation, however, we need an alternative approach.

Chapter 10

Non-linear response

10.1. Steady state solution

In Chapter 9 we have seen how the linear response to a weak sinusoidal field of a dilute system of polar and polarizable particles can be obtained in the presence of a fixed background field. It is possible to go beyond the linear calculation however. To illustrate how this can be done we next consider a simplified problem in which there is no background field and we consider only permanent dipoles, $\boldsymbol{m} = m\boldsymbol{u}$, subject to an external field $\boldsymbol{E}_1 \cos\omega t$ with $\boldsymbol{E}_1 = E_1 \boldsymbol{e}_z$. The time-dependent potential energy of the dipole is then

$$V(\boldsymbol{u}, t) = -\boldsymbol{m} \cdot \boldsymbol{E}_1 \cos\omega t = -mE_1 \cos\theta \cos\omega t\,, \tag{10.1}$$

with θ the polar angle of $\boldsymbol{u}$ with respect to the axis defined by $\boldsymbol{E}_1$. After transients have decayed there will be a steady oscillation of the polarization which will be parallel to $\boldsymbol{E}_1$.

Thus, we have azimuthal symmetry about the z-axis so that the time-dependent distribution function $P(\boldsymbol{u}, t) = P(\cos\theta, t) = P(z, t)$ is independent of the azimuthal angle and satisfies the Smoluchowski equation

$$\frac{\partial P}{\partial t} = D^{\mathrm{r}} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial P}{\partial\theta} \right) \right) + \xi_1 \cos\omega t \left(2\cos\theta P + \sin\theta \frac{\partial P}{\partial\theta} \right), \tag{10.2}$$

with $\xi_1 = \beta m E_1$. It is convenient to write

$$P(z, t) = \frac{1}{4\pi} f(z, t)\,, \tag{10.3}$$

with normalization

$$\int P(z,t)d\boldsymbol{u} = \frac{1}{4\pi}\int f(z,t)d\boldsymbol{u} = \frac{1}{2}\int\limits_{-1}^{1} f(z,t)dz = 1\,. \tag{10.4}$$

From (8.2) and (8.30) the polarization $F_z(t)$ and the order parameter $F_2(t)$ are

$$F_z(t) = \frac{1}{2}\int\limits_{-1}^{1} zf(z,t)dz\,, \quad F_2(t) = \frac{1}{2}\int\limits_{-1}^{1} P_2(z)f(z,t)dz\,. \tag{10.5}$$

To solve the Smoluchowski equation (10.2) we proceed in two stages. First we expand the angular dependence in Legendre polynomials as in (8.18)

$$f(z,t) = \sum_{\ell=0}^{\infty} f_\ell(t)P_\ell(z)\,. \tag{10.6}$$

The normalization condition (10.4) gives, for all times t,

$$f_0(t) = 1\,, \tag{10.7}$$

while the polarization and order parameter $F_2(t)$ are simply

$$F_z(t) = \frac{1}{3}f_1(t)\,, \qquad F_2(t) = \frac{1}{5}f_2(t)\,. \tag{10.8}$$

As with the adjoint Smolochowski equation (8.22) the Smoluchowski equation (10.2) is transformed into an infinite set of coupled ordinary differential equations

$$\frac{df_\ell(t)}{dt} = -D^{\mathrm{r}}\ell(\ell+1)\left(f_\ell(t) + \xi_1\cos\omega t\left(\frac{1}{2\ell-1}f_{\ell-1}(t) - \frac{1}{2\ell+3}f_{\ell+1}(t)\right)\right)\,. \tag{10.9}$$

In the discussion of sudden change of field in Chapter 9 we solved similar equations as an initial value problem. In the present case, however, we are content to find the steady oscillatory solution of (10.9) which is time periodic with the period $T = 2\pi/\omega$ of the oscillating external field.

One can obtain the numerical solution to the system (10.9) in two distinct ways. The first method involves truncation of the system at order $\ell = \ell_{\max}$

followed by direct numerical integration of the resulting finite set of coupled first order equations with initial conditions $f_0^{(1)}(0) = 1$, $f_\ell^{(1)}(0) = 0$, $\ell = 1, 2, \ldots, \ell_{\max}$. This generates a particular solution $f_\ell^{(1)}(t)$. We then evaluate $f_\ell^{(1)}(t)$ at $T = 2\pi/\omega$ and use these values as initial conditions for a second solution, $f_\ell^{(2)}(0) = f_\ell^{(1)}(T)$. We iterate this procedure, $f_\ell^{(n)}(0) = f_\ell^{(n-1)}(T)$, and after a small number of iterations (in practice three iterations) the numerical solution is periodic with no transient components left. The polarization and order parameter follow then from (10.8).

An alternative solution uses the fact that we seek $f_\ell(t)$ as a function periodic with period $T = 2\pi/\omega$. Thus, in addition to the Legendre expansion of the angular dependence (10.6), we can also Fourier expand the time dependence [33, 34]

$$f_\ell(t) = \sum_{n=-\infty}^{\infty} f_{\ell n}\, e^{in\omega t}\,. \tag{10.10}$$

Inserting the Fourier expansion in (10.9) leads to a set of linear algebraic equations for the Fourier coefficients $f_{\ell n}$,

$$\begin{aligned} in\omega f_{\ell n} = -D^{\mathrm{r}}\ell(\ell+1)\Bigg(f_{\ell n} &- \frac{\xi_1}{2(2\ell-1)}\left(f_{\ell-1 n-1} + f_{\ell-1 n+1}\right) \\ &+ \frac{\xi_1}{2(2\ell+3)}\left(f_{\ell+1 n-1} + f_{\ell+1 n+1}\right)\Bigg). \end{aligned} \tag{10.11}$$

The normalization (10.7) gives

$$f_{00} = 1, \quad f_{0n} = 0, \quad n \neq 0\,, \tag{10.12}$$

and from the requirement that $f_\ell(t)$ be real we have

$$f_{\ell n}^* = f_{\ell -n}\,. \tag{10.13}$$

Since the values of f_{0n} are given explicitly in (10.12), the system (10.11) is an inhomogeneous linear system which we can solve for all $f_{\ell n}$, $\ell > 0$. Inspection of (10.11) shows that the $f_{\ell n}$ for odd values of $\ell + n$ do not couple to the $f_{\ell n}$ with even values of $\ell + n$. Thus we have also

$$f_{\ell n} = 0, \quad \ell + n \text{ odd}\,. \tag{10.14}$$

If, for $\ell > 0$, we express $f_{\ell n}$ in terms of real and imaginary parts, $f_{\ell n} = A_{\ell n} - iB_{\ell n}$, we obtain $f(z,t)$ in the explicitly real form

$$f(z,t) = 1 + 2\sum_{\ell=1}^{\infty}\left(\sum_{n=0}^{\infty} A_{\ell n}\cos n\omega t + \sum_{n=1}^{\infty} B_{\ell n}\sin n\omega t\right) P_\ell(z)\,. \qquad (10.15)$$

Calculating $F_z(t)$ and $F_2(t)$ we obtain

$$\begin{aligned} F_z(t) &= \frac{2}{3}\left(\sum_{n=1}^{\infty}(A_{1n}\cos n\omega t + \sum_{n=1}^{\infty}(B_{1n}\sin n\omega t\right)\,, \\ F_2(t) &= \frac{2}{5}\left(\sum_{n=0}^{\infty}(A_{2n}\cos n\omega t + \sum_{n=1}^{\infty}(B_{2n}\sin n\omega t\right)\,. \end{aligned} \qquad (10.16)$$

For numerical study we solve the system (10.11) by truncating at $\ell = \ell_{\max}$, $n = \pm n_{\max}$ and using the linear algebra routines of *Mathematica 4.0*. The solution so obtained can be checked against the direct integration described above. For the largest amplitude studied, $\xi_1 = 20$, we found convergence for $\ell_{\max} = 16$, $n_{\max} = 16$. For smaller values of ξ_1, significantly smaller truncations give good accuracy.

To compare with the linear response calculation in Chapter 9 we introduce the quantities

$$\begin{aligned} P(\xi_1,\omega) &= \xi_1\omega\int_0^T F_z(t)\cos\omega t\,dt\,, \\ Q(\xi_1,\omega) &= \xi_1\int_0^T \frac{dF_z(t)}{dt}\cos\omega t\,dt = \xi_1\omega\int_0^T F_z(t)\sin\omega t\,dt\,. \end{aligned} \qquad (10.17)$$

These represent non-linear generalizations of the susceptibilities $\chi'(\omega)$, $\chi''(\omega)$ with P equal to $-2\pi\beta$ times the time average of the mean potential energy of a dipole in the oscillating field and Q representing dissipation, the work done by the field in one period T. Both P and Q can be represented by a single complex expression

$$P(\xi_1,\omega) + iQ(\xi_1,\omega) = \xi_1\omega\int_0^{2\pi/\omega} F_z(t)e^{i\omega t}\,dt\,,\ \omega > 0\,. \qquad (10.18)$$

In the weak-field limit ($\xi_1 \ll 1$) we find

$$P_w(\xi_1,\omega) = \frac{\pi}{3}\xi_1^2 \frac{1}{1+\omega^2\tau_D^2}\,, \qquad Q_w(\xi_1,\omega) = \frac{\pi}{3}\xi_1^2 \frac{\omega\tau_D}{1+\omega^2\tau_D^2}\,, \tag{10.19}$$

which is proportional to the Debye result for the susceptibility (9.39). To compare with the linear susceptibilities we can normalize P and Q by dividing each by the zero frequency value $P(\xi_1, 0)$,

$$P(\xi_1,0) = \xi_1 \int_0^{2\pi} L(\xi_1 \cos\tau)\cos\tau\, dt\,, \tag{10.20}$$

where L is the Langevin function. To obtain (10.20) we use the fact that as $\omega \to 0$, the distribution function $P(\boldsymbol{u}, t)$ becomes simply the equilibrium distribution functions in the instantaneous field [34] ,

$$P_{ad}(\boldsymbol{u},t) = \frac{1}{Z(\xi_1\cos\omega t)} e^{\xi_1 \cos\theta \cos\omega t}\,. \tag{10.21}$$

Plots of $P(\xi_1,\omega)/P(\xi_1,0)$, $Q(\xi_1,\omega)/P(\xi_1,0)$ can be found in [34] where they are compared with the weak field result which follows from (10.19). In Fig. 10.1 we give one such example. There, for the strong field value $\xi_1 = 20$, we show $Q(\xi_1,\omega)/P(\xi_1,\omega)$ as computed by the full non-linear method sketched above (solid curve) and the weak field Debye result (dashed curve) plotted against $\log_{10}(\omega\tau_D)$. We see that the peak of absorption increases in magnitude and is shifted to higher frequencies compared with the weak field limit.

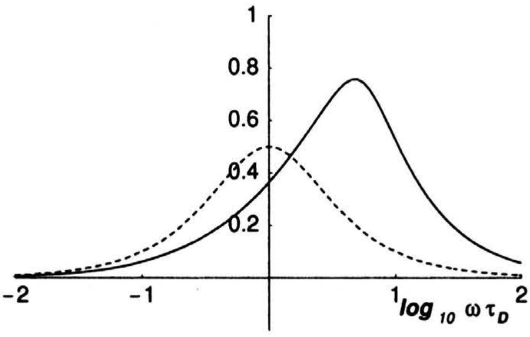

FIGURE 10.1.

10.2. Effective field approximation

Thus far in the lectures I have used the Smoluchowski equation to define the fundamental dynamics. Because the Smoluchowski equation is not always easy to solve, people have looked for phenomenological effective field theories to bypass the direct solution of the Smoluchowski equation. This approach has been particularly important in the case of ferrofluids (magnetic colloids) [28, 35]. I will derive one of these effective field equations to illustrate the approach and then compare its predictions with those of the full Smoluchowski equation. This approach, due to Martsenyuk *et al* [35] can be applied to the situation of axially symmetric systems such as those treated just above and also in Chapter 8 and 9.

If we denote the dimensionless external field by $\xi(t)$, we have the axisymmetric Smoluchowski equation (also called the Fokker–Planck equation in the magnetic system literature)

$$\frac{\partial P(z,t)}{\partial t} = \frac{\partial}{\partial z}\left((1-z^2)\left(\frac{\partial P}{\partial z} - \xi(t)P\right)\right). \tag{10.22}$$

In the magnetic problem the quantity $F_z(t)$ has the significance of the magnetization rather than the polarization and it is just the first moment of $P(z,t)$ defined as

$$F_z(t) = \langle z\rangle_t = \int z\, P(z,t)\, d\boldsymbol{u} = 2\pi \int_{-1}^{1} z\, P(z,t)\, dz\,. \tag{10.23}$$

Using (10.22) and an integration by parts we calculate the time derivative of the first moment as

$$\frac{d}{dt}\langle z\rangle_t = 2\pi \int_{-1}^{1} z \frac{\partial P}{\partial t} dz = D^{\mathrm{r}}\left(\xi(t) - 2\langle z\rangle_t - \xi(t)\langle z^2\rangle_t\right). \tag{10.24}$$

Clearly this is the first of an infinite set of coupled moment equations.

However, we can break the coupling to higher moments if we approximate $P(z,t)$ by assuming that the system is described by an equilibrium distribution, but in an effective field $\xi_e(t)$,

$$P(z,t) \approx \frac{1}{Z(\xi_e(t))} e^{\xi_e(t) z}\,. \tag{10.25}$$

For a distribution of this form the moments simplify so that by use of (8.20) we calculate

$$\begin{aligned} \langle z \rangle_t &= L_1(\xi_e(t)) , \\ \langle z^2 \rangle_t &= \frac{2}{3} \langle P_2(z) \rangle_t + \frac{1}{3} = \frac{2}{3} L_2(\xi_e(t)) + \frac{1}{3} . \end{aligned} \tag{10.26}$$

However, from the recursion relation for the Legendre polynomials one can derive

$$L_2(\xi_e) = -\frac{3}{\xi_e} L_1(\xi_e) + 1 . \tag{10.27}$$

Putting these results into (10.24) gives the effective field equations for the mean field magnetization $F_{zM}(t)$ as

$$\begin{aligned} \frac{dF_{zM}(t)}{dt} &= -2D^{\mathrm{r}} \left(F_{zM}(t) - \frac{\xi(t)}{\xi_e(t)} F_{zM}(t) \right) , \\ F_{zM}(t) &= L_1(\xi_e(t)) . \end{aligned} \tag{10.28}$$

Exercise 10.1: *Show that (10.28) can be written in terms of* $\xi(t)$, $\xi_e(t)$ *alone in the form*

$$\frac{d\xi_e(t)}{dt} = 2D^{\mathrm{r}} \xi_e(t) \sinh \xi_e(t) \frac{\xi_e(t) \cosh \xi_e(t) - \sinh \xi_e(t)}{\xi_e^2(t) - \sinh^2 \xi_e(t)} \left(1 - \frac{\xi(t)}{\xi_e(t)} \right) . \tag{10.29}$$

By integrating (10.29) numerically for $\xi_e(t)$ we get approximate values for the polarization and order parameter as $F_{zM}(t) = L_1(\xi_e(t))$, $F_{2M}(t) = L_2(\xi_e(t))$. We have calculated these approximate values and compared them with the exact results from the Smoluchowski equation [34]. We find that even in strong external fields, the effective field equations (10.28) give quite a good approximation. As an illustration of this, for field strength $\xi_1 = 20$, and frequency $\omega = 9.588/\tau_r$, we plot in Fig. 10.2 $F_z(t)$ as calculated by the non-linear method (solid curve) and $F_{zM}(t)$ as calculated from the effective field equations (10.28) (dashed curve). The functions are plotted against dimensionless time t/T where T is the period of steady oscillation.

Other forms of effective field models are also studied in [34] which are not so accurate. However, the one-particle Smoluchowski equation is only valid for dilute systems so that in dense suspensions, a good effective field approximation would be of great utility. There is further discussion of such macroscopic relaxation equations in [34] from the viewpoint of irreversible thermodynamics and the free energy of the system.

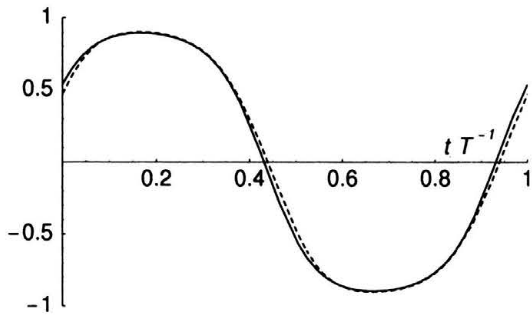

FIGURE 10.2.

Finally, we note an interesting feature of the analytic properties of the non-linear response functions as functions of frequency ω. In the linear response susceptibility (9.30) we see that, as a function of ω, $\chi(\omega)$ is analytic in the upper half complex ω-plane with poles in the lower half plane. Such analytic structure represents causality in the linear response framework. However, if one calculates explicitly to third order in ξ, one obtains [36],

$$P(\xi,\omega) + iQ(\xi,\omega) = \frac{\pi\xi^2}{3}\left(\frac{1}{1-i\omega\tau_D} - \frac{\xi^2}{60}\frac{1}{1+\omega^2\tau_D^2}\frac{1}{1-i\omega\tau_D}\frac{9-i\omega\tau_D}{3-2i\omega\tau_D} + \mathcal{O}(\xi^4)\right). \tag{10.30}$$

Clearly the higher order terms have a pole in the upper half ω-plane. Thus the non-linear response functions P, Q do not satisfy the Kramers–Kronig relation which is obeyed by the real and imaginary parts of the linear response susceptibility.

Chapter 11

The generalized Smoluchowski equation

Thus far we have considered dilute suspensions in which it was sufficient to calculate the single particle response to external probe fields. However, if suspensions are not dilute, new phenomena appear as the particles interact with each other as well as with external fields. The theoretical description of such a system has to be extended to a many-body formalism and we must consider what experimental observations are possible in such systems. For simplicity we consider a suspension of N identical spherical particles whose centres are located at points $\boldsymbol{R}_i$, $i = 1, 2 \ldots, N$, and which are characterized in addition by a direction fixed in each particle and described by a unit vector $\boldsymbol{u}_i$, $i = 1, 2 \ldots, N$. For example, they may be polar particles with a permanent dipole moment, $\boldsymbol{m}_i = m\boldsymbol{u}_i$, or they may have an axisymmetric polarizability tensor $\boldsymbol{\alpha}_i$ as in (7.12) with $\boldsymbol{u}_i$ specifying the optic axis. The configuration of the entire system now includes a position and an orientation variable for each particle which we can describe by a $6N$ dimensional vector

$$X = (X^{\mathrm{t}}, X^{\mathrm{r}}) = (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N, \boldsymbol{u}_1, \ldots, \boldsymbol{u}_N)\,, \tag{11.1}$$

where X^{t}, X^{r} are $3N$ dimensional vectors specifying only positions or orientations respectively. The particles may interact by potential interactions which we assume to be given by a sum of two-body potentials. These potentials may depend only on positions (hard-sphere or Lennard–Jones potentials for example) or on both positions and orientations (dipole-dipole interactions).

We denote the many-body potential function by

$$V(X) = \sum_{i<j} v_{ij}(\boldsymbol{R}_i, \boldsymbol{u}_i; \boldsymbol{R}_j, \boldsymbol{u}_j)\,, \tag{11.2}$$

with v_{ij} the two-body potential.

The particles undergo Brownian motion in position and orientation on the slow time scale $t \gg \tau_p, \tau_L$ and we describe this by a normalized time-dependent probability density in the N-particle configuration space, $P(X,t)$,

$$\int P(X,t)\, dX = \int P(X,t) d\boldsymbol{R}_1 \dots d\boldsymbol{R}_N d\boldsymbol{u}_1 \dots d\boldsymbol{u}_N = 1\,. \tag{11.3}$$

We postulate that on the slow time scale the dynamics is given by a generalized Smoluchowski equation (GSE) of the form

$$\frac{\partial P(X,t)}{\partial t} = -\nabla \cdot J(X,t)\,, \tag{11.4}$$

where J is the probability flux and the generalized gradient operator ∇ is a $6N$ dimensional operator of the form $\nabla = (\partial/\partial \boldsymbol{R}_1, \dots, \partial/\partial \boldsymbol{R}_N, \partial/\partial \boldsymbol{u}_1, \dots, \partial/\partial \boldsymbol{u}_N)$ or, alternatively, $\nabla = (\partial/\partial \boldsymbol{R}_1, \dots, \partial/\partial \boldsymbol{R}_N, \boldsymbol{L}_1, \dots, \boldsymbol{L}_N)$ where $\partial/\partial \boldsymbol{u}_i$ is the gradient on the unit sphere which is the orientational configuration space of particle i and $\boldsymbol{L}_i = \boldsymbol{u}_i \times \partial/\partial \boldsymbol{u}_i$ is the corresponding rotation generator as in Chapter 5.

The current density J has two distinct components, $J = J_B + J_K$, (compare (2.25), (2.58) and (5.19)) where J_B is a Brownian component and J_K is associated with the forces $\boldsymbol{F}_i$ and torques $\boldsymbol{T}_i$ arising from interactions. We denote a $6N$ dimensional generalized force vector $K(X)$ by

$$\begin{aligned} K(X) = (F,T) &= (\boldsymbol{F}_1, \dots, \boldsymbol{F}_N, \boldsymbol{T}_1, \dots, \boldsymbol{T}_N) \\ &= \left(-\frac{\partial V}{\partial \boldsymbol{R}_1}, \dots, -\frac{\partial V}{\partial \boldsymbol{R}_N}, -\boldsymbol{L}_1 V, \dots, -\boldsymbol{L}_N V \right), \end{aligned} \tag{11.5}$$

where F and T are $3N$ dimensional vectors of forces and torques respectively. The Brownian component of the current has the form

$$J_B = -D(X) \cdot \nabla P(X,t)\,, \tag{11.6}$$

where $D(X)$ is a $6N \times 6N$ many-body diffusion matrix. To understand how J_K is related to the force K we recall from the single particle problem of Chapter 2 that on the slow time scale where we can neglect inertia, there is a simple relation between applied force and the resultant steady velocity of the particle. This relation, given in (2.24) defines the mobility of a mesoparticle. In the many-body situation there is a generalization of the concept of mobility. To see how this arises, consider the motion of our N particles characterized by rigid body translational and angular velocities $\boldsymbol{U}_i$, $\boldsymbol{\Omega}_i$ in the suspending fluid. On the slow time scale we can describe the fluid response by the zero Reynolds number Stokes' equations

$$\eta\nabla^2\boldsymbol{v}(\boldsymbol{r}) - \boldsymbol{\nabla}p(\boldsymbol{r}) = 0\,, \qquad \boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}) = 0 \tag{11.7}$$

where $\boldsymbol{v}(\boldsymbol{r})$, $p(\boldsymbol{r})$ are velocity and pressure fields respectively. In this continuum approximation for the suspending fluid we have a boundary value problem in which we solve (11.7) subject to stick boundary conditions at the surface of the moving particles [37]. For given $\boldsymbol{U}_i$, $\boldsymbol{\Omega}_i$ we find the velocity field $\boldsymbol{v}(\boldsymbol{r})$ and can then evaluate the stress tensor which in turn can be integrated over the particle surfaces to give the forces and torques $\boldsymbol{F}_i$, $\boldsymbol{T}_i$ exerted on the fluid by the moving particles. Since the inertia of both the mesoparticles and the fluid is neglected, the forces $\boldsymbol{F}_i$ and torques $\boldsymbol{T}_i$ are identical with the externally applied forces and torques necessary to produce the velocities $\boldsymbol{U}_i$, $\boldsymbol{\Omega}_i$. Since (11.7) is a linear system we find a linear relation between the $\boldsymbol{F}_i$, $\boldsymbol{T}_i$ and the $\boldsymbol{U}_i$, $\boldsymbol{\Omega}_i$

$$\begin{aligned}\boldsymbol{F}_i &= \sum_{j=1}^{N}\zeta_{ij}^{\mathrm{tt}}\cdot\boldsymbol{U}_j + \sum_{j=1}^{N}\zeta_{ij}^{\mathrm{tr}}\cdot\boldsymbol{\Omega}_j\,,\\ \boldsymbol{T}_i &= \sum_{j=1}^{N}\zeta_{ij}^{\mathrm{rt}}\cdot\boldsymbol{U}_j + \sum_{j=1}^{N}\zeta_{ij}^{\mathrm{rr}}\cdot\boldsymbol{\Omega}_j\,,\end{aligned} \tag{11.8}$$

which can be abbreviated to

$$\begin{pmatrix} F \\ T \end{pmatrix} = \begin{pmatrix} \zeta^{\mathrm{tt}} & \zeta^{\mathrm{tr}} \\ \zeta^{\mathrm{rt}} & \zeta^{\mathrm{rr}} \end{pmatrix}\begin{pmatrix} U \\ \Omega \end{pmatrix}, \tag{11.9}$$

or

$$K(X) = \zeta(X)\cdot U_K\,. \tag{11.10}$$

The $6N \times 6N$ matrix $\zeta(X)$ is called the grand resistance matrix [13]. By inverting the linear relations (11.8)-(11.10) we obtain the many-body grand mobility matrix $\mu(X)$ [37],

$$\mu(X) = \zeta^{-1}(X)\,, \tag{11.11}$$

$$U_K = \mu(X) \cdot K(X), \tag{11.12}$$

$$\begin{pmatrix} U \\ \Omega \end{pmatrix} = \begin{pmatrix} \mu^{\mathrm{tt}} & \mu^{\mathrm{tr}} \\ \mu^{\mathrm{rt}} & \mu^{\mathrm{rr}} \end{pmatrix} \begin{pmatrix} F \\ T \end{pmatrix}, \tag{11.13}$$

$$\begin{aligned} \boldsymbol{U}_i &= \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{\mathrm{tt}} \cdot \boldsymbol{F}_j + \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{\mathrm{tr}} \cdot \boldsymbol{T}_j, \\ \boldsymbol{\Omega}_i &= \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{\mathrm{rt}} \cdot \boldsymbol{F}_j + \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^{\mathrm{rr}} \cdot \boldsymbol{T}_j. \end{aligned} \tag{11.14}$$

Using the mobility matrix, the advective contribution to the current density is expressed as

$$J_K = U_K \, P(X,t), \qquad U_K = \mu(X) \cdot K(X). \tag{11.15}$$

The generalized Smoluchowski equation (GSE) now takes the form

$$\begin{aligned} \frac{\partial P}{\partial t} &= -\nabla \cdot J = -\nabla \cdot (J_B + J_K) \\ &= \nabla \cdot (D(X) \cdot \nabla P - \mu(X) \cdot K(X) P) \\ &= \nabla \cdot (D(X) \cdot \nabla P + \mu(X) \cdot (\nabla V) P). \end{aligned} \tag{11.16}$$

Just as in the single particle case, to determine the diffusion matrix $D(X)$ we require that (11.16) has an equilibrium solution of Boltzmann type,

$$P_{\mathrm{eq}}(X) = \frac{1}{Z} e^{-\beta V(X)}, \tag{11.17}$$

for which the total current vanishes, $J_{\mathrm{eq}} = 0$. These two conditions give

$$D(X) = k_B T \mu(X) = k_B T \zeta^{-1}(X), \tag{11.18}$$

the generalization of the Einstein relation (2.10). Using this relation we write the GSE as

$$\frac{\partial P}{\partial t} = \nabla \cdot D \cdot (\nabla P + \nabla(\beta V) P) = \mathcal{D} P, \tag{11.19}$$

defining the many-body Smoluchowski operator to be

$$\mathcal{D} = \nabla \cdot D(X) \cdot (\nabla + \nabla(\beta V(X))) = \nabla \cdot D(X) e^{-\beta V(X)} \cdot \nabla e^{\beta V(X)}. \tag{11.20}$$

The generalized Einstein relation (11.18) enables us to express the GSE as a continuity equation in the space of $6N$ dimensional variables X. We have defined an advective velocity U_K and current J_K in (11.15). Correspondingly we express the Brownian current J_B of (11.6) in terms of a Brownian force K_B and velocity U_B,

$$J_B = U_B\, P(X,t)\,, \qquad U_B = \mu(X) \cdot K_B(X)\,, \tag{11.21}$$

where K_B arises from a Brownian potential V_B,

$$K_B = -\nabla V_B(X,t)\,, \qquad V_B(X,t) = k_B T \ln P(X,t)\,. \tag{11.22}$$

The GSE as expressed in (11.16) now has the form of a generalized continuity equation

$$\frac{\partial P}{\partial t} + \nabla \cdot (UP) = 0\,, \tag{11.23}$$

with $U = U_B + U_K$. This many-body continuity equation generalizes the one-body equations of (2.59) and (5.16). In the discussion above we have considered only internal forces arising from two-body potentials. The continuity equation form of the GSE is readily extended to include external forces and externally imposed flow fields in the suspending fluid [38].

The formal properties of the Smoluchowski equation for translational diffusion sketched in Chapter 2 can all be extended to the GSE. For many-body functions of configuration $A(X)$, $B(X)$ we define a scalar product generalizing (2.32), (2.33) and (2.44) to

$$\begin{aligned}(A(X), B(X)) &= \int A(X)B(X)\,dX\,,\\ (A(X), \mathcal{D}B(X)) &= (\mathcal{L}A(X), B(X))\,,\\ \mathcal{D}P_{\text{eq}}(X)f(X) &= P_{\text{eq}}(X)\mathcal{L}f(X)\,.\end{aligned} \tag{11.24}$$

Here, in exact analogy to the one-particle case, we define the adjoint Smoluchowski operator $\mathcal{L}$ by integration by parts to get

$$\begin{aligned}\mathcal{L} = \mathcal{D}^\dagger &= (\nabla - \nabla(\beta V(X))) \cdot D(X) \cdot \nabla\\ &= e^{\beta V(X)}\nabla \cdot D(X)e^{-\beta V(X)} \cdot \nabla\,.\end{aligned} \tag{11.25}$$

The time correlation formulae which generalize (2.40), (2.41) are

$$\begin{aligned}C_{AB}(t) &= \langle A(X(0))B(X(t))\rangle = \int dX\, P_{\text{eq}}(X)A(X)e^{\mathcal{L}t}B(X)\,,\\ \hat{C}_{AB}(s) &= \int_0^\infty e^{-st}C_{AB}(t)dt = \langle A(s-\mathcal{L})^{-1}B\rangle\,.\end{aligned} \tag{11.26}$$

Because $\mu(X)$, $D(X)$ are functions of configuration, the GSE (11.19) is said to contain hydrodynamic interactions [39, 40] as well as potential interactions which appear in $V(X)$. The interactions between particles which are mediated by the intervening fluid are extremely complicated. They are long-ranged, and by their definition are many-body in character. Unlike $V(X)$ which may be given as a sum of two-body terms as in (11.2) above, $\mu(X)$ is not simply a sum of two-body contributions.

Exercise 11.1: *Generalize the method of exercise (7.3) to the many-body situation with time translation operator $\mathcal{L}$ given by (11.25). Consider the change of configuration from X_0 at time $t = 0$ to X at time $t = dt$ a short time later. Show that to first order in dt we have the relations [41]*

$$\langle \boldsymbol{R}_i(dt) - \boldsymbol{R}_i(0)\rangle_{X_0} = dt \sum_{j=1}^{N} \left(\boldsymbol{\nabla}_j \cdot \boldsymbol{D}^{\mathrm{tt}}_{ji}(X_0) + \beta \boldsymbol{D}^{\mathrm{tt}}_{ij} \cdot \boldsymbol{F}_j(X_0) \right.$$
$$\left. + \beta \boldsymbol{D}^{\mathrm{tr}}_{ij} \cdot \boldsymbol{T}_j(X_0)\right),$$

$$\langle \boldsymbol{u}_i(dt) - \boldsymbol{u}_i(0)\rangle_{X_0} = dt \sum_{j=1}^{N} \Big(\boldsymbol{\nabla}_j \cdot \boldsymbol{D}^{\mathrm{tr}}_{ji}(X_0) \times \boldsymbol{u}_i(0)$$
$$+ \beta \boldsymbol{F}_j(X_0) \cdot \boldsymbol{D}^{\mathrm{tr}}_{ji}(X_0) \times \boldsymbol{u}_i(0) + \beta \boldsymbol{T}_j(X_0) \cdot \boldsymbol{D}^{\mathrm{rr}}_{ji}(X_0) \times \boldsymbol{u}_i(0)\Big)$$
$$+ \boldsymbol{D}^{\mathrm{rr}}_{ii}(X_0) \cdot \boldsymbol{u}_i(0) - (Tr \boldsymbol{D}^{\mathrm{rr}}_{ii}(X_0)) \boldsymbol{u}_i(0),$$

$$\langle (\boldsymbol{R}_i(dt) - \boldsymbol{R}_i(0))(\boldsymbol{R}_j(dt) - \boldsymbol{R}_j(0))\rangle_{X_0} = 2dt \boldsymbol{D}^{\mathrm{tt}}_{ij}(X_0),$$

$$\langle (\boldsymbol{R}_i(dt) - \boldsymbol{R}_i(0))(\boldsymbol{u}_j(dt) - \boldsymbol{u}_j(0))\rangle_{X_0} = 2dt \boldsymbol{D}^{\mathrm{tr}}_{ij}(X_0) \times \boldsymbol{u}_j(0),$$

$$\langle (\boldsymbol{u}_i(dt) - \boldsymbol{u}_i(0))(\boldsymbol{u}_j(dt) - \boldsymbol{u}_j(0))\rangle_{X_0} = -2dt\big(\boldsymbol{u}_i(0) \times \boldsymbol{D}^{\mathrm{rr}}_{ij}(X_0) \times \boldsymbol{u}_j(0)\big).$$

Here an expression like $\boldsymbol{D} \times \boldsymbol{u}$ is shorthand for the tensor quantity $D_{\alpha\beta}\epsilon_{\gamma\beta\rho}u_\rho$ with repeated component labels summed over.

These equations can be used to define a Brownian dynamics algorithm [41, 42] for use in computer simulation of an interacting suspension.

Chapter 12

Probing the particle environment

Thus far we have treated particles such as polar particles which interact directly with an external field that we can control. By observing the response to the field we can learn about diffusion of individual particles. Another situation is possible, however, in which there may be no external fields but only internal fields. What can we observe experimentally in such cases and what can we deduce from it?

First consider a very simple example. Suppose that a single mesosphere of radius a is suspended in a fluid which itself fills a spherical chamber of

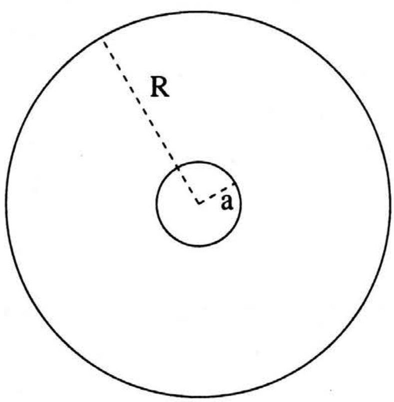

FIGURE 12.1.

radius R. Moreover, suppose that the mesosphere is located instantaneously at the centre of the fluid chamber.

A simple Stokes' flow hydrodynamic calculation gives the tra slational and rotational diffusion coefficients in this special geometry as

$$D^{\mathrm{t}} = D_0^{\mathrm{t}} \frac{(1-x)^3(4+7x+4x^2)}{4(1+x+x^2+x^3+x^4)} \tag{12.1}$$

and

$$D^{\mathrm{r}} = D_0^{\mathrm{r}}(1-x^3)\,, \tag{12.2}$$

where $x = a/R$ and D_0^{t}, D_0^{t} are the diffusivities in unbounded fluid. As the caging gets tighter, $R \to a$, rotational diffusion survives much better than does translational diffusion. If we could measure this diffusion coefficient we would learn something about the size and nature of the confining walls of the chamber. If instead of a fixed chamber, the surroundings comprised a dense glassy colloidal suspension, or a nematic liquid crystal, or a gel, or the space inside a fluid filled zeolite structure, the measured diffusivity would give information about the internal environment of the moving particle.

12.1. Depolarized light scattering

One way to monitor rotational diffusion in such circumstances is by using particles that are optically non-isotropic [43] and then making observations of light scattering with the initial and final polarizations controlled. This technique is described in great detail by Berne and Pecora [14] in their book on dynamic light scattering. A closely related technique uses fluorescence depolarization [14] or polarized fluorescence recovery [23] to measure rotational diffusion. It will be necessary to summarize briefly some experimental details to explain what can be measured and how it can be interpreted.

To be specific, I consider a suspension of N spherical particles with axisymmetric polarizabilities $\boldsymbol{\alpha}^j$, $j = 1, \ldots, N$, as in the earlier discussion of the Kerr effect in Chapter 7. An initial electromagnetic wave with wave vector $\boldsymbol{k}_i$ and linear polarization in the direction of the unit vector $\boldsymbol{n}_i$ scatters in the xy-plane producing an outgoing wave with wave vector $\boldsymbol{k}_f$ and polarization $\boldsymbol{n}_f$. The angle between $\boldsymbol{k}_i$ and $\boldsymbol{k}_f$ is the scattering angle θ and $\boldsymbol{k}_f$ is taken to lie in the direction of the positive x-axis, with the z-axis normal to the scattering plane in the direction of $\boldsymbol{k}_i \times \boldsymbol{k}_f$. The scattering vector $\boldsymbol{q}$ is defined by $\boldsymbol{q} = \boldsymbol{k}_i - \boldsymbol{k}_f$. There are certain standard polarization configurations which

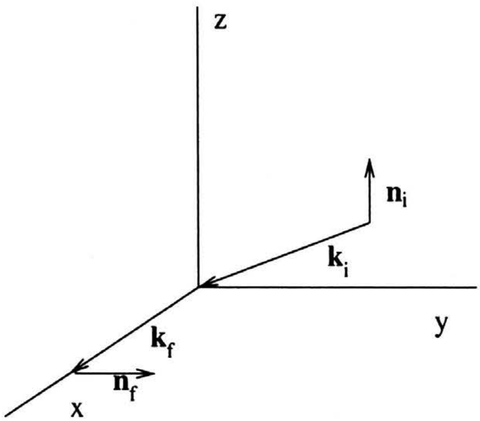

FIGURE 12.2.

are denoted as VV, $\boldsymbol{n}_i = \boldsymbol{e}_z$, $\boldsymbol{n}_f = \boldsymbol{e}_z$, or VH, $\boldsymbol{n}_i = \boldsymbol{e}_z$, $\boldsymbol{n}_f = \boldsymbol{e}_y$, with HV and HH configurations defined analogously [14]. Each suspended particle contributes to the scattered field which has the form

$$E_{\text{scattered}}(t) = C \sum_{j=1}^{\infty} \boldsymbol{n}_i \cdot \boldsymbol{\alpha}^j(t) \cdot \boldsymbol{n}_f e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j(t)}, \tag{12.3}$$

with C a normalization constant. In a dynamic light scattering experiment, what is observed is the autocorrelation function of the scattered light, $\langle E_S^*(0)E_S(t)\rangle$ where the brackets indicate a thermal equilibrium average over the suspension of N particles. The measured autocorrelation function is then proportional to

$$I_{if}(\boldsymbol{q},t) = \sum_{j,k=1}^{N} \langle \alpha_{if}^j(0)\alpha_{if}^k(t) e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_k(t)-\boldsymbol{R}_j(0))}\rangle . \tag{12.4}$$

The polarizability components that contribute to the scattering have been abbreviated to α_{if}^j where

$$\alpha_{if}^j = \boldsymbol{n}_i \cdot \boldsymbol{\alpha}^j \cdot \boldsymbol{n}_f = n_{i\beta} n_{f\gamma} \alpha_{\beta\gamma}^j , \tag{12.5}$$

with Greek subscripts denoting Cartesian components of vectors and tensors. The thermal average, in the absence of external fields is

$$\langle \cdots \rangle = \frac{1}{(4\pi)^N Z^{\text{t}}} \int e^{-\beta V(X^{\text{t}})} \cdots d\boldsymbol{R}_1 \ldots d\boldsymbol{R}_N d\boldsymbol{u}_1 d\boldsymbol{u}_N . \tag{12.6}$$

Note that here I assume potentials that depend only on the position configuration $X^{\mathrm{t}} = (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$, thus ruling out dipolar particles with dipole-dipole interactions which couple the orientation variables $\boldsymbol{u}_i$ to position variables $\boldsymbol{R}_j$. The $I_{if}(\boldsymbol{q},t)$ can be expressed in terms of the polarization tensor [14] $w^{if}_{\beta\gamma} = n_{i\beta}n_{f\gamma}$ as

$$I_{if}(\boldsymbol{q},t) = w^{if}_{\beta\gamma} w^{if}_{\rho\sigma} \sum_{j,k=1}^{N} \langle \alpha^j_{\beta\gamma}(0) \alpha^k_{\rho\sigma}(t) e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_k(t)-\boldsymbol{R}_j(0))} \rangle . \tag{12.7}$$

The time-correlation function that appears in (12.7) is quite complex but it simplifies somewhat in various limiting situations. For example, in a dilute suspension with no orientation dependent interactions, or in a dense suspension at large values of the scattering vector $\boldsymbol{q}$, the cross-particle correlations can be neglected so that only the $j = k$ terms survive. For identical particles these diagonal terms are all identical reducing (12.7) to

$$I_{if}(\boldsymbol{q},t) = w^{if}_{\beta\gamma} w^{if}_{\rho\sigma} N \langle \alpha_{\beta\gamma}(0) \alpha_{\rho\sigma}(t) e^{i\boldsymbol{q}\cdot(\boldsymbol{R}(t)-\boldsymbol{R}(0))} \rangle , \tag{12.8}$$

where $\boldsymbol{\alpha}$ and $\boldsymbol{R}$ refer to the same single particle. A second simplifying assumption is often made to interpret I_{if}, called the de-coupling appproximation. This consists of assuming that translational and rotational motions are uncoupled. For spherical particles this may be reasonable, for non-spherical particles it is at best a pious hope. With this second approximation we have

$$I_{if}(\boldsymbol{q},t) = w^{if}_{\beta\gamma} w^{if}_{\rho\sigma} N \langle \alpha_{\beta\gamma}(0) \alpha_{\rho\sigma}(t) \rangle \langle e^{i\boldsymbol{q}\cdot(\boldsymbol{R}(t)-\boldsymbol{R}(0))} \rangle , \tag{12.9}$$

where the second factor now defines the dynamic scattering function for self or tracer translational diffusion,

$$F_S(\boldsymbol{q},t) = \langle e^{i\boldsymbol{q}\cdot(\boldsymbol{R}(t)-\boldsymbol{R}(0))} \rangle . \tag{12.10}$$

In a suspension of non-interacting spherical particles whose motion is described by the simple Gaussian Langevin process of Chapter 2 , we would have the result

$$F_S(\boldsymbol{q},t) = e^{-q^2 \langle (\boldsymbol{R}(t)-\boldsymbol{R}(0))^2 \rangle /6} = e^{-D^{\mathrm{t}}_0 q^2 t} , \tag{12.11}$$

with D^{t}_0 the non-interacting self-diffusion coefficient introduced in Chapter 2. Deviations of $F_S(\boldsymbol{q},t)$ from the single exponential result in (12.11) give information about particle interactions [14, 39, 40]. The other correlation function

$\langle \alpha_{\beta\gamma}(0)\alpha_{\rho\sigma}(t)\rangle$ contains information about rotational diffusion. There are two common polarization measurements made [14, 40], one (VV) with initial and final polarization states normal to the scattering plane ($\boldsymbol{n} = \boldsymbol{e}_z$), the other (VH) with $\boldsymbol{n}_i = \boldsymbol{e}_z$, $\boldsymbol{n}_f = \boldsymbol{e}_y$. Thus we obtain by measurement

$$\begin{aligned} I_{VV}(\boldsymbol{q},t) &= N\langle \alpha_{zz}(0)\alpha_{zz}(t)\rangle F_S(\boldsymbol{q},t)\,, \\ I_{VH}(\boldsymbol{q},t) &= N\langle \alpha_{yz}(0)\alpha_{yz}(t)\rangle F_S(\boldsymbol{q},t)\,, \end{aligned} \tag{12.12}$$

where we have used the symmetry of $\boldsymbol{\alpha}$. The VH measurement is referred to as the depolarized scattering.

We can say quite a lot more about the form of $\langle \alpha_{\beta\gamma}(0)\alpha_{\rho\sigma}(t)\rangle$ for suspensions in which potential interactions are independent of orientation and depend only on the interparticle distances $|\boldsymbol{R}_i - \boldsymbol{R}_j|$. We recall from (7.14) and (7.15) the form of $\boldsymbol{\alpha}$ for an axisymmetric optical polarizability,

$$\boldsymbol{\alpha} = \alpha_0 \mathbf{1} + b\boldsymbol{S} = \alpha_0 \mathbf{1} + b\,(\boldsymbol{uu} - \frac{1}{3}\mathbf{1})\,,$$

where $\alpha_0 = (\alpha_\parallel + 2\alpha_\perp)$ and $b = (\alpha_\parallel - \alpha_\perp)$ is the anisotropy parameter. We have

$$\begin{aligned} \langle \alpha_{\beta\gamma}(0)\alpha_{\rho\sigma}(t)\rangle &= \alpha_0^2 \delta_{\beta\gamma}\delta_{\rho\sigma} \\ &+ \alpha_0 b \delta_{\beta\gamma}\langle S_{\rho\sigma}(t)\rangle + \alpha_0 b\langle S_{\beta\gamma}(0)\rangle\delta_{\rho\sigma} + b^2\langle S_{\beta\gamma}(0)S_{\rho\sigma}(t)\rangle\,, \end{aligned} \tag{12.13}$$

where by time translation invariance $\langle S_{\beta\gamma}(0)\rangle = \langle S_{\beta\gamma}(t)\rangle$, and, for an isotropic suspension (isotropy being a consequence of the assumed potential interactions) $\langle S_{\beta\gamma}\rangle = 0$. The isotropy of the suspension allow us to decompose the time-correlation function into isotropic Cartesian tensors as [14]

$$\langle S_{\beta\gamma}(0)S_{\rho\sigma}(t)\rangle = u(t)\delta_{\beta\gamma}\delta_{\rho\sigma} + v(t)(\delta_{\beta\rho}\delta_{\gamma\sigma} + \delta_{\beta\sigma}\delta_{\rho\gamma})\,, \tag{12.14}$$

with $u(t)$, $v(t)$ scalar functions. By the tracelessness of $\boldsymbol{S}$ we have (using the summation convention for repeated subscripts)

$$\langle S_{\beta\beta}(0)S_{\rho\sigma}(t)\rangle = (3u(t) + 2v(t))\delta_{\rho\sigma} = 0\,,$$

giving $u(t) = -(2/3)\,v(t)$ and the simplified form of (12.14)

$$\langle S_{\beta\gamma}(0)S_{\rho\sigma}(t)\rangle = v(t)\left(\delta_{\beta\rho}\delta_{\gamma\sigma} + \delta_{\beta\sigma}\delta_{\rho\gamma} - \frac{2}{3}\delta_{\beta\gamma}\delta_{\rho\sigma}\right). \tag{12.15}$$

From this result we further calculate (again using the summation convention)

$$\langle S_{\beta\gamma}(0)S_{\gamma\beta}(t)\rangle = 10v(t)\,, \tag{12.16}$$

but from the definition of $\boldsymbol{S}$ in (7.15) we also have

$$\langle S_{\beta\gamma}(0)S_{\gamma\beta}(t)\rangle = \frac{2}{3}\langle\frac{3}{2}\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)^2 - \frac{1}{2}\rangle = \frac{2}{3}\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle\,. \tag{12.17}$$

Putting together (12.13), (12.15)-(12.17) gives [14]

$$\begin{aligned}\langle\alpha_{\beta\gamma}(0)\alpha_{\rho\sigma}(t)\rangle &= \alpha_0^2\delta_{\beta\gamma}\delta_{\rho\sigma}\\ &\quad + \frac{b^2}{15}\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle\left(\delta_{\beta\rho}\delta_{\gamma\sigma} + \delta_{\beta\sigma}\delta_{\rho\gamma} - \frac{2}{3}\delta_{\beta\gamma}\delta_{\rho\sigma}\right).\end{aligned} \tag{12.18}$$

Thus the polarizability time-correlation function measures the correlation between the directions $\boldsymbol{u}(0)$ and $\boldsymbol{u}(t)$.

From the calculation of (5.26) we have, for completely non-interacting particles, $\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle = \exp(-6D_0^{\mathrm{r}}t)$ so that in very dilute suspensions we can measure the "bare" rotational diffusion coefficient of an isolated single particle from the polarizability correlations. If we apply (12.18) to the two special scattering configurations VV and VH we find

$$\begin{aligned}I_{VV}(\boldsymbol{q},t) &= N\left(\alpha_0^2 + \frac{4b^2}{45}\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle\right)F_S(\boldsymbol{q},t)\,,\\ I_{VH}(\boldsymbol{q},t) &= N\frac{b^2}{15}\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle F_S(\boldsymbol{q},t)\,.\end{aligned} \tag{12.19}$$

For isotropic suspensions the result (12.19) can be cast in a variety of different forms. We had the identity (5.25) which on averaging becomes

$$\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle = \frac{4\pi}{5}\sum_{m=-2}^{2}\langle Y_{2m}^*(\boldsymbol{u}(0))Y_{2m}(\boldsymbol{u}(t))\rangle.$$

However, in an isotropic suspension one can show [44] that $\langle Y_{2m}^*(\boldsymbol{u}(0))$ $Y_{2m}(\boldsymbol{u}(t))\rangle$ is independent of m so that we can also write

$$\langle P_2\left(\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\right)\rangle = 4\pi\langle Y_{2m}^*(\boldsymbol{u}(0))Y_{2m}(\boldsymbol{u}(t))\rangle = F_R(t)\,. \tag{12.20}$$

Thus (12.19) can be expressed as

$$\begin{aligned}I_{VV}(\boldsymbol{q},t) &= N\left(\alpha_0^2 + \frac{4b^2}{45}F_R(t)\right)F_S(t)\,,\\ I_{VH}(\boldsymbol{q},t) &= N\frac{b^2}{15}F_R(t)F_S(t)\,.\end{aligned} \tag{12.21}$$

Yet other forms of the scattering functions are given in Berne and Pecora [14] which arise from expressing α_{zz} and α_{yz} in (12.12) in terms of the spherical polar angles θ, φ of $\boldsymbol{u}$ with respect to a laboratory frame of reference,

$$\begin{aligned}\alpha_{zz} &= \alpha_0 - \frac{b}{3} + bu_z u_z = \alpha_0 - \frac{b}{3} + b\cos^2\theta = \alpha_0 + b\sqrt{\frac{16\pi}{45}}Y_{20}(\theta,\varphi)\,,\\ \alpha_{yz} &= bu_y u_z = b\sin\theta\cos\theta\sin\varphi = i\sqrt{\frac{2\pi}{15}}\,(Y_{21}(\theta,\varphi) + Y_{2-1}(\theta,\varphi))\,.\end{aligned} \tag{12.22}$$

Experimental measurements in the VV and VH configurations enable one to extract separately [43] the two single-particle correlation functions $F_S(\boldsymbol{q},t)$ and $F_R(t)$.

12.2. Hydrodynamic interactions

For a suspension of spherical polarizable particles, the depolarized light scattering gives a way to measure the hydrodynamic interactions buried inside the GSE description. To examine this further, we assume that the potential energy for the suspension consists of a sum of central two-body potentials that depend only on particle separation but not on orientation,

$$V(X) = \sum_{i<j} v_{ij}(|\boldsymbol{R}_i - \boldsymbol{R}_j|)\,. \tag{12.23}$$

With this assumption the adjoint Smoluchowski operator takes the form

$$\begin{aligned}\mathcal{L} = \sum_{i,j=1}^{N}\Bigg\{ &\left(\frac{\partial}{\partial \boldsymbol{R}_i} - \frac{\partial(\beta V)}{\partial \boldsymbol{R}_i}\right)\cdot\left(\boldsymbol{D}^{\mathrm{tt}}_{ij}(X^{\mathrm{t}})\cdot\frac{\partial}{\partial \boldsymbol{R}_j} + \boldsymbol{D}^{\mathrm{tr}}_{ij}(X^{\mathrm{t}})\cdot\boldsymbol{L}_j\right)\\ &+ \boldsymbol{L}_i\cdot\left(\boldsymbol{D}^{\mathrm{rt}}_{ij}(X^{\mathrm{t}})\cdot\frac{\partial}{\partial \boldsymbol{R}_j} + \boldsymbol{D}^{\mathrm{rr}}_{ij}(X^{\mathrm{t}})\cdot\boldsymbol{L}_j\right)\Bigg\}\,,\end{aligned} \tag{12.24}$$

$$\mathcal{L} = \mathcal{L}^{\mathrm{tt}} + \mathcal{L}^{\mathrm{tr}} + \mathcal{L}^{\mathrm{rt}} + \mathcal{L}^{\mathrm{rr}}\,. \tag{12.25}$$

We have indicated that for spherical particles the diffusion tensors $\boldsymbol{D}^{\mathrm{ab}}(X^{\mathrm{t}})$ are functions of position only but not of orientation. We have broken $\mathcal{L}$ into a sum of four operators, corresponding to the four types of diffusion tensors involved in each. Note that because of the position dependence of the $\boldsymbol{D}^{\mathrm{ab}}(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N)$ and the occurrence of configuration derivatives $\partial/\partial\boldsymbol{R}_i$, the different operators $\mathcal{L}^{\mathrm{ab}}$ do not commute with each other. As we have seen above, the typical time-correlation function that enters into the light scattering has the form

$$
\begin{aligned}
F_{\ell m}(\boldsymbol{q},t) &= \frac{4\pi}{N}\sum_{j,k=1}^{N}\langle Y^*_{\ell m}(\boldsymbol{u}_j(0))e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_j(0)}Y_{\ell m}(\boldsymbol{u}_k(t))e^{i\boldsymbol{q}\cdot\boldsymbol{R}_k(t)}\rangle \\
&= \frac{4\pi}{N}\sum_{j,k=1}^{N}\langle Y^*_{\ell m}(\boldsymbol{u}_j)e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_j}e^{\mathcal{L}t}Y_{\ell m}(\boldsymbol{u}_k)e^{i\boldsymbol{q}\cdot\boldsymbol{R}_k}\rangle\,,
\end{aligned}
\tag{12.26}
$$

where we have made use of $\mathcal{L}$ as a time translation operator as in (11.26). Because we cannot rigorously factor the time-translation operator owing to the non-commutativity of the $\mathcal{L}^{\mathrm{ab}}$, $(\exp\mathcal{L}t \neq \exp\mathcal{L}^{\mathrm{tt}}t\,\exp\mathcal{L}^{\mathrm{tr}}t\,\exp\mathcal{L}^{\mathrm{rt}}t\,\exp\mathcal{L}^{\mathrm{rr}}t)$, we see that the de-coupling approximation cannot be exact. However, for an isotropic suspension as assumed above, we can observe [43] that to order t there is de-coupling of translations and rotations. Indeed, in the absence of orientation dependent potentials, $\mathcal{L}$ cannot couple $\boldsymbol{u}_i$ to $\boldsymbol{u}_j$ for $i \neq j$ so in the equilibrium thermal average (12.6) all collective terms with $i \neq j$ vanish, and for identical particles we need look only at

$$
F_{\ell m}(\boldsymbol{q},t) = 4\pi\langle Y^*_{\ell m}(\boldsymbol{u}_1)e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_1}e^{\mathcal{L}t}Y_{\ell m}(\boldsymbol{u}_1)e^{i\boldsymbol{q}\cdot\boldsymbol{R}_1}\rangle\,. \tag{12.27}
$$

Expanding the time translation operator to first order in t, $\exp\mathcal{L}t = 1 + t(\mathcal{L}^{\mathrm{tt}}+\mathcal{L}^{\mathrm{tr}}+\mathcal{L}^{\mathrm{rt}}+\mathcal{L}^{\mathrm{rr}})+\mathcal{O}(t^2)$, and using the isotropy of the suspension [43], we find no contribution from $\mathcal{L}^{\mathrm{tr}}$, $\mathcal{L}^{\mathrm{rt}}$ leaving only the contributions

$$
\begin{aligned}
&4\pi\langle Y^*_{\ell m}(\boldsymbol{u}_1)e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_1}\mathcal{L}^{\mathrm{tt}}Y_{\ell m}(\boldsymbol{u}_1)e^{i\boldsymbol{q}\cdot\boldsymbol{R}_1}\rangle \\
&\qquad = 4\pi\langle Y^*_{\ell m}(\boldsymbol{u}_1)Y_{\ell m}(\boldsymbol{u}_1)\rangle\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_1}\mathcal{L}^{\mathrm{tt}}e^{i\boldsymbol{q}\cdot\boldsymbol{R}_1}\rangle = -\frac{q^2}{3}\langle Tr\boldsymbol{D}^{\mathrm{tt}}_{11}\rangle\,,
\end{aligned}
\tag{12.28}
$$

$$
\begin{aligned}
&4\pi\langle Y^*_{\ell m}(\boldsymbol{u}_1)e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_1}\mathcal{L}^{\mathrm{rr}}Y_{\ell m}(\boldsymbol{u}_1)e^{ii\boldsymbol{q}\cdot\boldsymbol{R}_1}\rangle \\
&\qquad = 4\pi\langle Y^*_{\ell m}(\boldsymbol{u}_1)\mathcal{L}^{\mathrm{rr}}\,Y_{\ell m}(\boldsymbol{u}_1)\rangle = -\frac{\ell(\ell+1)}{3}\langle Tr\boldsymbol{D}^{\mathrm{rr}}_{11}\rangle\,.
\end{aligned}
\tag{12.29}
$$

Thus the short-time result for $F_{\ell m}(\boldsymbol{q},t)$ is

$$
F_{\ell m}(\boldsymbol{q},t) = 1 - \left(q^2 D^{\mathrm{t}}_0 H^{\mathrm{t}}_s + \ell(\ell+1)D^{\mathrm{r}}_0 H^{\mathrm{r}}_s\right)t + \mathcal{O}(t^2)\,, \tag{12.30}
$$

with D^{t}_0 and D^{r}_0 the "bare" translational and rotational diffusion coefficients for a single isolated sphere in the suspending fluid. The functions H^{t}_s and H^{r}_s

are many-body configurational averages of the respective tracer mobilities,

$$
\begin{aligned}
H_s^{\mathrm{t}} &= \frac{k_B T}{3D_0^{\mathrm{t}}}\langle Tr\boldsymbol{\mu}_{11}^{\mathrm{tt}}(X^{\mathrm{t}})\rangle = \frac{k_B T}{3D_0^{\mathrm{t}}}\int dX P_{\mathrm{eq}}(X) Tr\boldsymbol{\mu}_{11}^{\mathrm{tt}}(X^{\mathrm{t}})\,,\\
H_s^{\mathrm{r}} &= \frac{k_B T}{3D_0^{\mathrm{r}}}\langle Tr\boldsymbol{\mu}_{11}^{\mathrm{rr}}(X^{\mathrm{t}})\rangle = \frac{k_B T}{3D_0^{\mathrm{r}}}\int dX P_{\mathrm{eq}}(X) Tr\boldsymbol{\mu}_{11}^{\mathrm{rr}}(X^{\mathrm{t}})\,.
\end{aligned}
\tag{12.31}
$$

Thus from the short-time light scattering in the VV and VH polarization configurations we get information about the hydrodynamic interaction functions for the suspension.

For suspensions at low to medium particle density one can evaluate these many-body averages using a cluster expansion in powers of Φ, the volume fraction of the suspended mesoparticles [45, 46]. The cluster expansion looks like

$$
\begin{aligned}
\langle\boldsymbol{\mu}_{11}^{\mathrm{rr}}(X^{\mathrm{t}})\rangle &= \boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1) + \frac{n^2}{N}\int d\boldsymbol{R}_1 d\boldsymbol{R}_2 g(\boldsymbol{R}_1,\boldsymbol{R}_2)\left(\boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1,\boldsymbol{R}_2) - \boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1)\right)\\
&+ \frac{n^3}{2N}\int d\boldsymbol{R}_1 d\boldsymbol{R}_2 d\boldsymbol{R}_3 g(\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3)\Big(\left(\boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3) - \boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1)\right)\\
&- \left(\boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1,\boldsymbol{R}_2) - \boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1)\right) - \left(\boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1,\boldsymbol{R}_3) - \boldsymbol{\mu}_{11}^{\mathrm{rr}}(\boldsymbol{R}_1)\right)\Big) + \dots\,,
\end{aligned}
\tag{12.32}
$$

where $n = N/V$ is the number density of the suspension and $g(\boldsymbol{R}_1,\boldsymbol{R}_2)$, $g(\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3)$ are the pair and triplet distribution functions for the suspension. From this and a similar expression for $\langle\boldsymbol{\mu}_{11}^{\mathrm{tt}}\rangle$ we derive virial expansions to second order in the volume fraction Φ,

$$
\begin{aligned}
H_s^{\mathrm{t}}(\Phi) &= 1 + H_{s1}^{\mathrm{t}}\Phi + H_{s2}^{\mathrm{t}}\Phi^2 + \dots\,,\\
H_s^{\mathrm{r}}(\Phi) &= 1 + H_{s1}^{\mathrm{r}}\Phi + H_{s2}^{\mathrm{r}}\Phi^2 + \dots\,.
\end{aligned}
\tag{12.33}
$$

One experimental measurement on a heavily screened charged suspension [43] gave

$$
H_s^{\mathrm{r}} = 1 - (0.55 \pm 0.1)\Phi - (1.1 \pm 0.2)\Phi^2 + \dots\,,
\tag{12.34}
$$

while a theoretical calculation for hard spheres [47] gave

$$
H_s^{\mathrm{r}} = 1 - 0.6310\Phi - (0.726 \pm 0.001)\Phi^2 + \dots\quad.
\tag{12.35}
$$

Although screened charged particles are not hard spheres, their interactions are very short ranged with a strongly repulsive core so that the degree of agreement between (12.34) and (12.35) is encouraging.

It is now possible to make similar measurements for tracer spheres in suspensions of spheres of different sizes [23, 48, 49], in suspensions of rods and discs and in gels. Quite recently measurements of rotational diffusion of a tracer disc have been used to deduce the viscoelastic modulus of a polymer entanglement network [50]. There is as yet limited theoretical understanding of these more complicated suspensions as compared with suspensions of identical spheres. Good theoretical models of these more complicated systems will enable the experimental measurements to be interpreted in terms of detailed local properties of the suspension thus providing an ever more valuable diagnostic tool.

Chapter 13

Afterword

These lectures have traced some of the applications of rotational diffusion as they developed from Debye's original work in 1913. After introducing the mathematical description of rotational diffusion in terms of a Smoluchowski equation in orientation space, most of the applications from Chapter 7 to Chapter 12 concerned polar or dielectric particles and their interactions with static or dynamic electric fields. However, these examples are far from exhausting the many applications of rotational diffusion to systems of dispersed particles. This brief afterword points the reader to additional areas where rotational dynamics plays an important role and where there is scope for progress in theoretical modelling.

The dynamics of ferrofluids or magneto-rheological fluids (suspensions of magnetic or magnetizable colloidal particles) is a technologically significant area of application [51]. Although formally similar to dispersions of electrically polar particles, the magnetic systems have many applications in technology owing to the wide variety of particle size and magnetization properties achievable. A particularly interesting class of problems arises here from the coupling of flow fields, external magnetic fields and rotational diffusion which leads to phenomena like magneto-viscosity [52] and "negative" viscosity [53, 54, 55] seen in the flow of a ferrofluid down a tube in the presence of an oscillating field.

For suspensions of electrically or magnetically polar particles the dynamics of dense suspensions represents a difficult many-body problem. We have touched on the many-body problem in Chapters 11 and 12 but there studied only single-particle correlation functions while ignoring the effect of long-ranged dipole-dipole interactions. In addition to these tracer particle correlation functions there are correlation functions for collective rotational and translational properties which are equally important [56]. By approximating and truncating the dipole-dipole interaction to a finite range Heisenberg interaction and ignoring hydrodynamic interactions, the effect of two-body rotational dynamics in semi-dilute suspensions has been studied [57]. More recently progress has been made on the two-body problem with the full long-ranged dipole-dipole interaction present [58]. If hydrodynamic interactions are included as well as dipolar forces, computer simulation may be the only way to make progress in modelling dense suspensions.

For suspensions of non-spherical particles there are interesting problems both for dilute systems subject to external fields [20] and for dense systems of linear particles such as rigid rod polymers [24, 59]. Finally we mention an analogue problem suggested by the observation in Chapter 4 that the configuration space of orientations is compact and bounded. The extreme limit of a bounded configuration space would be one in which there were only a finite discrete set of orientations possible. We can map such a system onto a diffusion-reaction system where each particle has a finite set of internal chemical states between which transitions are possible. The analogue of the Smoluchowski equation in Chapter 4 becomes a discrete state master equation which can be used in a generalized Smoluchowski description instead of the continuous rotation operators [60]. These examples show that there are still many challenging applications of rotational diffusion ninety years after Debye's seminal paper.

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