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Memory function moment analysis of dynamic light scattering data

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Abstract. We consider the problem of obtaining long-time diffusivities $D^{L}(k)$ from dynamic light scattering data for suspensions of spherical particles. Starting from the integro-differential memory equation for the intermediate scattering function $F(k, t)$, we derive an infinite-order linear differential equation for $F(k, t)$ with coefficients $\mu_n(t)$ expressed as finite-time moments of the memory function. We obtain an exact analytic representation of these moments for a model suspension of low-density hard spheres; numerical results for the moments in this model suspension are presented for a range of values of wavenumber and time. The numerical study shows that at short or intermediate times t one may neglect all but the low-order moments leading to a simplified differential equation for $F(k, t)$. At intermediate times this differential equation may be inverted to obtain the lowest moment $\mu_0(t)$ in terms of the experimentally measured slope of ln $F(k, t)$. The numerical study of the moments for the hard-sphere system indicates that even at quite short times $\mu_0(t)$ gives an accurate estimate of $\mu_0(\infty)$ from which the diffusivities $D^{L}(k)$ can be obtained.

1. Introduction

Dynamic light scattering from particulate suspensions is a versatile probe of the dynamics of interacting Brownian particles (Berne and Pecora 1976, Pusey and Tough 1982). Excellent experimental data exist for suspensions of both neutral and charged spherical particles (Grüner 1980, Cebula *et al* 1981, Kops-Werkhoven and Fijnaut 1982, Kops-Werkhoven *et al* 1982) but the theoretical interpretation of such data has been difficult. If the logarithm of the experimentally measured intermediate scattering function, ln $F^{M}(k, t)$, is plotted against time, the graphs all show the qualitative features of an initial rapid decay followed by a region of slower decay at experimentally long times where the graphs are approximately linear in time. The initial slope of the graph determines a measured short-time diffusivity $D_{S}^{M}(k)$ while the slope of the longer-time part gives an experimental long-time diffusivity $D_{L}^{M}(k)$. To interpret these data one wishes to relate the measured diffusivities to theoretical calculations of the collective and self intermediate scattering functions $F_{c}(k, t)$ and $F_{s}(k, t)$.

In an ideal monodisperse suspension F^{M} and F_{c} should be identical but in real suspensions polydispersity interferes with such an identification. Consider spherical particles identical in size but with a spread of values of index of refraction (optical polydispersity). For such a case Weissman (1980) and Pusey (Cebula *et al* 1981) have argued that F^{M} is a sum of coherent and incoherent contributions

$$F^{M}(k, t) = (1-x)F_{c}(k, t) + xF_{s}(k, t) \tag{1.1}$$

where

$$x = 1 - (\bar{b})^2/\overline{b^2} \tag{1.2}$$

is a measure of the polydispersity of the light scattering amplitudes b of the different particles in the suspension (the bar denotes average values). If x can be varied in a controlled manner (Kops-Werkhoven and Fijnaut 1982, Kops-Werkhoven *et al* 1982) from one experiment to another then the polydispersity gives a tool to obtain separately experimental values of F_c and F_s. Alternatively it may be possible in different regimes of k, t or concentration to argue that F^M is dominated either by F_c or F_s. In what follows we will assume that F_c and F_s are known separately by experimental measurement.

The measured $F^M(k, t)$ is often fitted as a sum of exponentials in the time (Kops-Werkhoven and Fijnaut 1982, Kops-Werkhoven *et al* 1982)

$$F^M(k, t) = A_1(k) \exp(-D_S^M(k)k^2t) + A_2(k) \exp(-D_L^M(k)k^2t). \tag{1.3}$$

Such a procedure implicitly assumes that F_c and F_s are themselves exponential functions at long times. This latter assumption has been criticised by Hinch (1983) on the basis of numerical calculations on model suspensions and can be criticised on theoretical grounds away from the long-wavelength ($k = 0$) limit. In this article a new representation of the time dependence of F_c, F_s is introduced in order to understand better when simple exponential behaviour may be expected and it is shown how, even if there is no simple exponential behaviour, one may analyse the experimental data at short and intermediate times to extract parameters to compare with theoretically calculated long-time diffusivities. In § 2 we collect some definitions and introduce the theoretical long-time diffusivities. In § 3 we give a new differential equation representation of $F(k, t)$ by means of a finite-time moment expansion of the memory equation formalism. In § 4 we use a hard-sphere model to study the behaviour of the moments as functions of k and t. In § 5 we show how the differential equation representation may be used to fit experimentally measured curves of ln $F(k, t)$ in order to extract the theoretically defined long-time diffusivities.

2. Long-time diffusivities

The intermediate scattering functions for collective and self diffusion in a suspension of spherical particles are defined as density–density time correlation functions (Pusey and Tough 1982)

$$\begin{aligned} F_c(k, t) &= \frac{1}{N} \sum_{p,q=1}^{N} \langle \exp[-\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{R}_p(t) - \boldsymbol{R}_q(0))] \rangle, \\ F_s(k, t) &= \langle \exp[-\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{R}_1(t) - \boldsymbol{R}_1(0))] \rangle, \end{aligned} \tag{2.1}$$

where N is the number of particles in the suspension, $\boldsymbol{R}_p(t)$ is the position of particle p at time t, $\boldsymbol{k}$ is the scattering vector of the light and the angle brackets denote an equilibrium thermal average. At equal times ($t = 0$) these reduce to

$$F_c(k, 0) = S(k), \qquad F_s(k, 0) = 1, \tag{2.2}$$

with $S(k)$ the static structure factor for the suspension.

If we now introduce the Fourier–Laplace transform of each of these correlation functions

$$\hat{F}(k, \omega) = \int_0^\infty e^{i\omega t} F(k, t)\, dt \tag{2.3}$$

then it is possible to express F_c, F_s in terms of wavenumber and frequency dependent diffusion coefficients (Felderhof and Jones 1983a, Hess and Klein 1983) $\hat{D}_c(k, \omega)$ and $\hat{D}_s(k, \omega)$ as

$$\hat{F}_c(k, \omega) = S(k)/(-i\omega + k^2 \hat{D}_c(k, \omega)), \qquad \hat{F}_s(k, \omega) = (-i\omega + k^2 \hat{D}_s(k, \omega))^{-1}. \tag{2.4}$$

The limiting values of these diffusion coefficients at zero frequency and zero wavenumber are the phenomenological collective and self diffusion coefficients (Kadanoff and Martin 1963) measurable by macroscopic diffusion experiments. In this hydrodynamic limit (first $k \to 0$ then $\omega \to 0$) the functions $F(k, t)$ become simple exponentials in time corresponding to the hydrodynamic pole in frequency which appears in the expressions (2.4). In light scattering, however, the system is probed at finite k away from the hydrodynamic limit. In this situation the (theoretical) long-time diffusivities are defined by (Felderhof and Jones 1983a, b, c, Hess and Klein 1983)

$$D_c^L(k) = \lim_{\omega \to 0} \hat{D}_c(k, \omega), \qquad D_s^L(k) = \lim_{\omega \to 0} \hat{D}_s(k, \omega). \tag{2.5}$$

Short-time diffusivities are defined by an infinite frequency limit

$$D_c^S(k) = \lim_{\omega \to \infty} \hat{D}_c(k, \omega), \qquad D_s^S(k) = \lim_{\omega \to \infty} \hat{D}_s(k, \omega). \tag{2.6}$$

The short-time diffusivities are well understood (Pusey and Tough 1982) and can be expressed in terms of equilibrium correlations as

$$D_c^S(k) = D_0 H_c(k)/S(k), \qquad D_s^S(k) = D_0 H_s(k), \tag{2.7}$$

where the factors $H_c(k)$, $H_s(k)$ incorporate hydrodynamic interactions (Pusey and Tough 1982) and are equal to one if these can be neglected. By D_0 we denote the diffusion constant of a single particle in the infinite-dilution limit. The quantities $D^S(k)$ are obtained experimentally as the initial slopes of curves of $\ln F(k, t)$ and the dependence of $D_c^S(k)$ upon the structure factor has been well established (Pusey and Tough 1982). In principle the long-time diffusivities $D^L(k)$ can also be obtained from the experimental $F(k, t)$ by use of (2.3), (2.4) and (2.5) as

$$D_c^L(k) = \hat{D}_c(k, 0) = \frac{S(k)}{k^2 \hat{F}_c(k, 0)} = \frac{S(k)}{k^2} \left(\int_0^\infty F_c(k, t)\, dt \right)^{-1} \tag{2.8}$$

and similarly for $D_s^L(k)$ by the changes $S(k) \to 1$, $c \to s$. Thus long-time diffusivities can be obtained as the area under an experimental curve subject to errors arising from lack of absolute normalisation and from the fact that the data do not extend to $t = \infty$. The result (2.8), however, says nothing about whether $F(k, t)$ is a simple exponential function of time or whether $D^L(k)$ can be found from the slope of $\ln F(k, t)$.

3. Moment representation of the memory equation

To investigate whether $F(k, t)$ is, even approximately, a single exponential function of time we turn now to the memory equation (Ackerson 1978, Pusey and Tough 1982) which can be written for $F_c(k, t)$ in the form

$$\frac{\mathrm{d}F_c(k,t)}{\mathrm{d}t} = -D_c^S(k)k^2F_c(k,t) - \int_0^t M_c(k, t-t')F_c(k,t')\,\mathrm{d}t'$$

$$= -\frac{D_0k^2H_c(k)}{S(k)}F_c(k,t) - \int_0^t F_c(k, t-t')M_c(k,t')\,\mathrm{d}t'. \tag{3.1}$$

If we take the Fourier–Laplace transform of this equation and compare with (2.4) we obtain

$$k^2\hat{D}_c(k,\omega) = k^2D_c^S(k) + \hat{M}_c(k,\omega) \tag{3.2}$$

with

$$\hat{M}_c(k,\omega) = \int_0^\infty e^{i\omega t}M_c(k,t)\,\mathrm{d}t \tag{3.3}$$

where $M_c(k, t)$ is called the memory function (Berne and Pecora 1976, Ackerson 1978, Pusey and Tough 1982). To simplify (3.1) we introduce a dimensionless time τ by the definition

$$\tau = D_0k^2t \tag{3.4}$$

and note that the k dependence must also be of dimensionless form ka where a is a characteristic length (the sphere radius for neutral hard spheres or a screening length or interparticle distance for charged particles) to obtain the dimensionless equation

$$\frac{\mathrm{d}\mathscr{F}_c(ka,\tau)}{\mathrm{d}\tau} = -\frac{H_c(ka)}{S(ka)}\mathscr{F}_c(ka,\tau) - \int_0^\tau \mathscr{F}_c(ka,\tau-\tau')\mathscr{M}_c(ka,\tau')\,\mathrm{d}\tau' \tag{3.5}$$

where $F_c(k,t) \to \mathscr{F}_c(ka,\tau)$ and

$$\mathscr{M}_c(ka,\tau) = M_c(k,t)/(D_0k^2)^2. \tag{3.6}$$

Equation (3.5) is written in a form appropriate to a system with one characteristic length (hard spheres); it would be modified in an obvious manner if the system had more than one characteristic length.

The short-time behaviour of $\mathscr{F}_c(ka,\tau)$ has often been analysed by simple expansions about $\tau = 0$ such as the cumulant expansion (Pusey and Tough 1982). However, apart from the lowest term such expansions have not proved of great use and for hard-sphere systems it is known that $\mathscr{F}_c(ka,\tau)$ is not analytic at $\tau = 0$ (Ackerson and Fleishman 1982, Jones and Burfield 1982a, b) so that such an expansion does not exist for this case. An alternative procedure is to take the memory equation in the form (3.5) and to expand $\mathscr{F}_c(ka, \tau-\tau')$ in Taylor series about the point τ,

$$\mathscr{F}_c(ka,\tau-\tau') = \sum_{n=0}^\infty \frac{(-\tau')^n}{n!}\frac{\mathrm{d}^n\mathscr{F}_c(ka,\tau)}{\mathrm{d}\tau^n}, \tag{3.7}$$

and then integrate term by term to convert (3.5) into an infinite-order differential equation

$$\frac{\mathrm{d}\mathscr{F}_c(ka,\tau)}{\mathrm{d}\tau} = -\frac{H_c(ka)}{S(ka)}\mathscr{F}_c(ka,\tau) - \sum_{n=0}^\infty (-1)^n\mu_{cn}(ka,\tau)\frac{\mathrm{d}^n\mathscr{F}_c(ka,\tau)}{\mathrm{d}\tau^n} \tag{3.8}$$

in which the coefficients $\mu_{cn}(ka, \tau)$ are finite-time moments of the memory function

$$\mu_{cn}(ka, \tau) = \frac{1}{n!} \int_0^\tau \tau'^n \mathcal{M}_c(ka, \tau')\, d\tau'. \tag{3.9}$$

Although the representation (3.8) is formally an infinite-order differential equation, at small to intermediate values of the time we may expect it to give a good description of $\mathcal{F}_c(ka, \tau)$ if we keep only the lowest-order terms in the infinite series. The lowest-order moment $\mu_{c0}(ka, \tau)$ is related at long times ($\tau = \infty$) to the long-time diffusion coefficient by

$$D_c^L(k) = D_0[H_c(ka)/S(ka) + \mu_{c0}(ka, \infty)] \tag{3.10}$$

where (2.5), (3.2), (3.3) and (3.9) have been used. This lowest moment is also simply related to another measure of long-time diffusivity introduced by Grüner and Lehmann (1979) who measured a quantity

$$\Delta(k) = (D_c^S(k) - D_c^L(k))/D_c^S(k). \tag{3.11}$$

This $\Delta(k)$ is related to $\mu_{c0}(ka, \infty)$ by

$$\Delta(k) = -(S(ka)/H_c(ka))\mu_{c0}(ka, \infty). \tag{3.12}$$

The formulae (3.1)–(3.10) hold for self diffusion if $S(ka)$ is replaced by 1 and the subscript c by s.

The usefulness of the representation (3.8) depends on how the moments $\mu_n(ka, \tau)$ vary with time, wavenumber and concentration. If the memory function $\mathcal{M}(ka, \tau)$ were a delta function $\delta(\tau)$ then all moments but μ_0 would vanish and (3.8) would predict simple exponential decay of $\mathcal{F}(ka, \tau)$ for all τ. Evidently then deviation from simple exponential decay is expressed through the higher-order moments which give a measure of the lifetime of memory effects. We next turn to a model system in order to get an idea of how the moments $\mu_n(ka, \tau)$ depend upon ka and τ. For simplicity we ignore hydrodynamic interactions in the next two sections so that in the formulae above we put $H_c(ka)$ and $H_s(ka)$ equal to one. Hydrodynamic effects of course also contribute to the memory function (Ackerson 1978, Jones and Burfield 1982a, b) and we will neglect these as well. In the later discussion we will indicate what changes might be expected if the hydrodynamic interactions were included.

4. Hard-sphere model for the memory function

To study the moments $\mu_n(ka, \tau)$ we take as a model system a suspension of hard spheres at low density without hydrodynamic interactions for which we can give an analytic expression for $\mu_n(ka, \tau)$ that is easily evaluated numerically. The only other case in which something is known about the memory function is the case of a highly charged low-density suspension where graphs of the memory function have been published by Hess and Klein (1983) based on a mode coupling approximation.

The use of hard spheres should not be too restrictive a model, however, since for $ka \gtrsim 2$ the low-density result is thought to be qualitatively similar to the high-density hard-sphere result (Felderhof and Jones 1983c), which itself can be used as a rough model (after scaling of lengths) for a low-density charged suspension (van Megan and Snook 1983).

Specifically then we consider hard spheres of radius a and volume fraction $\phi = 4\pi a^3 n/3$ where $n = N/V$ is the number density of the suspension. By comparison of (3.2) with the calculation of $\hat{D}_c(k, \omega)$ by Felderhof and Jones (1983b), it follows that the memory function $\hat{M}_c(k, \omega)$ is given exactly to lowest order in volume fraction ϕ by

$$\hat{M}_c(k, \omega) = 24\phi D_0 k^2 \sum_{\substack{l=0 \\ l \text{ even}}}^{\infty} (2l+1) \frac{[j_l'(ka)]^2 k_l(2\mu a)}{(2\mu a) k_l'(2\mu a)} \tag{4.1}$$

where j_l, k_l are spherical Bessel functions, primes denote derivatives $(j_l'(z) = \mathrm{d}j_l(z)/\mathrm{d}z)$ and the variable μ is given by

$$\mu = (k^2/4 - \mathrm{i}\omega/2D_0)^{1/2}. \tag{4.2}$$

The memory function for self diffusion in this model is given by an expression like (4.1) with 24 replaced by 12 and the summation including both odd and even values of l.

To obtain $M_c(k, t)$ we use the inverse Fourier–Laplace transform

$$M_c(k, t) = (2\pi)^{-1} \int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}\omega t} \hat{M}_c(k, \omega)\, \mathrm{d}\omega \tag{4.3}$$

where the integration path is the real ω axis. From (4.1), (4.2) it is evident that $\hat{M}_c(k, \omega)$ is analytic in ω except for branch points at $\omega = -\mathrm{i}D_0k^2/2$ and $\omega = -\mathrm{i}\infty$ which may be joined by a cut along the negative imaginary axis of ω. By moving the contour of integration in (4.3) into the lower half ω-plane we express $M_c(k, t)$ as an integral around the cut as indicated in figure 1. Introducing a variable ρ along the cut by

$$\omega = -\tfrac{1}{2}\mathrm{i}D_0k^2[1 + \rho/4(ka)^2] \tag{4.4}$$

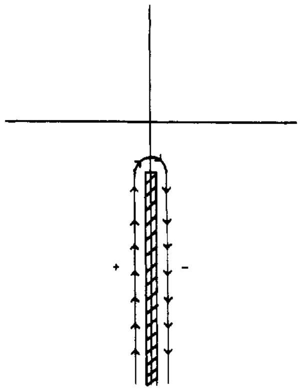

Figure 1. The complex ω plane showing the cut along the negative imaginary axis together with the contour of integration used in deriving (4.5).

we obtain for $M_c(k, t)$

$$M_c(k, t) = \frac{\mathrm{i}D_0k^2}{16\pi(ka)^2} \exp\left(-\frac{\tau}{2}\right) \int_0^{\infty} \exp\left(-\frac{\rho\tau}{8(ka)^2}\right) (\hat{M}_{c+}(k, \rho) - \hat{M}_{c-}(k, \rho))\, \mathrm{d}\rho \tag{4.5}$$

where $\hat{M}_{c\pm}(k, \rho)$ denotes $\hat{M}_c(k, \omega)$ evaluated on the $\pm$ sides of the cut respectively as in figure 1. To find the discontinuity across the cut, $\hat{M}_{c+} - \hat{M}_{c-}$, we must evaluate

$$k_l(2\mu_+a)/(2\mu_+a)k_l'(2\mu_+a) - k_l(2\mu_-a)/(2\mu_-a)k_l'(2\mu_-a) = \mathrm{i}D_l(\rho) \tag{4.6}$$

where

$$2\mu_{\pm}a = \pm iR = \pm\tfrac{1}{2}i\sqrt{\rho}. \tag{4.7}$$

For $l=0$ it is trivial to evaluate $D_0(\rho)$ as

$$D_0(\rho) = 2\sqrt{\rho}/(4+\rho^2). \tag{4.8}$$

For general l values it is still possible to evaluate $D_l(\rho)$ in simple explicit form by use of a sequence of Bessel function relations. The first transformation of the left-hand side of (4.6) uses the relations

$$\begin{aligned} &k_l'(z) = -[(l+1)/z]k_l(z) - k_{l-1}(z), \\ &k_l(R\,e^{-i\pi/2}) = \tfrac{1}{2}i\pi\, e^{i(l+1)\pi/2} h_l^{(1)}(R) = k_l^*(R\,e^{i\pi/2}), \\ &h_l^{(1)}(R) = j_l(R) + iy_l(R), \end{aligned} \tag{4.9}$$

where j_l, y_l and $h_l^{(1)}$ are standard spherical Bessel functions (Abramowitz and Stegun 1965), to obtain

$$D_l(\rho) = \frac{2R[j_l(R)y_{l-1}(R) - y_l(R)j_{l-1}(R)]}{[(l+1)j_l(R) - Rj_{l-1}(R)]^2 + [(l+1)y_l(R) - Ry_{l-1}(R)]^2}. \tag{4.10}$$

One can simplify the numerator of (4.10) by the identity

$$j_l(R)y_{l-1}(R) - j_{l-1}(R)y_l(R) = 1/R^2. \tag{4.11}$$

The denominator is simplified by expressing j_l, y_l in terms of modulus and phase (Abramowitz and Stegun 1965),

$$\begin{aligned} &j_l(R) = (\pi/2R)^{1/2} M_{l+1/2}(R)\cos\theta_{l+1/2}(R), \\ &y_l(R) = (\pi/2R)^{1/2} M_{l+1/2}(R)\sin\theta_{l+1/2}(R), \end{aligned} \tag{4.12}$$

and using

$$j_{l-1}(R) = j_l'(R) + [(l+1)/R]j_l(R), \qquad y_{l-1}(R) = y_l'(R) + [(l+1)/R]y_l(R), \tag{4.13}$$

to obtain

$$\begin{aligned} D_l(\rho) = \frac{2}{R}\bigg[&-(l+1)^2\left(\frac{\pi}{2R} M_{l+1/2}^2(R)\right) + R^2\left(\frac{\pi}{2R} M_{l-1/2}^2(R)\right) \\ &-(l+1)R\frac{d}{dR}\left(\frac{\pi}{2R} M_{l+1/2}^2(R)\right)\bigg]^{-1}. \end{aligned} \tag{4.14}$$

The function $(\pi/2R)M_{l+1/2}^2(R)$ is a polynomial

$$\frac{\pi}{2R} M_{l+1/2}^2(R) = \frac{1}{R^2}\sum_{p=0}^{l} C(l,p)(2R)^{2p-2l}, \tag{4.15}$$

with coefficients

$$C(l,p) = (2l-p)!(2l-2p)!/p![(l-p)!]^2. \tag{4.16}$$

Putting these last expressions into (4.14) gives finally

$$D_l(\rho) = \rho^{1/2}\left((\rho/4)\sum_{p=0}^{l-1} C(l-1,p)\rho^{p-l+1} - (l+1)\sum_{p=0}^{l}(2p-l-1)C(l,p)\rho^{p-l}\right)^{-1}. \tag{4.17}$$

Remembering (3.6) and combining (4.1), (4.5), (4.6) and (4.17) we obtain for the memory function $\mathcal{M}_c(ka, \tau)$ the expression

$$\mathcal{M}_c(ka, \tau) = -\frac{3\phi}{2\pi} \sum_{\substack{l=0 \\ l \text{ even}}}^{\infty} (2l+1)\left(\frac{j_l'(ka)}{ka}\right)^2 H_l\left(\frac{\tau}{(ka)^2}\right) \exp(-\tau/2) \tag{4.18}$$

with the function $H_l(z)$ defined by a definite integral

$$H_l(z) = \int_0^{\infty} \exp(-\rho z/8) D_l(\rho)\, d\rho. \tag{4.19}$$

The moments $\mu_{cn}(ka, \tau)$ are given by integration of the expression (4.18) over a finite time interval. After interchange of the order of the ρ and τ integrations the time integration can be evaluated analytically to give a function

$$g_n(\rho/(ka)^2, \tau) = (n!)^{-1} \int_0^{\tau} \tau'^n \exp[-(\tfrac{1}{2} + \rho/8(ka)^2)\tau']\, d\tau'. \tag{4.20}$$

For $n = 0$ this is

$$g_0(\rho/(ka)^2, \tau) = [\tfrac{1}{2} + \rho/8(ka)^2]^{-1}\{1 - \exp[-(\tfrac{1}{2} + \rho/8(ka)^2)\tau]\} \tag{4.21}$$

and at all higher n values g_n can similarly be expressed in terms of elementary functions. The remaining ρ integration defines a function

$$W_n^l(ka, \tau) = \int_0^{\infty} g_n(\rho/(ka)^2, \tau) D_l(\rho)\, d\rho \tag{4.22}$$

in terms of which the moments $\mu_{cn}(ka, \tau)$ are

$$\mu_{cn}(ka, \tau) = -\frac{3\phi}{2\pi} \sum_{\substack{l=0 \\ l \text{ even}}}^{\infty} (2l+1)\left(\frac{j_l'(ka)}{ka}\right)^2 W_n^l(ka, \tau). \tag{4.23}$$

To get $\mathcal{M}_s(ka, \tau)$ and $\mu_{sn}(ka, \tau)$ for self diffusion one simply replaces $\frac{3}{2}$ by $\frac{3}{4}$ in (4.18) and (4.23) and sums over both even and odd l values. In the last expression (4.23) there remains a one-dimensional definite integral which must be evaluated numerically to obtain $\mu_n(ka, \tau)$.

From (4.18) one sees that $\mathcal{M}(ka, \tau)$ has an overall slow exponential decay due to the factor $\exp(-\tau/2)$ which, in dynamical terms, arises from the diffusion of the centre of mass of a pair of particles in the suspension. A simple scaling of variables in the integral in (4.19) shows that as $\tau \to 0$, $\mathcal{M}(ka, \tau)$ diverges as $\tau^{-1/2}$ (Ackerson and Fleishman 1982) while the moments $\mu_n(ka, \tau)$ are finite, behaving as

$$\mu_n(ka, \tau) \sim \tau^{n+1/2}. \tag{4.24}$$

From the basic definition (3.9) or from (4.24) it is clear that for $\tau < 1$ the $\mu_n(ka, \tau)$ decrease rapidly in magnitude as n increases, but for $\tau > 1$ this need not be the case. To study the detailed behaviour of $\mu_n(ka, \tau)$ the first four moments ($n = 0, 1, 2, 3$) have been calculated throughout the ranges of ka and τ, $0.1 \leqslant ka \leqslant 6.0$ and $0 \leqslant \tau \leqslant 6.0$. A sample of these numerical results is presented in figures 2 and 3 as well as in tables 1 and 2. For a hard-sphere suspension the structure factor $S(ka)$ has its maximum at a value k_{max} which is given in terms of the radius a by $k_{max}a \approx 3$. In figures 2 and 3 are shown graphs of $-\mu_n/\phi$ against τ for both collective and self diffusion at a wavenumber ($ka = 2.0$) which is just below k_{max}, while in tables 1 and 2 the analogous results are

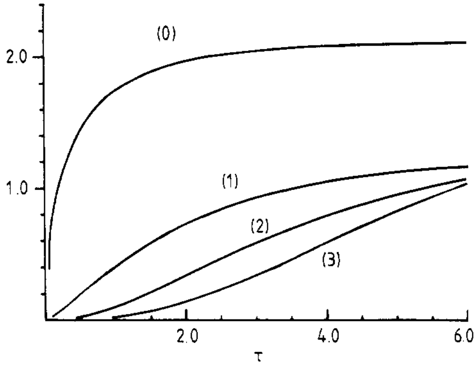

Figure 2. Graphs showing the dependence of the quantities $-\mu_{cn}(ka, \tau)/\phi$ $(n=0, 1, 2, 3)$ upon the time τ for wavenumber $ka = 2.0$.

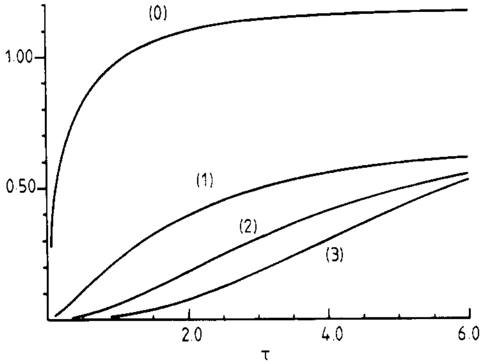

Figure 3. Graphs showing the dependence of the quantities $-\mu_{sn}(ka, \tau)/\phi$ $(n=0, 1, 2, 3)$ upon the time τ for wavenumber $ka = 2.0$.

Table 1. Collective diffusion at wavenumber $ka = 0.3$.

τ	$-\mu_{c0}/\phi$	$-\mu_{c1}/\phi$	$-\mu_{c2}/\phi$	$-\mu_{c3}/\phi$
0.10	0.174	0.0036	$9.1\,(10^{-5})$	$2.0\,(10^{-6})$
0.30	0.208	0.0096	$6.8\,(10^{-4})$	$4.4\,(10^{-5})$
0.50	0.221	0.0144	0.0016	$1.7\,(10^{-4})$
1.00	0.233	0.0231	0.0048	$9.7\,(10^{-4})$
1.50	0.238	0.0288	0.0083	0.0024
2.00	0.240	0.0327	0.0117	0.0044
2.50	0.241	0.0355	0.0148	0.0067
3.00	0.242	0.0375	0.0175	0.0092
3.50	0.242	0.0389	0.0198	0.0117
4.00	0.243	0.0399	0.0218	0.0142
4.50	0.243	0.0407	0.0234	0.0165
5.00	0.243	0.0413	0.0248	0.0186
5.50	0.243	0.0417	0.0259	0.0206
6.00	0.243	0.0420	0.0268	0.0223

presented numerically at a wavenumber ($ka = 0.3$) much less than k_{max} and close to the hydrodynamic limit $k = 0$.

The numerical study shows that throughout the range of wavenumbers $0.1 \leq ka \leq 6.0$ and for $\tau < 1$ the lowest moment $\mu_0(ka, \tau)$ is much the largest in magnitude; moreover it grows extremely rapidly in the time interval $0 \leq \tau \leq 0.5$. For $\tau > 1$ the moment $\mu_0(ka, \tau)$ quickly saturates at a plateau value which at $\tau = 2$ is already about nine-tenths of its $\tau = \infty$ value. The higher moments for $n > 1$ grow much more slowly than does μ_0 and themselves approach plateau values at successively later values of τ. From tables 1 and 2 it is seen that for $ka = 0.3$ the lowest moment μ_0 is much greater in magnitude than any of the higher moments at all times. However, in the graphs of figures 2 and 3 at $ka = 2.0$ one sees that the plateau values reached by the higher moments μ_n $(n \geq 1)$ are of the same order of magnitude as μ_0 itself. For the hard-sphere model over the time range $0 \leq \tau \leq 6$ the moment μ_0 is the dominant moment only for $ka \leq 0.5$ $(k \leq 0.15 k_{max})$. For $ka > 0.5$ and at times $\tau > 1$ one must include higher moments in the differential equation representation (3.8) of the memory equation.

Table 2. Self diffusion at wavenumber $ka = 0.3$.

τ	$-\mu_{s0}/\phi$	$-\mu_{s1}/\phi$	$-\mu_{s2}/\phi$	$-\mu_{s3}/\phi$
0.10	1.64	0.0326	8.1 (10^{-4})	1.7 (10^{-5})
0.30	1.86	0.0695	0.0042	2.5 (10^{-4})
0.50	1.91	0.0874	0.0077	7.1 (10^{-4})
1.00	1.94	0.108	0.0148	0.0025
1.50	1.95	0.116	0.0202	0.0047
2.00	1.95	0.121	0.0242	0.0070
2.50	1.95	0.124	0.0274	0.0094
3.00	1.95	0.126	0.0299	0.0117
3.50	1.95	0.127	0.0319	0.0138
4.00	1.95	0.128	0.0335	0.0158
4.50	1.95	0.128	0.0348	0.0176
5.00	1.95	0.129	0.0358	0.0192
5.50	1.95	0.129	0.0366	0.0206
6.00	1.95	0.129	0.0372	0.0218

5. Analysis of experimental data

In § 3 it was shown (3.10) that the theoretically defined long-time diffusivities $D_c^L(k)$, $D_s^L(k)$ are given in terms of the lowest moments $\mu_{c0}(ka, \tau)$, $\mu_{s0}(ka, \tau)$ at $\tau = \infty$. Is it possible then to extract a value for $\mu_0(ka, \infty)$ from experimental data which are mostly confined to the range $0 \leqslant \tau \leqslant 6$ with the most accurate data lying in a smaller range near $\tau = 0$? To try to answer this question one can use the behaviour of the moments in the hard-sphere model of § 4 as a qualitative guide. The results above suggest that if one is close enough to the hydrodynamic limit ($k \leqslant 0.15 k_{max}$) then all moments but μ_0 are negligible. In such a case the differential equation (3.8) reduces to

$$d\mathscr{F}_c(ka, \tau)/d\tau = -(1/S(ka) + \mu_{c0}(ka, \tau))\mathscr{F}_c(ka, \tau) \tag{5.1}$$

so that the slope of $\ln \mathscr{F}_c(ka, \tau)$ directly gives $1/S(ka) + \mu_{c0}(ka, \tau)$. Since, by $\tau = 2$, μ_{c0} has almost reached its $\tau = \infty$ value we conclude from (3.10) that a simple slope measurement will indeed give $D_c^L(k)$ and that $\mathscr{F}_c(ka, \tau)$ will behave as a simple exponential for times $\tau > 2$.

Unfortunately, at larger wavenumber k the higher moments ($n \geqslant 1$) begin to contribute significantly at times $\tau > 2$ so one must correct for their presence if one tries to extract μ_{c0} alone. The first possibility to consider is one in which the memory function (and hence also the moments μ_{cn}) is small in comparison with the term in (3.8) which includes $1/S(ka)$. Since the memory effects vanish as $\phi \to 0$ and at short times there will certainly be regimes where we can make the small memory function approximation (neglecting hydrodynamic interaction):

$$d\mathscr{F}_c(ka, \tau)/d\tau \approx -(S(ka))^{-1}\mathscr{F}_c(ka, \tau). \tag{5.2}$$

One can now use (5.2) to estimate all higher derivatives in (3.8) as

$$d^n\mathscr{F}_c(ka, \tau)/d\tau^n \approx (-1/S(ka))^n\mathscr{F}_c(ka, \tau) \tag{5.3}$$

to obtain from (3.8) the expression

$$d \ln \mathscr{F}_c(ka, \tau)/d\tau = -[1/S(ka) + \mu_{c0}(ka, \tau)] - \sum_{n=1}^{\infty} \mu_{cn}(ka, \tau)/S^n(ka). \tag{5.4}$$

One sees now that if μ_{c0} is not the dominant moment then the higher moments will reach non-negligible plateau values in succession as τ increases producing a steadily changing slope of $\ln \mathscr{F}_c(ka, \tau)$. Such a behaviour is seen qualitatively in some experimental data (Cebula *et al* 1981, Kops-Werkhoven and Fijnaut 1982, Kops-Werkhoven *et al* 1982). Suppose now that we know from experiment $\ln \mathscr{F}_c(ka, \tau)$ and its slope $E(\tau)$,

$$E(\tau) = \mathrm{d} \ln \mathscr{F}_c(ka, \tau)/\mathrm{d}\tau. \tag{5.5}$$

How can one extract μ_{c0} from these data which by (5.4) include higher-moment contributions as well? For the sake of illustration consider a time regime during which only the first three moments ($n = 0, 1, 2$) are of significant magnitude. Then we can truncate the summation in (5.4) at $n = 2$ and use the following identities:

$$\begin{aligned} \mu_{c1}(ka, \tau) &= \tau\mu_{c0}(ka, \tau) - \int_0^\tau \mu_{c0}(ka, \tau')\,\mathrm{d}\tau', \\ \mu_{c2}(ka, \tau) &= \tfrac{1}{2}\tau^2\mu_{c0}(ka, \tau) - \int_0^\tau \tau'\mu_{c0}(ka, \tau')\,\mathrm{d}\tau', \end{aligned} \tag{5.6}$$

to convert (5.4) into an integral equation giving $\mu_{c0}(ka, \tau)$ in terms of $E(\tau)$:

$$\begin{aligned} \mu_{c0}(ka, \tau) = {} & \left[1 + \frac{\tau}{S(ka)} + \frac{1}{2}\left(\frac{\tau}{S(ka)}\right)^2\right]^{-1} \left[-\left(\frac{1}{S(ka)} + E(\tau)\right)\right. \\ & \left. + \frac{1}{S(ka)}\int_0^\tau \mu_{c0}(ka, \tau')\,\mathrm{d}\tau' + \frac{1}{S^2(ka)}\int_0^\tau \tau'\mu_{c0}(ka, \tau')\,\mathrm{d}\tau'\right]. \end{aligned} \tag{5.7}$$

The integral terms here account for the presence of higher moments; since these effects should be small a simple iterative solution of (5.7) should suffice to extract a value for $\mu_{c0}(ka, \tau)$ out to perhaps $\tau \approx 2$ where as we have seen in § 4 it has almost reached its $\tau = \infty$ value.

Finally we consider the case that the memory function cannot be regarded as small (e.g. at high concentrations) so that the estimate (5.3) is invalid. In such a case the derivative terms on the right-hand side of (3.8) must be kept through some order n at which the moments μ_{cn} become negligible. As an example, suppose that up to some time τ only μ_{c0} and μ_{c1} are significant. Then (3.8) reduces to

$$E(\tau) = -(1/S(ka) + \mu_{c0}(ka, \tau))/(1 - \mu_{c1}(ka, \tau)). \tag{5.8}$$

Using (5.6) we express this as

$$\mu_{c0}(ka, \tau) = -\frac{(E(\tau) + 1/S(ka))}{(1 - \tau E(\tau))} - \frac{E(\tau)}{(1 - \tau E(\tau))}\int_0^\tau \mu_{c0}(ka, \tau')\,\mathrm{d}\tau' \tag{5.9}$$

which again can be solved for μ_{c0} in terms of $E(\tau)$. If both $n = 1$ and $n = 2$ terms are significant, as when the curvature of $\ln \mathscr{F}_c(ka, \tau)$ is not negligible, we have a second-order differential equation from (3.8)

$$\mathrm{d}\mathscr{F}_c/\mathrm{d}\tau = -(S^{-1} + \mu_{c0})\mathscr{F}_c + \mu_{c1}\,\mathrm{d}\mathscr{F}_c/\mathrm{d}\tau - \mu_{c2}\,\mathrm{d}^2\mathscr{F}_c/\mathrm{d}\tau^2. \tag{5.10}$$

Using (5.6) we can express this also as an integral equation

$$\begin{aligned} \mu_{c0}(ka, \tau) = {} & [1 - \tau E(\tau) + \tfrac{1}{2}\tau^2(\dot{E}(\tau) + E^2(\tau))]^{-1}\left[-\left(\frac{1}{S(ka)} + E(\tau)\right)\right. \\ & \left. - E(\tau)\int_0^\tau \mu_{c0}(ka, \tau')\,\mathrm{d}\tau' - (\dot{E}(\tau) + E^2(\tau))\int_0^\tau \tau'\mu_{c0}(ka, \tau')\,\mathrm{d}\tau'\right] \end{aligned} \tag{5.11}$$

where now the curvature of $\ln \mathcal{F}_c(ka, \tau)$ is taken account of through the combination $\dot{E}(\tau) + E^2(\tau)$. A similar analysis holds for self diffusion after the replacements $S(ka) \to 1$ and $c \to s$.

6. Conclusions

Consideration of the model memory function of § 4 in conjunction with the differential equation form of the memory equation in (3.8) leads to the following conclusions about obtaining long-time diffusivities from experimental curves of $\ln \mathcal{F}_c(ka, \tau)$ or $\ln \mathcal{F}_s(ka, \tau)$. First of all, the hydrodynamic limit regime consists of the wavenumber range $0 \leqslant k \leqslant 0.15 k_{max}$. In this range of k, $\mathcal{F}(ka, \tau)$ should appear to be a simple exponential for all experimentally accessible times $\tau > 1$ and the slope of $\ln \mathcal{F}(ka, \tau)$ in this region should give the long-time diffusivity $D^L(k)$. At larger values of k the slope of $\ln \mathcal{F}(ka, \tau)$ depends on several moments μ_n when $\tau > 1$ and there should be a slowly changing slope as τ increases, implying that $\mathcal{F}(ka, \tau)$ is not a simple exponential in this regime. In § 5 it is shown how one can take account of these higher moments in order to extract only the lowest moment μ_0 from the experimental curves. A determination of $\mu_0(\tau)$ out to about $\tau \approx 2$ should give a good estimate of $\mu_0(\infty)$ and hence of $D^L(k)$. A measurement of $D^L(k)$ obtained in this way from short-time data should be a useful alternative to the measurement of $D^L(k)$ by the area determination method of (2.8).

The fact that the moments $\mu_n(\tau)$ for $n \geqslant 1$ are of significant magnitude indicates that the hard-sphere memory function decays slowly. The memory function curves of Hess and Klein (1983) for charged suspensions show a qualitatively similar behaviour. In both high-density hard-sphere systems and low-density charged systems (Pusey and Tough 1982) the structure factor $S(k)$ shows great variability with wavenumber, ranging from $S(k) \approx 0.1$ at small k to $S(k) > 1.5$ at k_{max}. For small values of $S(k)$ the initial decay of $\mathcal{F}_c(\tau)$ is exceedingly rapid and the graph of $\ln \mathcal{F}_c(\tau)$ shows a rapidly changing slope so that an analysis like that of § 5 should include at least the second derivative of $\mathcal{F}_c(\tau)$ as indicated in (5.11). For $k > k_{max}$ when $S(k)$ is of order 1 it should be possible to ignore the second derivative and use (5.9) instead. Finally we remark that if hydrodynamic forces are included in the hard-sphere model the qualitative effect at moderate concentrations will be to reduce the magnitude of the memory function since the small radial mobility near contact reduces the effect of the large hard-sphere contact force (Jones and Burfield 1982a, b). This suggests that the small memory function approximation of (5.4) and (5.7) may be appropriate for real low-density hard-sphere systems if one takes account of the short-time hydrodynamic effects by the replacement $1/S(ka) \to H(ka)/S(ka)$.

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