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The coupling between translational and rotational motions

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The coupling between molecular reorientation and translational displacement is studied in a fluid of rough spheres. The correlation functions frequently encountered in thermal neutron scattering and laser light scattering are computed using a binary collision approximation. These are compared with the corresponding uncoupled results. In the diffusion limit coupled and uncoupled diffusion coefficients are found. The Hubbard relation is generalized. The maximum deviation between the coupled and uncoupled results occur for wavenumbers commonly found in thermal neutron scattering. The ratio of uncoupled and coupled correlation times displays regions where translation–rotation coupling is clearly important. In these regions there are important differences in the computed coupled and uncoupled correlation functions.

1. INTRODUCTION

Spectroscopic techniques rarely if ever determine the pure reorientational correlation functions [1]

$$C_l(t) \equiv \langle P_l(\mathbf{u}(0) \,.\, \mathbf{u}(t))\rangle, \tag{1.1}$$

where $P_l(x)$ is the Legendre polynomial of order l and $\mathbf{u}$ is a unit vector embedded in a molecule. Instead, the correlation functions [2]

$$C_l(\mathbf{q}, t) \equiv \langle P_l(\mathbf{u}(t) \,.\, \mathbf{u}(0)) \exp [i\mathbf{q} \,.\, \Delta\mathbf{r}(t)]\rangle \tag{1.2}$$

are determined where $\Delta\mathbf{r}(t) = \mathbf{r}(t) - \mathbf{r}(0)$ is the displacement of a molecule in the time t and $\mathbf{q}$ is the wave vector defining the scattering between the probing beam and the molecules of the fluid.

A good example of where such correlation functions arise is that of incoherent thermal neutron scattering [2]. Such functions also arise in connection with dipolar absorption, and Raman scattering processes [1, 3]. In these latter cases q is often small enough that the phase factor $\exp [i\mathbf{q} \,.\, \Delta\mathbf{r}(t)]$ is ignored. In neutron scattering [3] and light scattering [4] it is often assumed, on the other hand, that there is no coupling between the rotational and translational motions so that equation (1.2) becomes

$$C_l(\mathbf{q}, t) \simeq C_l(t)F_s(\mathbf{q}, t), \tag{1.3}$$

where $C_l(t)$ is given by equation (1.1), and

$$F_s(\mathbf{q}, t) \equiv \langle \exp [i\mathbf{q} \,.\, \Delta\mathbf{r}(t)]\rangle \tag{1.4}$$

is the frequently encountered Van Hove self-intermediate scattering function [5] which describes the self-translational motion of the molecules.

In this paper we study the orientational relaxation of a fluid of rough spherical molecules. The three correlation functions $C_l(t)$, $C_l(\mathbf{q}, t)$ and $F_s(\mathbf{q}, t)$ are calculated using a simple approximation recently introduced by Chandler in a different connection [6]. Although this approximation is not expected to give quantitatively accurate correlation functions [7], it is expected to provide a trustworthy picture of the coupling between translational and rotational motion.

In this paper the model of rough spheres is generalized and is studied as a function of a slip parameter λ. When $\lambda=0$ the spheres are perfectly smooth, whereas when $\lambda=1$ they are perfectly rough. For $0<\lambda<1$, the collisions between the spheres are less efficient transmitters of angular velocity. It is found that the coupling between rotations and translations is a very sensitive function of λ such that the coupling increases as λ decreases. Even in the limit in which $C_l(t)$, and $F_s(\mathbf{q}, t)$ are adequately described by rotational and translational diffusion equations, there are values of the parameters for which $C_l(\mathbf{q}, t)$ is not represented by equation (1.3).

Although the calculations performed here are for classical systems, the approach is easily generalized to quantum-mechanical systems. In addition the functions

$$C_{lm}(\mathbf{q}, t)=\langle Y_{lm}^*(\mathbf{u}(t))\, Y_{lm}(\mathbf{u}(0)) \exp(i\mathbf{q} \,.\, \Delta\mathbf{r})\rangle \tag{1.5}$$

are also easily computed.

2. Theory

It is useful to develop the theory in terms of irreducible tensorial sets [8]. To this end define the irreducible tensorial set of rank l:

$$\boldsymbol{\alpha}^{(l)}(\mathbf{q})=\mathbf{Y}_l(\mathbf{u}) \exp(i\mathbf{q} \,.\, \mathbf{r}), \tag{2.1}$$

where $\mathbf{u}$ is a unit vector rigidly embedded in the sphere and $\mathbf{r}$ is the position of the centre of mass of the sphere. $\mathbf{Y}_l(\mathbf{u})$ is an irreducible tensorial set consisting of the $2l+1$ spherical harmonics $\{Y_{lm}(\mathbf{u})\}$. In addition it should be recalled that the tensor dot product $\odot$ is defined† such that $\mathbf{Y}_l(\mathbf{u}_1)\odot\mathbf{Y}_l(\mathbf{u}_2)=P_l(\mathbf{u}_1 \,.\, \mathbf{u}_2)$, where $P_l(x)$ is a Legendre polynomial of rank l.

From this it is clear that equation (1.3) can also be written as

$$C_l(\mathbf{q}, t)=\langle(\exp iLt\boldsymbol{\alpha}^{(l)}(\mathbf{q}))\odot\boldsymbol{\alpha}^{(l)}(\mathbf{q})\rangle \tag{2.2}$$

where L is the Liouville operator.‡

The aim of this paper is to compute these correlation functions for a rough sphere fluid.

In Appendices A and B it is shown that in the independent binary collision

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† In particular

$$\mathbf{Y}_l(\mathbf{u}_1) \,.\, \mathbf{Y}_l(\mathbf{u}_2)\equiv\frac{4\pi}{2l+1}\sum_{m=-l}^{+l} Y_{lm}(\mathbf{u}_1)\,Y_{lm}^*(\mathbf{u}_2).$$

Application of the spherical harmonic addition theorem then gives $P_l(\mathbf{u}_1 \,.\, \mathbf{u}_2)$.

‡ The Liouvillian, L, is the generator of the motion in phase space. Its properties for hard and rough spheres are discussed in references [6] and [7] and the references cited therein, particularly to papers by Zwanzig, and Dorfman and Cohen.

approximation the rough sphere fluid is characterized by the following parameters :

$$\frac{1}{\tau_c} \equiv \left(\frac{16\pi kT}{m}\right)^{1/2} n g^{(2)}(\sigma)\sigma^2, \tag{2.3 a}$$

$$\kappa \equiv \frac{4I}{m\sigma^2}, \tag{2.3 b}$$

$$\frac{1}{\tau_v} = \tfrac{2}{3}\left(\frac{(1+\lambda)\kappa+1}{\kappa+1}\right)\frac{1}{\tau_c}, \tag{2.3 c}$$

$$\frac{1}{\tau_\omega} = \tfrac{2}{3}\left(\frac{\lambda}{\kappa+1}\right)\frac{1}{\tau_c}, \tag{2.3 d}$$

i.e.

$$\frac{\tau_\omega}{\tau_v} = \frac{(1+\lambda)\kappa+1}{\lambda}, \tag{2.3 e}$$

where τ_c is the mean free time, m is the mass, n is the number density, σ is the sphere diameter, $g^{(2)}(\sigma)$ is the contact pair correlation function [9]†, I is the moment of inertia, κ is the loading parameter, λ is the coefficient of slip and τ_v and τ_ω are respectively the linear and angular velocity correlation times.

It should be noted that τ_v and τ_ω are very sensitive to the values of κ and λ. κ specifies the mass distribution in the sphere and takes the values 0, $\tfrac{2}{5}$ and $\tfrac{2}{3}$ respectively when the mass is distributed entirely in the centre, uniformly, or entirely on the surface of the sphere. The coefficient of slip varies between $\lambda=0$ for perfectly smooth spheres to $\lambda=1$ for perfectly rough spheres. It is important to observe that τ_v/τ_ω is a very strong function of λ and a weak function of κ. Mixtures are treated in Appendix B.

It is useful to express the time in units of the free rotational tumbling time $(I/kT)^{1/2}$. The above parameters then become

$$\beta_c = \left(\frac{I}{kT}\right)^{1/2}\frac{1}{\tau_c}, \quad \beta_v = \left(\frac{I}{kT}\right)^{1/2}\frac{1}{\tau_v}, \quad \beta_\omega = \left(\frac{I}{kT}\right)^{1/2}\frac{1}{\tau_\omega}. \tag{2.4}$$

To proceed we define the generalized scalar product of two tensorial sets $\mathbf{A}^{(l)}$ and $\mathbf{B}^{(l)}$ as

$$(A^{(l)}, B^{(l)}) = \langle \mathbf{A}^{(l)} \odot \mathbf{B}^{(l)} \rangle, \tag{2.5}$$

where $\langle \ldots \rangle$ denotes an ensemble average. Then we note that

$$C_l(\mathbf{q}, t) = ((\exp(iLt)\alpha^{(l)}(\mathbf{q})), \alpha^{(l)}(\mathbf{q})). \tag{2.6}$$

Clearly the correlation functions introduced in equations (1.2) and (1.1) are respectively,

$$F_s(\mathbf{q}, t) = C_0(\mathbf{q}, t), \tag{2.7}$$

$$C_l(t) = \lim_{q\to 0} C_l(\mathbf{q}, t). \tag{2.8}$$

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† The contact pair correlation function is well approximated by

$$g(\sigma) = (2-\eta)[2(1-\eta)^3]^{-1},$$

where $\eta = \sqrt{2}\pi\hat{\rho}/6$ with $\hat{\rho}$ being the reduced number density. This was first recognized by N. F. Carnahan and K. E. Starling.

This definition of the scalar product can be used in conjunction with the Zwanzig–Mori formalism [10]† to derive the equation

$$\frac{\partial C_l}{\partial t}(\mathbf{q}, t) = -\int_0^t dt\, K_l(\mathbf{q}, \tau) C_l(\mathbf{q}, t-\tau) \tag{2.9}$$

where $K_l(t)$ is the memory function

$$K_l(\mathbf{q}, t) = (\exp(iQLt)\dot{\alpha}^{(l)}(\mathbf{q}), \dot{\alpha}^{(l)}(\mathbf{q})), \tag{2.10}$$

where Q and P are projection operators

$$Q = 1 - P, \tag{2.11 a}$$

$$P = (\ldots, \alpha^{(l)}(\mathbf{q}))\boldsymbol{\alpha}^{(l)}(\mathbf{q}). \tag{2.11 b}$$

$\dot{\alpha}^{(l)}$ is the instantaneous rate of change of $\boldsymbol{\alpha}^{(l)}$ which can be expressed as [11]

$$\dot{\boldsymbol{\alpha}}^{(l)}(\mathbf{q}) = i\boldsymbol{\omega} \cdot \hat{\mathbf{l}}\boldsymbol{\alpha}^{(l)}(\mathbf{q}) + i\mathbf{q} \cdot \mathbf{v}\boldsymbol{\alpha}^{(l)}(\mathbf{q}), \tag{2.12}$$

where $\boldsymbol{\omega}$ and $\mathbf{v}$ are respectively the angular and linear velocity of the sphere and where $\hat{\mathbf{l}}$ is the dimensionless angular momentum operator (generator of the rotation) of the sphere.

It is useful to evaluate the quantity $(\dot{\alpha}^{(l)}(\mathbf{q}), \dot{\alpha}^{(l)}(\mathbf{q}))$. This is readily accomplished by noting that $\hat{\mathbf{l}}$ is hermitian and $\mathbf{v}$ and $\boldsymbol{\omega}$ are statistically independent. It follows from this that (see Appendix A)

$$(\dot{\alpha}^{(l)}(\mathbf{q}), \dot{\alpha}^{(l)}(\mathbf{q})) = \tfrac{1}{3}(l(l+1)\langle\omega^2\rangle + q^2\langle v^2\rangle). \tag{2.13}$$

To proceed we adopt an approximation first proposed by Chandler in a different context [6]. This approximation includes all sequences of independent binary collisions in which any two spheres collide with each other only once. Thus back-scattering events are not treated properly [12]‡. Nevertheless, this approximation yields results consistent with the Chapman–Enskog solution of the Enskog equation. We therefore call this the independent binary collision approximation (IBCA). Thus, applying the IBCA we find that $K_l(\mathbf{q}, t)$ of equation (2.10) can be expressed in terms of $K_l^{(0)}(\mathbf{q}, t)$, the memory function corresponding to $C_l^{(0)}(\mathbf{q}, t)$ of an ideal gas ; that is

$$K_l(\mathbf{Q}, \tau) = K_l^{(0)}(\mathbf{Q}, \tau)\exp(-\beta_l(Q)\tau), \tag{2.14}$$

where the time τ is in units of $(I/kT)^{1/2}$, the dimensionless wavenumber Q is

$$Q^2 \equiv \frac{\kappa}{4}(q\sigma)^2 \tag{2.15}$$

and the relaxation rate $\beta_l(Q)$ is (see Appendix B)

$$\beta_l(Q) = \beta_\omega \left(\frac{l(l+1) + \dfrac{(1+\lambda)\kappa + 1}{\lambda} Q^2}{l(l+1) + Q^2} \right). \tag{2.16}$$

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† See, in particular, the didactic presentation given in reference [4].

‡ A renormalizable theory would be required to account for the back-scattering events. See, for example, the excellent didactic treatment given by Yip and Mazenko.

The memory function $K_l^{(0)}(\mathbf{Q}, \tau)$ is given by

$$\frac{\partial C_l^{(0)}}{\partial \tau}(\mathbf{Q}, \tau) = -\int_0^{\tau} d\tau' \, K_l^{(0)}(\mathbf{Q}, \tau') C_l^{(0)}(\mathbf{Q}, \tau - \tau'), \tag{2.17}$$

where $C_l^{(0)}(\mathbf{Q}, \tau)$ is the translation–rotation correlation function of an ideal gas.

Combining the Laplace transforms of equations (2.9), (2.14) and (2.17) then gives

$$\tilde{C}_l(\mathbf{Q}, p) = \frac{\tilde{C}_l^{(0)}(\mathbf{Q}, p + \beta_l(Q))}{1 - \beta_l(\mathbf{Q}) \tilde{C}_l^{(0)}(\mathbf{Q}, p + \beta_l(Q))}, \tag{2.18}$$

where p is the Laplace variable in units of $(kT/I)^{1/2}$.

Equation (2.18) is the primary equation of this section. In the remaining sections we shall Laplace invert equation (2.18) and shall study $C_l(\mathbf{Q}, \tau)$ in the diffusion limit and in general.

3. Diffusion limit

In dense fluids where the collision rate β_c and concommitantly the relaxation rates β_ω and $\beta_l(Q)$ are very large, it is often assumed for both $F_s(\mathbf{q}, t)$ and $C_l(t)$, that the translational and rotational diffusion equations are valid [4, 13]. What would be the form of $C_l(\mathbf{Q}, \tau)$ in the diffusion approximation?

In Appendix C we show that should $F_s(\mathbf{q}, t)$ and $C_l(t)$ ever be validly described by the diffusion approximation, then

$$C_l(\mathbf{Q}, \tau) = \exp(-D_l(Q)\tau), \tag{3.1}$$

where the coupled translation–rotation diffusion coefficient is

$$Dl(Q) = \frac{(l(l+1) + Q^2)^2}{\beta_\omega \left(l(l+1) + \frac{(1+\lambda)\kappa + 1}{\lambda} Q^2 \right)}. \tag{3.2}$$

This should be compared with the uncoupled result:

$$C_l^{(\mathrm{unc})}(\mathbf{Q}, \tau) = \exp(-D_l^{(\mathrm{unc})}(Q)\tau), \tag{3.3}$$

where the uncoupled diffusion coefficient is

$$\begin{aligned} D^{(\mathrm{unc})}(Q) &= D_0(Q) + D_l(Q=0) \\ &= \frac{1}{\beta_\omega}\left(l(l+1) + \frac{\lambda}{(1+\lambda)\kappa + 1} Q^2 \right). \end{aligned} \tag{3.4}$$

The ratio

$$\frac{D_l^{(\mathrm{unc})}(Q)}{D_l(Q)} = 1 + \left(\frac{\lambda}{(1+\lambda)\kappa + 1} + \frac{(1+\lambda)\kappa + 1}{\lambda} - 2 \right) \frac{Q_l^2}{(1 + Q_l^2)^2} \tag{3.5}$$

varies very strongly with λ, κ and Q_l, where

$$Q_l \equiv \frac{Q}{\sqrt{[l(l+1)]}} = \frac{\sqrt{\kappa}}{2} \frac{q\sigma}{\sqrt{[l(l+1)]}}. \tag{3.6}$$

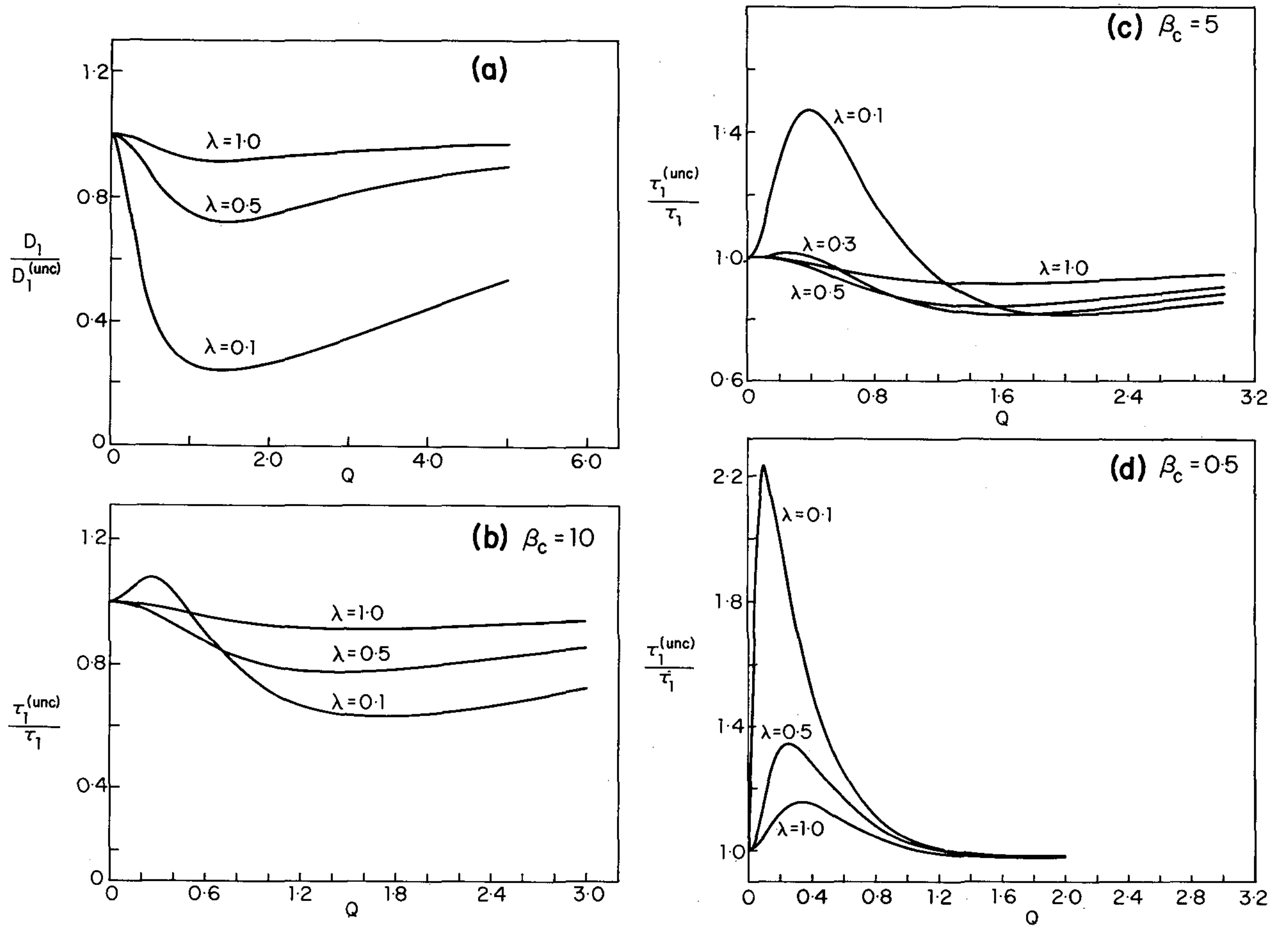

Figure 1. (*a*) The ratio of the coupled and uncoupled diffusion coefficients D_1 and $D_1^{(unc)}$ (cf. equation (3.5)) is plotted versus the dimensionless wavenumber Q for values of the slip parameter λ corresponding to perfect stick ($\lambda=1$), partial stick ($\lambda=0{\cdot}5$) and nearly perfect slip ($\lambda=0{\cdot}1$). (*b*) The ratio of the uncoupled and coupled correlation times $\tau_1^{(unc)}$ and τ_1 (cf. equations (4.1) and (4.4)) is plotted versus Q for $\lambda=0{\cdot}1$, 0·5, and 1 with $\beta_e=10$, where β_e is the dimensionless collision rate defined in the text. (*c*) $\tau_1^{(unc)}/\tau_1$ is plotted versus Q for $\lambda=0{\cdot}1$, 0·5, and 1 with $\beta_e=5$. (*d*) $\tau_1^{(unc)}/\tau_1$ is plotted versus Q for 0·1, 0·5, and 1 with $\beta_c=0{\cdot}5$.

This ratio or rather its inverse $D_l(Q)/D_l^{(\mathrm{unc})}(Q)$ is plotted versus Q for $\kappa = 0{\cdot}4$ and for several values of λ in figure 1 (*a*). It should be noted that $D_l(Q)$ deviates maximally from $D_l^{(\mathrm{unc})}(Q)$ when $Q_l \cong 1$ and this deviation grows dramatically as $\lambda \to 0$. In fact the maximum value of the ratio is

$$\left(\frac{D_l^{(\mathrm{unc})}}{D_l}\right)_{\max} = \tfrac{1}{2} + \tfrac{1}{4}\left(\frac{\lambda}{(1+\lambda)\kappa+1} + \frac{(1+\lambda)\kappa+1}{\lambda}\right). \tag{3.7}$$

Equations (3.5) and (3.7) can be also expressed as

$$\frac{D_l^{(\mathrm{unc})}(Q)}{D_l(Q)} = 1 + \left(\frac{\tau_v}{\tau_\omega} + \frac{\tau_\omega}{\tau_v} - 2\right)\frac{Q_l^2}{(1+Q_l^2)^2}, \tag{3.8 a}$$

$$\left(\frac{D^{(\mathrm{unc})}(Q)}{D_l(Q)}\right)_{\max} = \tfrac{1}{2} + \tfrac{1}{4}\left[\left(\frac{\tau_\omega}{\tau_v}\right) + \left(\frac{\tau_v}{\tau_\omega}\right)\right]. \tag{3.8 b}$$

τ_ω is always greater than τ_v. The larger the coefficient of slip, the greater τ_ω/τ_v. From this it follows that the greater the difference between τ_ω and τ_v the more likely will we see strong coupling between the translation and rotation in the diffusion limit. This difference increases as λ decreases. In addition the maximum deviation occurs for $Q_l \simeq 1$ but the deviation persists as Q_l varies over a decade. Thus we should look at

$$q \sim \frac{1}{\sigma}\sqrt{\left(\frac{l(l+1)}{\kappa}\right)}. \tag{3.9}$$

Wavenumbers of this magnitude are attainable in neutron scattering [15].

4. GENERALIZED HUBBARD RELATION

The correlation time $\tau_l(Q)$ of the coupled correlation function $C_l(Q, \tau)$ is defined as

$$\tau_l(Q) = \int_0^\infty d\tau\, C_l(\mathbf{Q}, \tau). \tag{4.1}$$

This correlation time is a strong function of Q and of (τ_ω/τ_v). Combining equations (4.1) and (2.18) gives the explicit form

$$\tau_l(Q) = \frac{\tilde{C}_l^{(0)}(\mathbf{Q}, \beta_l(Q))}{1 - \beta_l(Q)\tilde{C}_l^{(0)}(\mathbf{Q}, \beta_l(Q))}, \tag{4.2}$$

where $\tilde{C}_l^{(0)}(Q, P)$ is given in equation (2.18). Equation (4.2) shows that $\tau_l(Q)$ is a function of $\beta_l(Q)$ and Q. In the limit of large $\beta_l(Q)$ it is not very difficult to show that (see Appendix C)

$$\tau_l(Q)\cdot\tau_{v\omega}(Q) = \frac{1}{l(l+1)+Q^2}, \tag{4.3}$$

where $\tau_{v\omega}(Q) \equiv \beta_l^{-1}(Q)$ is the coupled 'velocity correlation time'. This is a generalization of the Hubbard relation [14]. It shows that there is an inverse relation between the twi relaxation times $\tau_l(Q)$ and $\tau_{v\omega}(Q)$ such that the smaller $\tau_{v\omega}(Q)$ the larger $\tau_l(Q)$. Equation (4.3) only results from the high $\beta_l(Q)$ limit; that is, in the diffusion limit.

The correlation time for the uncoupled function equation (1.3), is

$$\tau_l^{(\mathrm{unc})}(Q)=\int_0^\infty d\tau\, F_s(\mathbf{Q},\tau)C_l(\tau). \tag{4.4}$$

This time is a function of $\beta_l(Q=0)$ and $\beta_0(Q)$, and also varies explicitly with Q.

To locate where we expect the largest effect of coupling to occur we plot the ratio $\tau_l(Q)/\tau_l^{(\mathrm{unc})}(Q)$ in figure 1 (*b–c*) as a function of Q for several values of κ and λ and β_e where $\beta_e=\frac{2}{3}\beta_c$. It is clear from these curves that the effects of translation–rotation coupling are largest for small values of the slip parameter λ. Physically, this reflects the need of a ‘ nearly smooth ’ sphere to translate further than a ‘ rough ’ one in order to suffer enough collisions to undergo reorientation. The figures also show that the coupled functions relax faster than the uncoupled functions for small values of β_c (low collision rates) and slower than the uncoupled functions for large β_c (high collision rates). The transition between these two cases occurs roughly for β_c in the neighbourhood of $\beta_c=7$.

To demonstrate the possible observable effects of translation–rotation coupling we have numerically computed coupled and uncoupled power spectra, $I_l(\omega)$, where

$$I_l(\omega)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} d\tau\, C_l(\mathbf{Q},\tau)\exp(-i\omega\tau) \tag{4.5}$$

in two cases where the ratios of coupled and uncoupled correlation times show large deviations from unity. These are displayed in figures 2 (*a*) and (*b*). We note in passing that even larger effects may be possible for mixtures (see Appendix B) as there is a greater range of mechanical parameters in that case.

5. Conclusion

It is clear from the foregoing that there are significant differences between the coupled and uncoupled correlation functions for values of q often probed in neutron-scattering experiments. The larger the separation in the time scales characterizing the linear and angular momentum decays, the larger will be the differences between the coupled and uncoupled correlation functions. The differences are most easily perceived in connection with dense fluids where the coupled diffusion approximation might well apply, and where we have derived explicit results for the coupled diffusion coefficient (cf. equations (3.2), (3.5), (3.8).

This work should serve to point out the danger in analysing thermal neutron-scattering data according to the uncoupled approximation.

The binary collision model used here is easily generalized to quantum rotors and may be very useful in the discussion of Dicke narrowing of spectral lines in dilute gases.

It is important to note that this paper is based on the rough sphere model. Real molecules, unlike rough spheres, sweep out a volume larger than the molecular volume when they rotate. Thus, in dense fluids volume fluctuations must occur if these molecules are to rotate in certain directions. This should lead to a much stronger coupling between rotational and translational motion in real molecular fluids than in rough sphere fluids. Thus, by establishing the

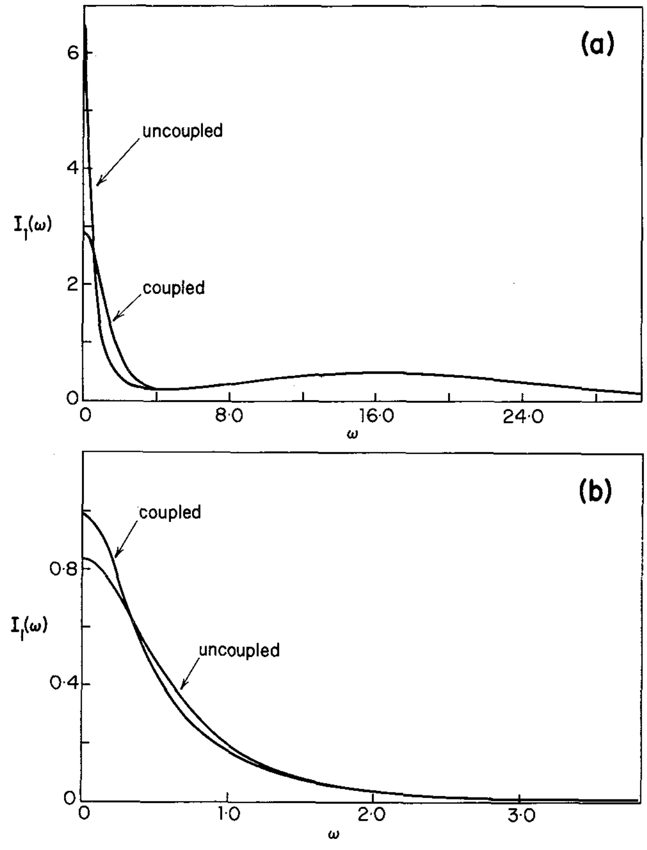

Figure 2. The power spectrum $I_1(\omega)$ (cf. equation (4.5)) of the correlation functions $C_1(Q, \tau)$ and $C_1^{(\mathrm{unc})}(Q, \tau)$ is plotted versus the dimensionless frequency ω (*a*) for $\lambda=0{\cdot}1$, $\kappa=0{\cdot}4$, $Q=0{\cdot}1$, and $\beta_e=0{\cdot}5$ and (*b*) for $\lambda=0{\cdot}5$, $\kappa=0{\cdot}4$, $Q=1{\cdot}5$, and $\beta_e=5$.

importance of coupling in the rough sphere fluid, it becomes all the more obvious that these effects should be heeded in real molecular fluids.

We are grateful to Dr. Jon S. Gethner for making available to us his computer code for calculation of the error function for complex values of its argument.

Appendix A

The binary collision approximation for neat fluids and mixtures

The parameter $\beta_l(Q)$ of equation (2.14) is given in the Chandler [6] approximation by

$$\beta_l(Q)=\left(\frac{I}{k_B T}\right)^{1/2}\frac{(T\dot{\alpha}^{(l)}, \dot{\alpha}^{(l)})}{(\dot{\alpha}^{(l)}, \dot{\alpha}^{(l)})}, \qquad \text{(A 1)}$$

where $\dot{\boldsymbol{\alpha}}^{(l)}$ is the instantaneous rate of change of $\boldsymbol{\alpha}^{(l)}$. T is the total binary collision operator

$$T=\sum_{i>j} T_{ij} \qquad \text{(A 2)}$$

and T_{ij} is the binary collision operator for collisions between particles i and j which only has an effect when acting on dynamical properties that depend on either the linear velocity or angular velocity of particle i or j. The property $\dot{\alpha}^{(l)}$ in equation (2.12) refers to one particle—say particle labelled 1, so that

$$(T\dot{\alpha}_1{}^{(l)}, \dot{\alpha}_1{}^{(l)}) = (N_1-1)(T_{12}{}^{(11)}\dot{\alpha}_1{}^{(l)}, \dot{\alpha}_1{}^{(l)}) + N_2(T_{12}{}^{(12)}\dot{\alpha}_1{}^{(l)}, \dot{\alpha}_1{}^{(l)}), \qquad \text{(A 3)}$$

where $T_{12}{}^{(11)}$ corresponds to a collision between two spheres labelled 1 and 2 both of the same species, whereas $T_{12}{}^{(12)}$ corresponds to two spheres of different species.

The quantities $(T\dot{\alpha}_1{}^{(l)}, \dot{\alpha}_1{}^{(l)})$ must be further simplified. First we note from the explicit form of $\dot{\alpha}_1{}^{(l)}(q)$ given by equation (2.12) that

$$\dot{\boldsymbol{\alpha}}_1{}^{(l)}(\mathbf{q}) = (i\mathbf{q} \,.\, \mathbf{v}_1 + i\boldsymbol{\omega}_1 \,.\, \hat{\mathbf{I}}_1)\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}), \qquad \text{(A 4)}$$

where $\hat{\mathbf{I}}_1$ is the generator of the rotation. This is none other than the dimensionless angular momentum operator of quantum mechanics. Now $\hat{\mathbf{I}}_1\boldsymbol{\alpha}_1{}^{(l)}(q)$ is a function of orientation and position but not of $\mathbf{v}_1$ or $\boldsymbol{\omega}_1$, meaning that in the averaging procedure it can be decoupled from the $\boldsymbol{\omega}_1$ and $\mathbf{v}_1$ averages. In addition in an equilibrium ensemble $\mathbf{v}_1$ and $\boldsymbol{\omega}_1$ are not correlated. Thus

$$(\dot{\alpha}_1{}^{(l)}, \dot{\alpha}_1{}^{(l)}) = \langle(\mathbf{q} \,.\, \mathbf{v}_1)^2 + \langle(\boldsymbol{\omega}_1 \,.\, \hat{\mathbf{I}}_1\boldsymbol{\alpha}_1{}^{(l)}) \odot (\boldsymbol{\omega}_1 \,.\, \hat{\mathbf{I}}_1\boldsymbol{\alpha}_1{}^{(l)})\rangle. \qquad \text{(A 5)}$$

In cartesian components

$$\langle v_{1\alpha}v_{1\beta}\rangle = \langle v_{1\alpha}{}^2\rangle\delta_{\alpha\beta} = \tfrac{1}{3}\langle v_1{}^2\rangle\delta_{\alpha\beta}, \qquad \text{(A 6a)}$$

$$\langle \omega_{1\alpha}\omega_{1\beta}\rangle = \tfrac{1}{3}\langle \omega_1{}^2\rangle\delta_{\alpha\beta}. \qquad \text{(A 6b)}$$

Then equation (A 5) becomes

$$(\dot{\alpha}_1{}^{(l)}, \dot{\alpha}_1{}^{(l)}) = \tfrac{1}{3}q^2\langle v_1{}^2\rangle + \tfrac{1}{3}\langle\omega_1{}^2\rangle \left\langle \sum_{j=1}^{3} (\hat{\mathbf{I}}_{1j}\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q})) \odot (\hat{\mathbf{I}}_{1j}\boldsymbol{\alpha}^{(l)}(\mathbf{q})) \right\rangle. \qquad \text{(A 7)}$$

The quantity $\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}) \odot \boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}) = P_l(\mathbf{u} \,.\, \mathbf{u}) = 1$ is a scalar quantity ; that is, it is invariant to a rotation of the system. This means that it is unchanged when acted upon by the generator of the rotation

$$I_{1j}{}^2(\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}) \odot \boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q})) = 0. \qquad \text{(A 8)}$$

Applying I_{1j} serially then gives the relation

$$\begin{aligned}(I_{1j}{}^2\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q})) \odot \boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}) + \boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}) \odot (I_{1j}{}^2\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q}))& \\ = 2(\mathbf{I}_{1j}\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q})) \odot (\mathbf{I}_{1j}\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q})).& \qquad \text{(A 9)}\end{aligned}$$

Now summing over j we see that the right-hand product can be identified with a term in brackets in equation (A 7). Since $\sum_j I_j{}^2 = \hat{I}^2$ is the square of the square of the total angular momentum and the tensorial set $\boldsymbol{\alpha}_1{}^{(l)}(\mathbf{q})$ transforms like the spherical harmonics it follows that

$$\hat{I}^2\boldsymbol{\alpha}_1{}^{(l)} = l(l+1)\boldsymbol{\alpha}_1{}^{(l)}. \qquad \text{(A 10)}$$

The left-hand side of equation (A 9) is then $2l(l+1)$.

Combining this with equation (A 7) then gives

$$(\dot{\alpha}_1^{(l)}, \dot{\alpha}_1^{(l)}) = \tfrac{1}{3}(q^2\langle v_1^2\rangle + l(l+1)\langle \omega_1^2\rangle) \tag{A 11}$$

as was asserted in equation (2.13). In like manner we find that

$$(T\dot{\alpha}_1^{(l)}(q), \dot{\alpha}_1^{(l)}(q)) = \tfrac{1}{3}(q^2\langle \mathbf{v}_1 \cdot T\mathbf{v}_1\rangle + l(l+1)\langle \boldsymbol{\omega}_1 \cdot T\boldsymbol{\omega}_1\rangle. \tag{A 12}$$

Equation (A 1) then becomes

$$\beta_l(Q) = \left(\frac{I}{k_B T}\right)^{1/2} \left(\frac{q^2\langle \mathbf{v}_1 \cdot T\mathbf{v}_1\rangle + l(l+1)\langle \boldsymbol{\omega}_1 \cdot T\boldsymbol{\omega}_1\rangle}{q^2\langle v_1^2\rangle + l(l+1)\langle \omega_1^2\rangle}\right). \tag{A 13}$$

It remains to compute the quantities $\langle \boldsymbol{\omega}_1 \cdot T_{12}\boldsymbol{\omega}_1\rangle$ and $\langle \mathbf{v}_1 \cdot T_{12}\mathbf{v}_1\rangle$. Chandler has already computed these quantities for the perfectly rough sphere. Actually we would like to generalize this model to arbitrary roughness. This is done in Appendix B.

APPENDIX B

The rough sphere model with arbitrary roughness for our neat fluids and mixtures

It is useful to generalize the rough sphere model to arbitrary roughness. This we do by introducing a coefficient of slip λ into the collision dynamics of the rough sphere fluid. λ is chosen such that when $\lambda = 1$ the spheres are completely rough. Taking $0 < \lambda < 1$ gives intermediate cases.

In the usual rough sphere model [15] the relative velocity of the points of contact on the surfaces of the colliding spheres,

$$\mathbf{g}_{21} = \mathbf{v}_2 - \mathbf{v}_1 - \tfrac{1}{2}\mathbf{n}(\sigma_2\boldsymbol{\omega}_2 + \sigma_1\boldsymbol{\omega}_1) \tag{B 1}$$

is completely reversed by the collision that is

$$\mathbf{g}_{21}' = -\mathbf{g}_{21} \tag{B 2}$$

In equation (B 1) $\mathbf{v}_2 - \mathbf{v}_1 \equiv \mathbf{v}_{21}$ is the relative velocity of the centres of mass, σ_1 and σ_2 are the diameters of the two spheres and $\mathbf{n}$ is a unit vector pointing from the centre of sphere 2 to sphere 1 at contact, i.e. the direction of the line of centres. Primed quantities indicate values of properties after collision and unprimed quantities indicate the values before collision. The dynamical law embodied in equation (B 2) gives rise to no slip whatsoever of the surfaces past each other.

For the purposes of generalizing the model, we imagine that the surface of each sphere of type 1 is covered by domains of roughness between which there are domains of perfect smoothness. These domains are randomly distributed and are such that the fraction of surface area that is rough will be denoted α_1 whereas the fraction that is smooth is $(1-\alpha_1)$. Contact between the rough domain of one sphere and the smooth domain of another must give rise to a perfect slippery collision whereas collision between two rough domains gives rise to a perfect rough collision. The probability p of a rough collision is therefore equal to $\alpha_1\alpha_2 = \lambda_{21}$ and the probability of a smooth collision is equal to $q = 1 - \alpha_1\alpha_2 = 1 - \lambda_{21}$.

To generalize, we resolve $\mathbf{g}_{21}$ into a part parallel to $\mathbf{n}$ and a part perpendicular to $\mathbf{n}$ labelled $\mathbf{g}_{\parallel}$ and $\mathbf{g}_{\perp}$, respectively, then in a collision we take

$$\mathbf{g}_{\parallel}' = -\mathbf{g}_{\parallel}, \tag{B 3a}$$

$$\mathbf{g}_{\perp} = (1-2b_{21})\mathbf{g}_{\perp}, \tag{B 3b}$$

$$\mathbf{g}' = \mathbf{g}_{\parallel}' + \mathbf{g}_{\perp}' = -\mathbf{g}_{\parallel} + (1-2b_{21})\mathbf{g}_{\perp}, \tag{B 3c}$$

where $b_{21}=1$ for a ' rough contact ' and $b_{21}=0$ for a smooth contact. Now it is clear from the foregoing that when b_{21} is averaged over all collisions between a particle of type 1 with that of a particle of type 2

$$\langle b_{21}\rangle = \lambda_{21} = \alpha_1\alpha_2. \tag{B 3d}$$

Following Chapman and Cowling we then find that

$$\mathbf{C}_1' = \mathbf{C}_1 + \frac{2M_2}{(\kappa_1\kappa_2+\kappa_0)}((\kappa_0+(1-b_{21})\kappa_2\kappa_1)\mathbf{n}(\mathbf{n}\,.\,\mathbf{g}_{21}) + b_{21}\kappa_1\kappa_2\mathbf{g}_{21}) \tag{B 4a}$$

$$\mathbf{C}_2' = \mathbf{C}_2 - \frac{2M_1}{(\kappa_1\kappa_2+\kappa_0)}((\kappa_0+(1-b_{21})\kappa_2\kappa_1)\mathbf{n}\,.\,(\mathbf{n}\,.\,\mathbf{g}_{21}) + b_{21}\kappa_1\kappa_2\mathbf{g}_{21}) \tag{B 4b}$$

$$\boldsymbol{\omega}_1' = \boldsymbol{\omega}_1 - \frac{4M_2\kappa_2}{(\kappa_1\kappa_2+\kappa_0)\sigma_1}\, b_{21}(\mathbf{n}\times\mathbf{g}_{21}), \tag{B 4c}$$

$$\boldsymbol{\omega}_2' = \boldsymbol{\omega}_2 - \frac{4M_1\kappa_1}{(\kappa_1\kappa_2+\kappa_0)\sigma_2}\, b_{21}(\mathbf{n}\times\mathbf{g}_{21}), \tag{B 4d}$$

where $\mathbf{C}_1'$ and $\mathbf{C}_2'$ are, respectively, the linear velocities of the points of contact and $\boldsymbol{\omega}_1'$ and $\boldsymbol{\omega}_2'$ are the angular velocities of the two spheres after collision, and

$$M_1 = \frac{m_1}{m_1+m_2}\,; \qquad \kappa_1 = \frac{4I_1}{m_1{\sigma_1}^2}\,;$$

$$M_2 = \frac{m_2}{m_1+m_2}\,; \qquad \kappa_2 = \frac{4I_2}{m_2{\sigma_2}^2}\,;$$

$$\kappa_0 \equiv M_1\kappa_1 + M_2\kappa_2,$$

where m_1 and m_2 are the masses of the two spheres. Equation (B 3*c*) and (B 4*a*–*d*) completely define the collision.

A formula due to Zwanzig [16] that is suitably generalized to the excluded volume problem by the insertion of the contact pair correlation function is

$$(\mathbf{A}_2\,.\,{T_{12}}^{12}\mathbf{A}_1) = -\frac{g(\sigma_{12}){\sigma_{12}}^2}{4V}\left\langle \int d\Omega|v_{21}|\mathbf{A}_2\,.\,(\mathbf{A}_1'-\mathbf{A}_1)\right\rangle, \tag{B 5}$$

where the average† is over the Maxwell distribution of unprimed linear and angular velocities, $\mathbf{A}_1'-\mathbf{A}_1$ is the change in the property $\mathbf{A}_1$ of particle 1 on collision with particle 2 and $d\Omega$ is the solid angle specifying the orientation of $\hat{\mathbf{n}}$. Here

$$\sigma_{12} = \frac{(\sigma_1+\sigma_2)}{2}$$

† The average is also over all orientations of the spheres, so that wherever b_{21} appears in the foregoing dynamics it is replaced by its average value, λ_{21} (cf. equation (B 3*d*)) in equation (B 6).

is the distance of closest approach of the spheres, and $g(\sigma_{12})$ is the contact pair correlation function.

Combining equations (A 3), (B 1), (B 4*a*–*d*), and (B 5) gives the following formulae :

$$\frac{1}{\tau_v(1,\,1)}=\frac{(N_1-1)\langle \mathbf{V}_1\,.\,T_{12}{}^{(11)}\mathbf{V}_1\rangle}{\langle V_1{}^2\rangle}=\frac{(1+\lambda_{11})\kappa_1+1}{\kappa_1+1}\Gamma_{11}, \tag{B 6a}$$

$$\frac{1}{\tau_v(1,\,2)}=\frac{N_2\langle \mathbf{V}_1\,.\,T_{12}{}^{12}\mathbf{V}_1\rangle}{\langle V_1{}^2\rangle}=4M_2{}^2\left(\frac{\kappa_0+(1+\lambda_{21})\kappa_1\kappa_2}{\kappa_1\kappa_2+\kappa_0}\right)\Gamma_{12}, \tag{B 6b}$$

$$\frac{1}{\tau_\omega(1,\,1)}=\frac{(N_1-1)\langle \boldsymbol{\omega}_1\,.\,T_{12}{}^{(11)}\boldsymbol{\omega}_1\rangle}{\langle \omega_1{}^2\rangle}=\frac{\lambda_{11}}{\kappa_1+1}\,\Gamma_{11}, \tag{B 6c}$$

$$\frac{1}{\tau_\omega(1,\,2)}=\frac{N_2\langle \boldsymbol{\omega}_1\,.\,T_{12}{}^{12}\boldsymbol{\omega}_1\rangle}{\langle \omega_1{}^2\rangle}=\frac{2M_2\kappa_2\lambda_{21}}{\kappa_1\kappa_2+\kappa_0}\,\Gamma_{12}, \tag{B 6d}$$

where $(1/\tau_v)(1,\,j)$ and $(1/\tau_\omega)(1,\,j)$ are respectively the contributions to the linear velocity and angular velocity relaxation rates of particle 1 due to collisions with particles of type j. The quantities $\Gamma_{\alpha\beta}$ are defined as

$$\Gamma_{\alpha\beta}=\frac{2\pi}{3}\,n_\beta g(\sigma_{\alpha\beta})\sigma_{\alpha\beta}{}^2\left(\frac{8k_{\mathrm{B}}T}{\pi\mu_{\alpha\beta}}\right)^{1/2}. \tag{B 7}$$

These quantities are equal to $\frac{2}{3}$ multiplied by the collision frequency for collisions between a particle of type α and particles of type β. These quantities depend on the concentration through n_β and $g(\sigma_{\alpha\beta})$. $g(\sigma_{\alpha\beta})$ has been computed by Lebowitz [17] from the Percus–Yevick approximation. Equations (B 6*a*–*d*) contain the two parameters λ_{11} and λ_{12} which can be different since collisions between different pairs of particles may be more or less sticky.

Thus the parameter $\beta_l(Q)$ appearing in equation (2.14) for a mixture is

$$\beta_l(Q)=\left(\frac{I_{\mathrm{B}}}{kT}\right)^{1/2}\left\{\frac{l(l+1)\dfrac{\langle\omega_1{}^2\rangle}{\tau_\omega{}^{(1)}}+q^2\dfrac{\langle v_1{}^2\rangle}{\tau_v{}^{(1)}}}{l(l+1)\langle\omega_1{}^2\rangle+q^2\langle v_1{}^2\rangle}\right\}, \tag{B 8}$$

where

$$\frac{1}{\tau_v(1)}=\frac{1}{\tau_v(1,\,1)}+\frac{1}{\tau_v(1,\,2)}, \tag{B 9a}$$

$$\frac{1}{\tau_\omega(1)}=\frac{1}{\tau_\omega(1,\,1)}+\frac{1}{\tau_\omega(1,\,2)}, \tag{B 9b}$$

where the various terms in equation (B 9) are given in equation (B 6).

In the case of a pure fluid

$$\frac{1}{\tau_v(1)}=\frac{1}{\tau_v}=\frac{(1+\lambda)\kappa+1}{\kappa+1}\,\Gamma_{11}, \tag{B 10a}$$

$$\frac{1}{\tau_\omega(1)}=\frac{1}{\tau_\omega}=\frac{\lambda}{\kappa+1}\,\Gamma_{11}, \tag{B 10b}$$

and

$$\frac{\tau_\omega}{\tau_v} = \frac{(1+\lambda)\kappa+1}{\lambda}. \tag{B 10c}$$

This quantity increases without bound as $\lambda \to 0$. Equation (B 8) then reduces to

$$\beta_l(Q) = \beta_\omega \left[\frac{l(l+1) + \left(\dfrac{(1+\lambda)\kappa+1}{\lambda} \right) Q^2}{l(l+1)+Q^2} \right], \tag{B 11}$$

where

$$Q^2 \equiv \frac{\kappa(q\sigma)^2}{4} \tag{B 12a}$$

is the dimensionless wavenumber and

$$\beta_\omega \equiv \left(\frac{I}{k_{\mathrm{B}}T} \right)^{1/2} \frac{1}{\tau_\omega} \tag{B 12b}$$

is the dimensionless angular velocity relaxation rate. Equation (B 11) is identical to equation (2.16).

Appendix C

The coupled diffusion equation and the generalized Hubbard relation

The free particle correlation function is [7]

$$C_l^{(0)}(\mathbf{Q}, \tau) = \left\langle \frac{1}{2l+1} \sum_{m=-l}^{l} \exp\left(i(m\omega + Qv_z)\tau\right) \right\rangle \tag{C 1}$$

where ω, v_z and τ are in reduced units and $\langle \omega^2 \rangle = 3$, $\langle v_z^2 \rangle = 1$. The Laplace transform required in equation (2.18) is thus

$$\tilde{C}_l^{(0)}(\mathbf{Q}, p+\beta_l) = \left\langle \frac{1}{2l+1} \sum_{m=-l}^{l} \frac{1}{p+\beta_l - i(m\omega + v_z Q)} \right\rangle. \tag{C 2}$$

If $\beta_l \gg l$, Q this can be expanded in powers of $(p+\beta_l)^{-1}$. To second order

$$\tilde{C}_l^{(0)}(\mathbf{Q}, p+\beta_l) = \frac{1}{p+\beta_l} - \frac{(l(l+1)+Q^2)}{(p+\beta_l)^3} \tag{C 3}$$

where we have used

$$\frac{1}{2l+1} \sum_{m=-l}^{l} 1 = 1\,; \quad \frac{1}{2l+1} \sum_{m=-l}^{l} m^2 = \frac{l(l+1)}{3}.$$

The memory function $K_l(\mathbf{Q}, \tau)$ is related to the time correlation function $C_l(\mathbf{Q}, \tau)$ through the memory function equation (cf. equation (2.9)). Laplace transformation then gives

$$\tilde{C}_l(\mathbf{Q}, p) = \frac{1}{p + K_l(\mathbf{Q}, p)}. \tag{C 4}$$

Comparison of this with equation (2.18) then gives a formula for the memory function

$$\tilde{K}_l(\mathbf{Q}, p) = \frac{1-(p+\beta_l)\tilde{C}_l^{(0)}(Q, p+\beta_l)}{\tilde{C}_l^{(0)}(Q, p+\beta_l)}. \tag{C 5}$$

Substitution of equation (C 3) into equation (C 5) and retaining the term that is lowest order in $(p+\beta_l)^{-1}$ gives

$$\tilde{K}_l(\mathbf{Q}, p) = \frac{l(l+1)+Q^2}{p+\beta_l(Q)}. \tag{C 6}$$

The orientational correlation time $\tau_l(Q)$ is

$$\tau_l(Q) = \lim_{p\to 0} C_l(Q, p). \tag{C 7}$$

Substitution of equations (C 4) and (C 6) into equation (C 7) then gives

$$\tau_l(Q)\tau_{v\omega}(Q) = \frac{1}{l(l+1)+Q^2}, \tag{C 8}$$

where we have defined the coupled velocity correlation time as

$$\tau_{v\omega}(Q) \equiv (\beta_l(Q))^{-1}. \tag{C 9}$$

This is the analogue of the Hubbard relation in the theory of rotational reorientation [14].

Next we solve the memory function equation subject to equation (C 6) :

$$\tilde{C}_l(\mathbf{Q}, p) = \frac{p+\beta_l}{p^2+\beta_l p+(l(l+1)+Q^2)}. \tag{C 10}$$

Inverse Laplace transformation gives

$$C_l(\mathbf{Q}, \tau) = \frac{(p_+ +\beta_l)\exp(p_+\tau)-(p_- +\beta_l)\exp(p_-\tau)}{(p_+ - p_-)}, \tag{C 11}$$

where

$$p_\pm = -\tfrac{1}{2}\beta_l \pm \tfrac{1}{2}\beta_l\left[1-4\left(\frac{l(l+1)+Q^2}{\beta_l^2}\right)\right]^{1/2}. \tag{C 12}$$

Now because $\beta_l \gg l, Q$, it follows that these roots can be well approximated by

$$p_\pm = \begin{cases} -D(Q), \\ -\beta_l(Q)+D_l(Q), \end{cases} \tag{C 13}$$

where we define

$$D_l(Q) \equiv \frac{l(l+1)+Q^2}{\beta_l(Q)}. \tag{C 14}$$

This is the coupled rotation–translation diffusion coefficient of equation (3.2). Substituting these roots into equation (C 11) gives

$$C_l(\mathbf{Q}, \tau) = \frac{(\beta_l - D_l)\exp(-D_l\tau) - D_l(Q)\exp(-(\beta_l - D_l)\tau)}{(\beta_l - 2D_l)}. \tag{C 15}$$

Because $D_l \ll \beta_l$, this consists of a very fast decay $\exp(-(\beta_l - D_l)\tau)$ followed by a much slower decay $\exp(-D_l\tau)$; clearly then, for times $\tau > \beta_l^{-1}$, the correlation function decays as the simple exponential

$$C_l(\mathbf{Q},\tau) = \exp(-D_l(Q)\tau). \tag{C 16}$$

This is the simple diffusion result mentioned in equation (3.1)

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