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Time-dependent self-diffusion coefficient of interacting Brownian particles

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We study the time-dependent self-diffusion coefficient for a suspension of interacting, spherical Brownian particles. Guided by an exact result for a dilute suspension of hard spheres, we conjecture that the Fourier transform of the memory function may be represented as a meromorphic function of the square root of the frequency. We show that a two-pole approximation provides a suitable framework for the analysis of experimental data.

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I. INTRODUCTION

The mean-square displacement of an isolated Brownian particle grows with time at a rate proportional to the diffusion coefficient. In a suspension of interacting Brownian particles, the time dependence of the mean-square displacement is more complicated. At short and long times the growth is again linear, but with different rates, so that one must distinguish a short-time and a long-time diffusion coefficient. For dilute suspensions these coefficients may be evaluated to first order in the volume fraction [1–5]. The time dependence of the mean-square displacement may be characterized by a memory function [6,7]. Although one may derive a formal expression for this function on the basis of the generalized Smoluchowski equation [5–9], relatively little is known about its actual behavior. In this paper we suggest that the memory function of self-diffusion may be well approximated by a relatively simple expression involving only a small number of parameters, which may be determined either theoretically or experimentally.

It has been suggested by various authors [10,11] that the memory function depends exponentially on time. Such a time dependence would allow its calculation on the basis of initial time averages. The necessary averages have been evaluated for suspensions with direct pair interactions of the Debye-Hückel type and without hydrodynamic interactions by Nägele *et al.* [12]. However, the predicted time dependence of the mean-square displacement does not agree with the data from Brownian-dynamics simulations [13]. Similarly, Cichocki and Hinsen [14] found in a computer simulation of a dense hard-sphere suspension that an exponential dependence could not describe the data. Rather, they were led to a stretched-exponential behavior.

The time dependence of the memory function proposed here is suggested by an exact result for the case of a dilute suspension of hard spheres without hydrodynamic interactions [15–17]. Guided by this result, we conjecture that the Fourier transform of the memory function may be represented as a meromorphic function of the square root of the frequency. We show that a simple two-pole approximation leads to excellent agreement with the Brownian-dynamics data of Gaylor *et al.* [13]. A comparison with analytical results for dilute suspensions and an analysis of the simulation data of Cichocki and Hinsen [14] will be presented elsewhere. We have found that the two-pole approximation gives an excellent fit of the data. At high volume fraction the two-pole approximation provides a better description than the stretched exponential.

II. SELF-DIFFUSION COEFFICIENT

We consider N identical spherical particles performing Brownian motion in an incompressible fluid with shear viscosity η. The whole system is enclosed in a volume Ω. To study self-diffusion we consider the Brownian motion of a selected particle labeled 1. The particles interact via a direct pair potential and via hydrodynamic interactions, which are mediated by the Stokes flow response of the solvent fluid to the motion of the suspended macroparticles. If $\mathbf{R}_i$ denotes the position of the center of the ith sphere, then the configuration of the entire suspension may be described by the $3N$-dimensional vector $\mathbf{X}=(\mathbf{R}_1,\ldots,\mathbf{R}_N)$. The dynamical evolution of the configuration $\mathbf{X}$ is assumed to be described by a time-dependent probability distribution $P(\mathbf{X},t)$, which obeys the generalized Smoluchowski equation [8]. In abbreviated form this reads

$$\frac{\partial P}{\partial t}=\mathcal{D}P \ , \tag{2.1}$$

where $\mathcal{D}$ is the Smoluchowski operator defined by

$$\mathcal{D}P=\frac{\partial}{\partial \mathbf{X}}\cdot\underline{D}\cdot\left[\frac{\partial P}{\partial \mathbf{X}}+\frac{\partial \Phi}{\partial \mathbf{X}}P\right] . \tag{2.2}$$

Here $\underline{D}(\mathbf{X})$ is the $3N\times 3N$ diffusion matrix, which depends on configuration due to hydrodynamic interactions. Furthermore, $\beta=1/k_BT$ and the potential $\Phi(\mathbf{X})$ in Eq. (2.2) incorporates both a wall potential and the direct pair interactions. The Smoluchowski equation

(2.1) describes how the distribution function $P(\mathbf{X},t)$ tends to the equilibrium distribution

$$P_{\mathrm{eq}}(\mathbf{X})=\exp[-\beta\Phi(\mathbf{X})]/Z(\beta) \tag{2.3}$$

in the course of time. The partition function $Z(\beta)$ normalizes the distribution to unity.

The self-diffusion coefficient may be defined from the time-dependent scattering function at wave vector $\mathbf{q}$

$$F_S(\mathbf{q},t)=\lim_{\substack{N\to\infty\\ \Omega\to\infty}}\langle \exp i\mathbf{q}\cdot[\mathbf{R}_1(t)-\mathbf{R}_1(0)]\rangle\ , \tag{2.4}$$

where we take the thermodynamic limit $N\to\infty$, $\Omega\to\infty$ at constant $n=N/\Omega$. The angle brackets indicate an average over the equilibrium distribution (2.3), and the time dependence of the position $\mathbf{R}_1$ is governed by the adjoint Smoluchowski operator $\mathcal{L}$ such that $\mathbf{R}_1(t)=(\exp\mathcal{L}t)\mathbf{R}_1(0)$, with $\mathbf{R}_1(0)=\mathbf{R}_1$. The operator $\mathcal{L}$ is given by

$$\mathcal{L}=\left[\frac{\partial}{\partial\mathbf{X}}-\beta\frac{\partial\Phi}{\partial\mathbf{X}}\right]\cdot\underline{D}\cdot\frac{\partial}{\partial\mathbf{X}}\ . \tag{2.5}$$

In the thermodynamic limit, the scattering function is independent of the wall potential. The one-sided Fourier transform of the scattering function is given by

$$G_S(\mathbf{q},\omega)=\int_0^\infty e^{i\omega t}F_S(\mathbf{q},t)dt\ . \tag{2.6}$$

We define the wave-vector- and frequency-dependent self-diffusion coefficient $D_S(\mathbf{q},\omega)$ from the identity

$$G_S(\mathbf{q},\omega)=\frac{1}{-i\omega+q^2D_S(\mathbf{q},\omega)}\ . \tag{2.7}$$

By the projection operator technique [6,7] one can derive an equation of motion for the scattering function of the form

$$\frac{dF_S(\mathbf{q},t)}{dt}=-q^2D_S(\mathbf{q},\infty)F_S(\mathbf{q},t) -q^2\int_0^t M_S(\mathbf{q},t-t')F_S(\mathbf{q},t')dt'\ , \tag{2.8}$$

where the instantaneous term is given by

$$D_S(\mathbf{q},\infty)=\frac{-1}{q^2}\langle e^{-i\mathbf{q}\cdot\mathbf{R}_1}\mathcal{L}e^{i\mathbf{q}\cdot\mathbf{R}_1}\rangle\ , \tag{2.9}$$

and $M_S(\mathbf{q},t)$ is the memory function. In Eq. (2.9) and in the following, the thermodynamic limit is implied. By Fourier transform of Eq. (2.8) one finds that the generalized self-diffusion coefficient may be expressed as

$$D_S(\mathbf{q},\omega)=D_S(\mathbf{q},\infty)+\hat{M}_S(\mathbf{q},\omega)\ , \tag{2.10}$$

where $\hat{M}_S(\mathbf{q},\omega)$ is the Fourier transform of the memory function, defined as in Eq. (2.6).

We shall consider only the long-wavelength limit. In this limit the memory function is given by [5,16]

$$M_S(0,t)=-\tfrac{1}{3}\langle \mathbf{U}_1'\cdot e^{\mathcal{L}t}\mathbf{U}_1'\rangle\ , \tag{2.11}$$

where $\mathbf{U}_1'(\mathbf{X})$ is the velocity of the selected particle on the Smoluchowski time scale [18]:

$$\mathbf{U}_1'=\mathcal{L}\mathbf{R}_1=\sum_j\left[\frac{\partial}{\partial\mathbf{R}_j}-\beta\frac{\partial\Phi}{\partial\mathbf{R}_j}\right]\cdot\underline{D}_{j1}\ . \tag{2.12}$$

Thus, apart from the minus sign, the memory function may be identified with a velocity time-correlation function [10]. The latter may be related to the mean-square displacement of the selected particle, defined by

$$W(t)=\tfrac{1}{6}\langle[\mathbf{R}_1(t)-\mathbf{R}_1(0)]^2\rangle\ . \tag{2.13}$$

By cumulant expansion of the scattering function defined in Eq. (2.4) one finds that

$$W(t)=\lim_{q\to0}\frac{-1}{q^2}\ln F_S(\mathbf{q},t)\ . \tag{2.14}$$

It is straightforward to show from Eq. (2.8) that the rate of change of the mean-square displacement is given by

$$\frac{dW}{dt}\equiv D_S(t)=D_S^S+\int_0^t M_S(0,t')dt'\ , \tag{2.15}$$

where D_S^S is the short-time diffusion coefficient

$$D_S^S=D_S(0,\infty)\ . \tag{2.16}$$

Equation (2.15) is used to define the time-dependent diffusion coefficient $D_S(t)$. The long-time diffusion coefficient D_S^L is given by

$$D_S^L=D_S^S+\int_0^\infty M_S(0,t)dt=D_S^S+\tfrac{1}{3}\langle\mathbf{U}_1'\cdot\mathcal{L}^{-1}\mathbf{U}_1'\rangle\ . \tag{2.17}$$

The main purpose of this paper is to study the time-dependent diffusion coefficient $D_S(t)$.

III. MEMORY FUNCTION TIME SCALE

It follows from Eq. (2.17) and the fact that $\mathcal{L}$ is a negative definite operator that the time-dependent diffusion coefficient $D_S(t)$, defined in Eq. (2.15), shows a decrease from its short-time value D_S^S to the long-time value D_S^L. In this section we define the time scale for the rate of variation.

It is somewhat more convenient to consider the difference

$$\mu_S(t)=D_S(t)-D_S^L\ . \tag{3.1}$$

This is the relaxation function corresponding to the memory function

$$\mu_S(t)=-\int_t^\infty M_S(0,t')dt'\ . \tag{3.2}$$

It may be expressed as

$$\mu_S(t)=D_S^S-D_S^L-\tfrac{1}{3}\langle\mathbf{U}_1'\cdot[\mathbf{R}_1(t)-\mathbf{R}_1(0)]\rangle\ . \tag{3.3}$$

From Eqs. (2.15) and (3.1) we find that the Fourier transform

$$\hat{\mu}_S(\omega)=\int_0^\infty e^{i\omega t}\mu_S(t)dt \tag{3.4}$$

is given by

$$\hat{\mu}_S(\omega)=\frac{1}{i\omega}[D_S^L-D_S^S-\hat{M}_S(0,\omega)]\ . \tag{3.5}$$

This quantity has the dimension area.

The time scale characterizing the variation of the memory function, and hence that of the diffusion coefficient $D_S(t)$, may be defined by

$$\tau_M = \int_0^\infty t M_S(\mathbf{0},t)dt \Big/ \int_0^\infty M_S(\mathbf{0},t)dt \ . \tag{3.6}$$

The denominator is just $D_S^L - D_S^S$, and an integration by parts with use of Eq. (3.2) shows that the numerator may be expressed as $-\hat{\mu}_S(0)$. Thus we have

$$\tau_M = \hat{\mu}_S(0)/(D_S^S - D_S^L) \ . \tag{3.7}$$

From the definitions (2.17) and (3.1) it follows that the numerator may be expressed as

$$\hat{\mu}_S(0) = \lim_{t\to\infty} [W(t) - D_S^L t] \ . \tag{3.8}$$

Therefore, the time scale τ_M may be found experimentally from the short- and long-time self-diffusion coefficients, and from the asymptotic behavior of the mean-square displacement, as given by Eq. (2.14) in terms of the scattering function [14].

The definition of the time scale τ_M presupposes that $\hat{\mu}_S(\omega)$ has a finite zero-frequency limit. If the limit exists, then the low-frequency behavior of the memory function is given by

$$\hat{M}_S(\mathbf{0},\omega) = (D_S^L - D_S^S)[1 + i\omega\tau_M + o(\omega)] \ . \tag{3.9}$$

By expansion of the correlation function expression

$$\hat{M}_S(\mathbf{0},\omega) = \tfrac{1}{3}\langle \mathbf{U}_1' \cdot (i\omega + \mathcal{L})^{-1}\mathbf{U}_1' \rangle \tag{3.10}$$

in powers of ω we find

$$\hat{\mu}_S(0) = \tfrac{1}{3}\langle \mathbf{U}_1' \cdot \mathcal{L}^{-2}\mathbf{U}_1' \rangle \ , \tag{3.11}$$

which shows that $\hat{\mu}_S(0)$ is always positive. From Eqs. (2.17) and (3.7) it follows that the time scale τ_M may be expressed as

$$\tau_M = -\langle \mathbf{U}_1' \cdot \mathcal{L}^{-2}\mathbf{U}_1' \rangle / \langle \mathbf{U}_1' \cdot \mathcal{L}^{-1}\mathbf{U}_1' \rangle \ . \tag{3.12}$$

In model calculations on dilute systems we have found that both moments may be evaluated and take finite values. Henceforth we assume that the low-frequency behavior of the memory function is of the form (3.9).

IV. ANALYTIC BEHAVIOR

In this section we discuss the analytic behavior of the Fourier transform $\hat{M}_S(\mathbf{0},\omega)$ of the memory function in more detail. A number of properties may be derived exactly from its definition.

The expression (3.10) for $\hat{M}_S(\mathbf{0},\omega)$ may be regarded as a diagonal matrix element of the resolvent operator related to the Smoluchowski equation. Formally, the spectral decomposition of the resolvent operator reads

$$(i\omega + \mathcal{L})^{-1} = \sum_\lambda |\lambda) \frac{1}{i\omega - \lambda} (\lambda| \ , \tag{4.1}$$

where $|\lambda) \equiv \psi_\lambda(\mathbf{X})$ is the right eigenvector of $\mathcal{L}$ with eigenvalue $-\lambda$:

$$|\lambda) = -\lambda|\lambda) \ , \tag{4.2}$$

and $(\lambda|$ is the corresponding left eigenvector. Substituting in Eq. (3.10) we find

$$\hat{M}_S(\mathbf{0},\omega) = \tfrac{1}{3}\sum_\lambda \frac{|(\lambda|\mathbf{U}_1')|^2}{i\omega - \lambda} \ , \tag{4.3}$$

where the scalar product is defined by

$$(\lambda|\mathbf{U}_1') = \int P_{\text{eq}}(\mathbf{X})\psi_\lambda^*(\mathbf{X})\mathbf{U}_1'(\mathbf{X})d\mathbf{X} \ , \tag{4.4}$$

and we have used the property

$$(A|B) = (B|A)^* \ . \tag{4.5}$$

It follows from general properties of the Smoluchowski operator that all eigenvalues λ are real and positive, except for the eigenvalue 0, which corresponds to the equilibrium distribution. Hence $\hat{M}_S(\mathbf{0},\omega)$ may be represented as a sum of simple poles on the negative imaginary ω axis with positive residues. Correspondingly, the memory function itself is given by a sum of decaying exponentials with negative weights:

$$M_S(\mathbf{0},t) = -\tfrac{1}{3}\sum_\lambda |(\lambda|\mathbf{U}_1')|^2 e^{-\lambda t} \ . \tag{4.6}$$

We consider instead the relaxation function $\mu_S(t)$, defined in Eq. (3.1), which is given by

$$\mu_S(t) = \tfrac{1}{3}\sum_\lambda \lambda^{-1}|(\lambda|\mathbf{U}_1')|^2 e^{-\lambda t} \ . \tag{4.7}$$

In the thermodynamic limit we expect a continuous spectrum and therefore we replace the sum by an integral. We cast the result in the form

$$\mu_S(t) = (D_S^S - D_S^L)\gamma_S(t/\tau_M) \ , \tag{4.8}$$

with

$$\gamma_S(\tau) = \int_0^\infty p_S(u)e^{-u\tau}du . \tag{4.9}$$

The function $\gamma_S(\tau)$ was introduced by Cichocki and Hinsen [14]. The spectral distribution $p_S(u)$ is positive, dimensionless, and normalized to unity:

$$\int_0^\infty p_S(u)du = 1 \ . \tag{4.10}$$

Moreover, we find from Eq. (3.7)

$$\int_0^\infty \frac{1}{u} p_S(u)du = 1. \tag{4.11}$$

The expressions (4.8) and (4.9) may be related to the inverse Fourier transform

$$\mu_S(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \hat{\mu}_S(\omega)e^{-i\omega t}d\omega \ . \tag{4.12}$$

Here we introduce the new variable

$$v = -\frac{1+i}{\sqrt{2}}\sqrt{\omega} \ , \tag{4.13}$$

where $\sqrt{\omega}$ is defined with branch cut along the negative imaginary ω axis. The integral in Eq. (4.12) becomes

$$\mu_S(t) = \frac{1}{\pi}\int_C iv\hat{\mu}_S(-iv^2)e^{-v^2 t}dv \ , \tag{4.14}$$

where the contour C in the complex v plane runs along the diagonal from $-(1+i)\infty$ to 0 and along the other diagonal from 0 to $(1-i)\infty$. From the analytic properties of $\hat{\mu}_S(\omega)$ discussed above, it follows that the integrand in Eq. (4.14) is analytic in the lower half of the complex v plane. Hence for $t>0$ we can shift the contour to run along the real v axis and obtain

$$\mu_S(t)=\frac{1}{\pi}\int_{-\infty}^{\infty}F_S(v)e^{-v^2t}dv \; , \tag{4.15}$$

where $F_S(v)$ is defined by

$$F_S(v)=iv\hat{\mu}_S(-iv^2) \; . \tag{4.16}$$

The real v axis is a natural boundary for this function, corresponding to the negative imaginary ω axis. We decompose the limiting value along the real v axis into real and imaginary parts:

$$F_S(v)=F_S'(v)+iF_S''(v) \; . \tag{4.17}$$

It follows from Eq. (4.3) that these have the symmetry properties

$$F_S'(v)=F_S'(-v), \quad F_S''(v)=-F_S''(-v) \; . \tag{4.18}$$

Introducing the variable $u=v^2\tau_M$, we can therefore rewrite Eq. (4.15) in the form (4.8) with the identification

$$p_S(v^2\tau_M)=\frac{1}{\pi\tau_M(D_S^S-D_S^L)}\frac{F_S'(v)}{v} . \tag{4.19}$$

This identity allows the calculation of the spectral density $p_S(u)$ from the Fourier transform $\hat{\mu}_S(\omega)$.

V. HARD SPHERES WITHOUT HYDRODYNAMIC INTERACTIONS

As an example of the formalism developed in the preceding sections, we consider a dilute system of hard spheres of radius a, diffusion coefficient D_0, and without hydrodynamic interactions. For this system, the memory function may be calculated exactly [15–17] to first order in the volume fraction $\phi=\frac{4}{3}\pi n a^3$. To this order one finds [17]

$$\hat{M}_S(0,\omega)=-2D_0\phi\frac{1+iv\sqrt{2\tau_0}}{1+iv\sqrt{2\tau_0}-v^2\tau_0} \; , \tag{5.1}$$

where $\tau_0=a^2/D_0$. The short- and long-time diffusion coefficients are given by

$$D_S^S=D_0, \quad D_S^L=D_0(1-2\phi) \; . \tag{5.2}$$

From Eq. (3.5) one finds

$$\hat{\mu}_S(\omega)=\frac{2\phi a^2}{1+iv\sqrt{2\tau_0}-v^2\tau_0} \; . \tag{5.3}$$

According to Eq. (3.7), the memory function time scale is simply $\tau_M=\tau_0$. The function $F_S(v)$, defined in Eq. (4.16), is given by

$$F_S(v)=\frac{2i\phi a^2 v}{1+iv\sqrt{2\tau_0}-v^2\tau_0} \; . \tag{5.4}$$

One easily checks the symmetry properties (4.18). From Eq. (4.19) one finds the spectral density

$$p_S(u)=\frac{1}{\pi}\frac{\sqrt{2u}}{1+u^2} \; . \tag{5.5}$$

This is a very broad spectrum, decaying slowly for large u. In Fig. 1 we plot $p_S(u)$ versus $\log_{10}u$.

The explicit expression for the time-dependent diffusion coefficient $D_S(t)$ may be found from Eqs. (3.1), (4.15), and (5.4). Decomposing the right-hand side of Eq. (5.4) into partial fractions we find

$$F_S(v)=i\left[\frac{A_+}{v_+-v}+\frac{A_-}{v_--v}\right] , \tag{5.6}$$

with

$$A_\pm=(1\pm i)\phi D_0, \quad v_\pm=(\pm1+i)\frac{1}{\sqrt{2\tau_0}} \; . \tag{5.7}$$

The time-dependent diffusion coefficient is given by

$$D_S(t)=D_S^L+A_+w(v_+\sqrt{t}\,)+A_-w(v_-\sqrt{t}\,) \; , \tag{5.8}$$

where the function $w(z)$ is related to the error function of complex argument [19]. From the known properties of this function one finds the short-time behavior

$$D_S(t)\approx D_0[1-4\phi\sqrt{2t/\pi\tau_0}+O(t)] \quad \text{as } t\rightarrow 0+ \; , \tag{5.9}$$

and the long-time behavior

$$D_S(t)\approx D_0[1-2\phi+\sqrt{2/\pi}\,\phi(\tau_0/t)^{3/2}+O(t^{-2})] \quad \text{as } t\rightarrow\infty \; . \tag{5.10}$$

Both expressions may also be obtained from the behavior of the spectral density (5.5) at large and small u. In Fig. 2 we plot $\gamma_S(t)=\mu_S(t)/2\phi D_0$ as a function of t/τ_0.

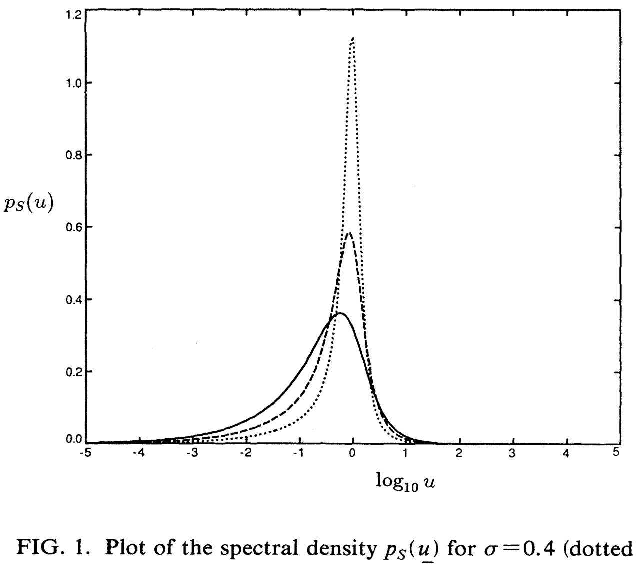

FIG. 1. Plot of the spectral density $p_S(u)$ for $\sigma=0.4$ (dotted curve), $\sigma=0.8$ (dashed curve), and $\sigma=\sqrt{2}$ (solid curve). The value $\sigma=\sqrt{2}$ corresponds to a dilute system of hard spheres without hydrodynamic interactions.

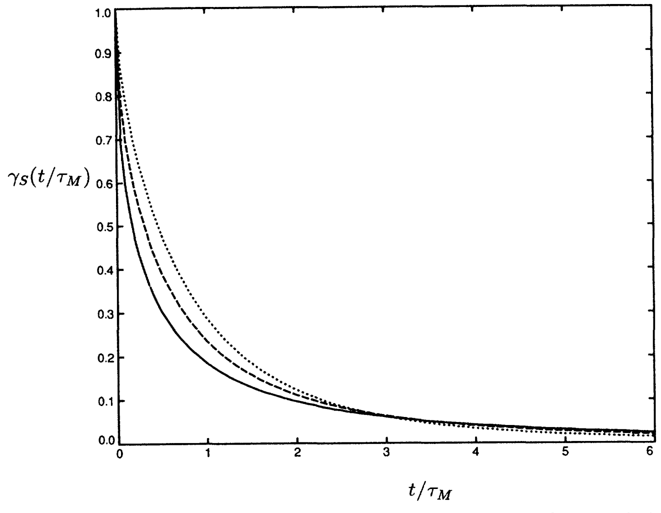

FIG. 2. Plot of the relaxation function $\gamma_S(t/\tau_M)$ for $\sigma=0.4$ (dotted curve), $\sigma=0.8$ (dashed curve), and $\sigma=\sqrt{2}$ (solid curve). The value $\sigma=\sqrt{2}$ corresponds to a dilute system of hard spheres without hydrodynamic interactions. The values $\sigma=0.4$ and 0.8 are typical for dense systems.

VI. CONJECTURE

It is a reasonable guess that the dynamics of a hard-sphere system at higher density, or of systems with more complicated interactions, is not too different from that of a dilute hard-sphere suspension, analyzed in the preceding section. Thus we conjecture that the function $F_S(v)$, defined in Eq. (4.16), may be analytically continued into the upper half of the complex v plane, where it is meromorphic. We have verified this conjecture for simple model systems. Together with additional assumptions on the location of the singularities, the conjecture allows an accurate description of the time dependence of the memory function in terms of a small number of parameters. In Sec. VIII we demonstrate this by way of example for some of the data of Gaylor *et al.* [13]. In a separate publication we shall validate our conjecture by a comparison with the simulation data of Cichocki and Hinsen [14].

We assume for simplicity that the singularities are simple poles. In analogy to Eq. (5.6) we conjecture that the function $F_S(v)$ may be expressed as

$$F_S(v)=i\sum_j \frac{A_j}{v_j-v}\ , \tag{6.1}$$

where all poles $\{v_j\}$ lie in the upper half of the complex v plane $I_+(v)$. It follows immediately from Eq. (4.15) that the corresponding relaxation function is given by

$$\mu_S(t)=\sum_j A_j w(v_j\sqrt{t}\,)\ . \tag{6.2}$$

It is clear that each pole v_j sets a time scale and that the residue A_j determines the corresponding amplitude. In this regard the expansion (6.2) is similar to an expansion in normal modes. However, the w functions vary over a much wider range. From the symmetry properties (4.18) it follows that the poles v_j either lie on the positive imaginary v axis with real residue, or occur in conjugate pairs

$$\begin{gathered} v_{j\pm}=\pm v_j'+iv_j'',\quad v_j''>0\ ,\\ A_{j+}'=A_{j-}',\quad A_{j+}''=-A_{j-}''\ . \end{gathered} \tag{6.3}$$

From Eq. (3.1) we find the sum rule

$$D_S^S-D_S^L=\sum_j A_j\ . \tag{6.4}$$

It follows from Eqs. (3.7) and (4.16) that the memory function time scale τ_M is finite provided

$$\sum_j \frac{A_j}{v_j}=0\ . \tag{6.5}$$

The time scale is then given by

$$\tau_M=\left[\sum_j A_j v_j^{-2}\right]\Big/\sum_j A_j\ . \tag{6.6}$$

For large t the w function behaves as

$$w(v\sqrt{t}\,)=\frac{i}{\sqrt{\pi}}\left[\frac{1}{v\sqrt{t}}+\frac{1}{2(v\sqrt{t}\,)^3}+O(t^{-5/2})\right]\ . \tag{6.7}$$

From Eqs. (6.2) and (6.5) we therefore find the long-time behavior

$$\mu_S(t)=\frac{i}{2\sqrt{\pi}}\left[\sum_j \frac{A_j}{v_j^3}\right]t^{-3/2}+O(t^{-5/2})\ . \tag{6.8}$$

Thus, for large t, the behavior of $\mu_S(t)$ is dominated by the poles near the origin. This suggests that the sum in Eq. (6.2) may be well approximated by only a small number of poles. We define the amplitudes of the long-time behavior C_L by

$$\mu_S(t)=(D_S^S-D_S^L)C_L(\tau_M/t)^{3/2}+O(t^{-5/2})\ . \tag{6.9}$$

The long-time coefficient C_L may be obtained from theory or experiment. As we shall show in Sec. VIII, the values of the diffusion coefficients D_S^S and D_S^L, the relaxation time τ_M, and the coefficient C_L of the long-time tail suffice to determine the numbers necessary for a two-pole approximation of the time-dependent diffusion coefficient $D_S(t)$.

VII. CONTINUED FRACTION

If there are more than two poles in the sum (6.1), then there are additional constraints on the possible values of the residues and poles. These follow from the relation (4.16) between $F_S(v)$ and $\hat{\mu}_S(\omega)$, and the nature of the correlation function expression (4.7) for $\hat{\mu}_S(\omega)$. These realtions imply that $F_S'(v)$ must be positive along the real v axis. The constraints are best expressed in terms of the continued-fraction representation of the function $\hat{\mu}_S(\omega)$.

From Eqs. (3.4) and (3.8) we find

$$\hat{\mu}_S(\omega)=(D_S^S-D_S^L)\tau_M\int_0^\infty \frac{p_S(u)}{u-i\omega\tau_M}du\ . \tag{7.1}$$

We denote $z=-i\omega\tau_M$ and transform to the variables

$$y=\frac{z_0}{z_0+u},\quad w=\frac{z_0}{z_0-z}\,, \tag{7.2}$$

where z_0 is a positive number, which may be chosen conveniently at a larger stage. The integral in Eq. (7.1) transforms to

$$\int_0^\infty \frac{p_S(u)}{u-i\omega\tau_M}du=wG(w)\,, \tag{7.3}$$

where $G(w)$ is given by the Stieltjes integral

$$G(w)=\int_0^1 \frac{g(y)}{w-y}dy\,, \tag{7.4}$$

with the positive weight function

$$g(y)=y^{-1}p_S(z_0y^{-1}-z_0)\,. \tag{7.5}$$

The normalization conditions (4.10) and (4.11) imply

$$G(0)=-\int_0^1 \frac{g(y)}{y}dy=\frac{-1}{z_0}\,, \tag{7.6a}$$

$$G(1)=\int_0^1 \frac{g(y)}{1-y}dy=1\,. \tag{7.6b}$$

According to a general theorem, the function $G(w)$ may be expanded as the so-called J fraction [20]:

$$G(w)=\frac{a_0}{w-b_1-}\,\frac{a_1}{w-b_2-}\cdots\,, \tag{7.7}$$

with positive coefficients $\{a_j\},\{b_j\}$, which may be related to the moments of the weight function $g(y)$ by means of a known algorithm. The properties of the coefficients $\{a_j\},\{b_j\}$ are described in the monograph by Wall [20]. The continued fraction converges at any point in the w plane at a finite distance from the interval (0,1). The number z_0, introduced in Eq. (7.2), may be used to improve the rate of convergence.

Our conjecture of the preceding section amounts to the assumption that the coefficients $\{a_j\},\{b_j\}$ saturate to constant values $a_\infty=\frac{1}{16}$ and $b_\infty=\frac{1}{2}$. If we accept this limiting behavior, then the continued fraction can be extrapolated in a simple way. Suppose from level n we replace all coefficients by their asymptotic values. Then for the continued fraction starting at level n we have the closed expression

$$f(w)=\frac{\frac{1}{16}}{w-\frac{1}{2}-f(w)}\,, \tag{7.8}$$

which is immediately solved for $f(w)$ with the result

$$f(w)=\tfrac{1}{2}w-\tfrac{1}{4}-\tfrac{1}{2}\sqrt{w(w-1)}\,. \tag{7.9}$$

As a consequence, the weight function $g(y)$ in Eq. (7.4) has support over the whole interval (0,1). The transformation (7.2) maps this interval into the negative imaginary ω axis, with $w=1$ corresponding to $\omega=0$, and $w=0$ to $\omega=-i\infty$. The square root in Eq. (7.9) may be expressed as

$$\sqrt{w(w-1)}=\frac{iv\sqrt{z_0\tau_M}}{z_0+v^2\tau_M} \tag{7.10}$$

in terms of the variable v defined in Eq. (4.13). Thus the assumed behavior of the continued fraction corresponds to a meromorphic function $F_S(v)$. The properties of the coefficients $\{a_j\},\{b_j\}$ imply constraints for the amplitudes $\{A_j\}$ and the location of the poles $\{v_j\}$.

VIII. TWO-POLE APPROXIMATION

In this section we consider the simplest case, where the meromorphic function $F_S(v)$ has only two poles in $I_+(v)$. If the continued fraction (7.7) saturates at the second level, then the function $G(w)$ becomes

$$G(w)=\frac{a_0}{w-b_1-16a_1f(w)}\,. \tag{8.1}$$

Substituting Eq. (7.9) and using the conditions (7.6) we find that this may be written

$$G(w)=\frac{a_0}{(z_0+1)a_0w-z_0a_0+8a_1\sqrt{w(w-1)}}\,. \tag{8.2}$$

This corresponds to the Fourier transform

$$\hat{\mu}_S(\omega)=(D_S^S-D_S^L)\tau_M\frac{1}{1+\sigma\sqrt{-i\omega\tau_M}-i\omega_M}\,, \tag{8.3}$$

with the denominator depending on the dimensionless parameter

$$\sigma=\frac{8a_1}{a_0\sqrt{z_0}}\,. \tag{8.4}$$

From Eq. (4.16) we find for the function $F_S(v)$ the two-pole approximation

$$F_S(v)=(D_S^S-D_S^L)\tau_M\frac{iv}{1+i\sigma v\sqrt{\tau_M}-v^2\tau_M}\,. \tag{8.5}$$

The denominator has roots at $v=v_\pm$ with

$$v_\pm=[i\sigma\pm(4-\sigma^2)^{1/2}]/2\sqrt{\tau_M}\,. \tag{8.6}$$

The fact that σ is positive guarantees that these roots lie in $I_+(v)$. The function $F_S(v)$ may be written as in Eq. (5.6) with amplitudes

$$A_\pm=\pm(D_S^S-D_S^L)\left[\frac{\tau_M}{4-\sigma^2}\right]^{1/2}v_\pm\,. \tag{8.7}$$

For $0<\sigma<2$ the roots $v_\pm$ lie symmetrically on both sides of the imaginary v axis and the amplitudes $A_\pm$ are complex conjugates. For $\sigma>2$ the roots $v_\pm$ are purely imaginary and the amplitudes $A_\pm$ are real. From Eq. (4.19) we find for the spectral density

$$p_S(u)=\frac{1}{\pi}\frac{\sigma\sqrt{u}}{1+(\sigma^2-2)u+u^2}\,. \tag{8.8}$$

In Fig. 1 we plot the spectral density for three values of σ.

The time-dependent diffusion coefficient is given by Eq. (5.8). It may be written in the form

$$D_S(t)=D_S^L+(D_S^S-D_S^L)F(t/\tau_M;\sigma,1)\,, \tag{8.9}$$

where $F(t/\tau_M;\sigma,1)$ is a standard function encountered in the theory of the motion of a sphere in a viscous fluid [21]. The explicit expression is

$$F(t/\tau_M;\sigma,1)=\frac{1}{v_+-v_-}[v_+w(v_+\sqrt{t})-v_-w(v_-\sqrt{t})]\ . \tag{8.10}$$

For short times

$$F(t/\tau_M;\sigma,1)=1-\frac{2\sigma}{\sqrt{\pi}}\left[\frac{t}{\tau_M}\right]^{1/2}+O(t)\quad\text{as } t\to 0+\ , \tag{8.11}$$

and for long times

$$F(t/\tau_M;\sigma,1)=\frac{\sigma}{2\sqrt{\pi}}\left[\frac{\tau_M}{t}\right]^{3/2}+O(t^{-2})\quad\text{as } t\to\infty\ . \tag{8.12}$$

Hence in the two-pole approximation the long-time coefficient C_L, defined in Eq. (6.9), is given by

$$C_L=\frac{\sigma}{2\sqrt{\pi}}\ . \tag{8.13}$$

Conversely, the dimensionless parameter σ may be determined from the long-time coefficient C_L, obtained either in theory or in experiment. For $\sigma=0$

$$F(t/\tau_M;0,1)=\exp(-t/\tau_M)\ . \tag{8.14}$$

The deviations from the exponential function are strongest for large values of σ. The case of a dilute system of hard spheres, discussed in Sec. V, corresponds to the value $\sigma=\sqrt{2}$. In Fig. 2 we plot the function $\gamma_S(t/\tau_M)$, defined in Eq. (4.8), for three values of σ.

Finally, we consider the mean-square displacement $W(t)$, which is the quantity obtained directly from experiment according to Eq. (2.14). From Eqs. (2.15) and (8.9) we find in the two-pole approximation

$$W(t)=D_S^Lt+(D_S^S-D_S^L)\tau_MF_1(t/\tau_M;\sigma,1)\ , \tag{8.15}$$

where the function $F_1(t/\tau_M;\sigma,1)$ is given by

$$F_1(t/\tau_M;\sigma,1)=1-\frac{1}{\tau_M}\frac{1}{v_+-v_-}\left[\frac{1}{v_+}w(v_+\sqrt{t})-\frac{1}{v_-}w(v_-\sqrt{t})\right]\ . \tag{8.16}$$

From Eq. (8.11) we find for short times

$$F_1(t/\tau_M;\sigma,1)=\frac{t}{\tau_M}-\frac{4\sigma}{3\sqrt{\pi}}\left[\frac{t}{\tau_M}\right]^{3/2}+O(t^2)\quad\text{as } t\to 0+\ , \tag{8.17}$$

and from Eq. (8.12) for long times

$$F_1(t/\tau_M;\sigma,1)=1-\frac{\sigma}{\sqrt{\pi}}\left[\frac{\tau_M}{t}\right]^{1/2}+O(t^{-1})\ . \tag{8.18}$$

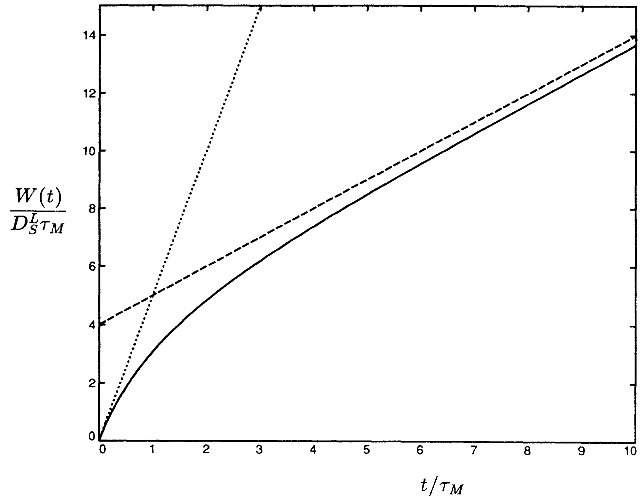

FIG. 3. Plot of the normalized mean-square displacement $W(t)/D_S^L\tau_M$ as a function of t/τ_M for $D_S^L/D_S^S=0.2$ and $\sigma=0.4$. The initial slope $D_S^S/D_S^L=5$ and the asymptote $4+t/\tau_M$ are indicated.

In Fig. 3 we plot the function $W(t)/D_S^L\tau_M$ for the values $D_S^L/D_S^S=0.2$ and $\sigma=0.4$. In the analysis of experimental data the time scale τ_M may be found from the intersection of the asymptote with the ordinate axis. One may find the parameter σ by fitting the intermediate and long-time behavior.

In Fig. 4 we demonstrate that the two-pole approximation may be used successfully in a comparison with experiment. We plot the ratio $W(t)/D_S^St$, as obtained in Brownian-dynamics simulations by Gaylor *et al.* [13], and compare with our theoretical curve, as given by Eq.

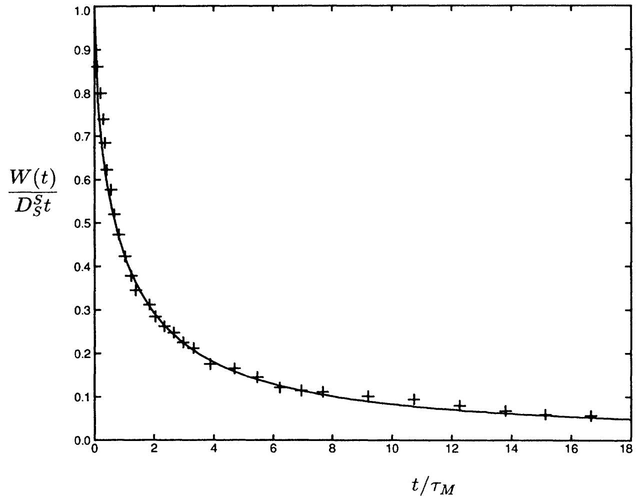

FIG. 4. Plot of the ratio $W(t)/D_S^St$ as a function of t/τ_M as obtained in Brownian-dynamics simulations [13]. We have used the data shown in Fig. 12(c) of Ref. [12]. We compare with the theoretical curve, as given by Eq. (8.15), for $D_S^L/D_S^S=0.29$, $\tau_M=0.3$ msec, and $\sigma=0.86$.

(8.15). From the data we find the ratio $D_S^L/D_S^S=0.29$ and the time scale $\tau_M=0.3$ msec. The theoretical curve is plotted for these values and for parameter $\sigma=0.86$. The agreement with the data is excellent. An earlier theory of Nägele *et al.* [12], in which the memory function was approximated by a single exponential, was not successful in the description of the time-dependent self-diffusion coefficient.

IX. DISCUSSION

In this paper we have discussed the time-dependent self-diffusion coefficient $D_S(t)$, as defined in terms of the mean-square displacement of a selected particle by Eq. (2.15). Guided by the exact expression for the Fourier transform of the memory function for a dilute suspension of hard spheres without hydrodynamic interactions, we have conjectured similar behavior in more general cases. Specifically, we have assumed that the Fourier transform of the memory function for self-diffusion may be represented as a meromorphic function of the square root of the frequency and is well approximated by an expression with a small number of poles. We have shown that a two-pole approximation leads to an accurate description of Brownian-dynamics data. We suggest that experimentalists analyze their data in terms of the representation proposed above.

From a theoretical point of view, our conjecture may be verified by comparison with exact calculations on dilute systems. The details of such a comparison will be presented elsewhere. It is of particular interest to study the dependence of the memory function on the parameters of the system, such as density and pair interaction. Our conclusion is that the theory presented above provides a suitable framework for the analysis of the time dependence of self-diffusion. We expect that the theory may be also applied to other transport properties of interacting Brownian particles.

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