Self-diffusion of interacting Brownian particles in a plane

B Cichocki† and B U Felderhof

Institut für Theoretische Physik A, RWTH Aachen, Templergraben 55, 52056 Aachen, Germany

Abstract. We study self-diffusion of interacting Brownian particles confined to a plane. The system is idealized as a set of discs interacting via a pair potential. We analyse the time-dependent mean square displacement of a selected disc. For long times the displacement grows linearly with time, and this defines the long-time self-diffusion coefficient, but there are important logarithmic correction terms. We present an exact expression for the time-dependent displacement in a semidilute suspension of discs with square-well interaction. An approximate expression is proposed which should be valid at any concentration for systems with repulsive interaction. The approximation is characterized by a small number of parameters which in principle can be determined from experimental or computer-simulation data.

1. Introduction

Transport phenomena in two dimensions show characteristic differences from their three-dimensional counterparts. In this paper we study Brownian motion of particles confined to a plane. Experimentally this may correspond to diffusion of particles adsorbed on a surface, or to Brownian particles immersed in a fluid bounded by two parallel plates [1, 2]. Computer simulations have been performed on systems of hard discs [3], and on discs with Yukawa interaction [4].

We study in particular the time-dependent self-diffusion of a selected particle. The mean square displacement grows linearly with time at long times, and this defines the long-time self-diffusion coefficient D_S^L, but in two dimensions there are characteristic logarithmic correction terms. The corrections are appreciable, and make it difficult to determine D_S^L from the data. A theoretical expression is needed which allows reliable determination of D_S^L from data in the intermediate-time regime. A study of the exact expression for the mean square displacement derived by Ackerson and Fleishman [5] for a semidilute suspension of hard discs reveals the nature of the correction terms to the long-time asymptote. We extend the analysis to a semidilute suspension of discs with square-well interaction to see how the time dependence depends on the nature of the interaction.

We show for a semidilute suspension with general pair interaction that the important parameters characterizing the mean square displacement may be determined from the steady-state density perturbation created by a constant force acting on the selected particle. The same method works at higher concentration, if a diffusion-type evolution equation for the pair distribution function is adopted. We propose an approximate expression for the Laplace transform of the memory function involving the same parameters. A

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† On leave of absence from: Institute of Theoretical Physics, Warsaw University, Hoza 69, 00-618 Warsaw, Poland and Institute of Fundamental Technological Research, Polish Academy of Sciences, Świętokrzyska 21, 00-049 Warsaw, Poland.

comparison with the exact result for a semidilute suspension with square-step interaction shows that the approximation works well for systems with repulsive interaction. The approximation captures the essential features of the time dependence of Brownian motion in two dimensions. It should describe the mean square displacement over a wide time range for systems at any concentration.

2. Self-diffusion coefficient

We consider N identical circular discs of radius a performing Brownian motion in the plane. A wall potential confines the discs to an area of size Σ. The bare diffusion coefficient of a disc is denoted as D_0. The diffusion is hindered due to interactions between the discs. In the simplest case there is a hard interaction potential preventing the discs from overlaping. More generally, we consider a pair potential $v(r)$ depending only on the distance r between the two centres. If R_i denotes the position of the centre of the ith disc, then the configuration of the whole set may be described by the $2N$-dimensional vector $X = (R_1, \ldots, R_N)$. The dynamical evolution of the configuration X is assumed to be described by a time-dependent probability distribution $P(X, t)$, which obeys the generalized Smoluchowski equation [6]. In the course of time the distribution function $P(X, t)$ tends to the equilibrium distribution

$$P_{eq}(X) = \exp[-\beta \, \Phi(X)]/Z(\beta) \qquad (1)$$

where $\beta = 1/k_B T$, the potential $\Phi(X)$ incorporates both the wall potential and the pair interactions, and the partition function $Z(\beta)$ normalizes the distribution to unity. We shall consider self-diffusion of a selected disc in the thermodynamic limit $N \to \infty$, $\Sigma \to \infty$ at constant $n = N/\Sigma$.

The self-diffusion coefficient is defined from the mean square displacement of the selected particle, labelled 1,

$$W(t) = \tfrac{1}{4} \langle [R_1(t) - R_1(0)]^2 \rangle \qquad (2)$$

where the time dependence of the position R_1 is governed by the adjoint Smoluchowski operator $\mathcal{L}$ such that $R_1(t) = (\exp \mathcal{L}t)R_1(0)$, with $R_1(0) = R_1$, and the angle brackets denote an average over the equilibrium distribution (1). The thermodynamic limit is implied. The time-dependent diffusion coefficient $D_S(t)$ is defined as the derivative

$$D_S(t) = \frac{\mathrm{d}W(t)}{\mathrm{d}t}. \qquad (3)$$

It may be expressed as

$$D_S(t) = D_S^S + \int_0^t M_S(t') \, \mathrm{d}t' \qquad (4)$$

where D_S^S is the short-time diffusion coefficient and $M_S(t)$ is the memory function. For the model under consideration, which does not include 'hydrodynamic interactions', the short-time coefficient D_S^S simply equals the bare diffusion coefficient D_0. The memory function $M_S(t)$ arises due to the interactions between discs.

The time dependence of the diffusion coefficient $D_S(t)$ is dominated by the behaviour at long times. It is therefore more convenient to write

$$D_S(t) = D_S^L + \mu_S(t) \qquad (5)$$

where D_S^L is the long-time self-diffusion coefficient, and the relaxation function $\mu_S(t)$ is related to the memory function by

$$\mu_S(t) = - \int_t^\infty M_S(t') \, \mathrm{d}t'. \qquad (6)$$

The long-time coefficient D_S^L may in principle be obtained from a steady-state calculation, in which one considers the linear response to a constant force applied to the selected disc. The relaxation function $\mu_S(t)$ describes the relaxation to the steady state. In two-dimensional diffusion the relaxation is extremely slow.

The mean square displacement may be expressed as

$$W(t) = D_S^L t + \int_0^t \mu_S(t')\, dt'. \tag{7}$$

It follows from the exact calculation by Ackerson and Fleishman [5] for a semidilute system of hard discs that for long times the relaxation function $\mu_S(t)$ decays as $1/t$. The mean square displacement therefore behaves for large t as

$$W(t) = D_S^L t + (D_S^S - D_S^L)\tau_L \ln(t/\tau_M) + O(1) \tag{8}$$

where τ_L and τ_M are typical time scales. The $1/t$ singularity of the relaxation function is characteristic of Brownian motion in two dimensions. Therefore the behaviour (8) holds also for a system of hard discs at any concentration, as well as for systems with different interactions. The coefficient D_S^L and the relaxation times τ_L and τ_M depend of course on the nature of the interactions, and on the concentration.

3. Analysis of mean square displacement data

In the following we shall derive theoretical expressions for the coefficient D_S^L and the time scales τ_L and τ_M for semidilute dispersions of discs. In this section we discuss how the coefficient D_S^L and the time scales τ_L and τ_M may be determined from data obtained in experiment or simulation.

The theoretical expression (8) shows that the approach of the ratio

$$\tilde{D}_S(t) = \frac{W(t)}{t} \tag{9}$$

to the long-time value D_S^L is extremely slow, with a long-time tail proportional to $\ln t/t$. Therefore in experiments and in simulations it will be difficult to determine the coefficient D_S^L from the value of $\tilde{D}_S(t)$ at long times. However, both the long-time diffusion coefficient D_S^L and the time scales τ_L and τ_M can be determined from the behaviour at intermediate times, if we assume that the time dependence of the mean square displacement is indeed dominated by the long-time expression (8). A similar analysis was used in three dimensions by Cichocki and Hinsen [7].

We choose a fixed intermediate time t_1. It follows from equation (8) that the behaviour of the ratio $R(t, t_1)$, defined by

$$R(t, t_1) = \frac{W(t) - W(t_1)}{t - t_1} \tag{10}$$

is given by

$$R(t, t_1) \simeq D_S^L + (D_S^S - D_S^L)\tau_L \frac{\ln(t/t_1)}{t - t_1}. \tag{11}$$

This suggests that if the ratio $R(t, t_1)$, as found from experiment or simulation, is plotted as a function of the variable

$$l = \frac{\ln(t/t_1)}{t - t_1} \tag{12}$$

then the graph should tend to a straight line as l tends to zero. The intercept of the asymptote with the ordinate axis gives the long-time diffusion coefficient D_S^L. The slope of the asymptote gives the time scale τ_L. We assume that the short-time self-diffusion coefficient D_S^S either equals D_0, as valid in the absence of hydrodynamic interactions, or is calculated or measured separately. Finally the time scale τ_M in principle can be determined from the asymptotic constant value of the difference

$$\Delta(t) = W(t) - D_S^L t - (D_S^S - D_S^L)\tau_L \ln t. \tag{13}$$

However, this requires very good data.

We demonstrate for a semidilute system of hard discs that the long-time expression (8) provides a good approximation over a wide range. To first order in density, the long-time diffusion coefficient of hard discs is given by [5]

$$D_S^L = D_0[1 - 2\phi] \tag{14}$$

where $\phi = \pi na^2$ is the fraction of the plane covered by discs. From the Laplace transform of the diffusion coefficient $D_S(t)$, as given by Ackerson and Fleishman [5], we find by use of a Tauberian theorem [8] the time scale $\tau_L = \tau_0$, where $\tau_0 = a^2/D_0$ is the diffusion time for a single disc. Correspondingly the relaxation function has asymptotic behaviour $\mu_S(t) \simeq 2a^2\phi/t$ for large t. The function decays to zero from the initial value $\mu_S(0) = 2\phi D_0$. Ackerson and Fleishman's conjecture [5] concerning the long-time behaviour was incorrect. In figure 1 we plot the reduced function $\gamma_S(\tau) = \mu_S(t)/2\phi D_0$ as a function of $\tau = t/\tau_0$, and compare with the long-time behaviour $\gamma_S(\tau) \simeq 1/\tau$. It is evident that the exact function, as calculated from the inverse Laplace transform, rapidly tends to the long-time behaviour. In figure 2 we plot the ratio $R(t, t_1)$, defined in equation (10), for $\phi = 0.2$ and $t_1 = 10\tau_0$, as a function of the variable l, defined in equation (12), and compare with the asymptotic behaviour given by equation (11). It is evident that the diffusion coefficient D_S^L and the time scale τ_L can be determined accurately from the plot.   We remark that the long-time behaviour of the function $\tilde{D}_S(t)$ is given incorrectly
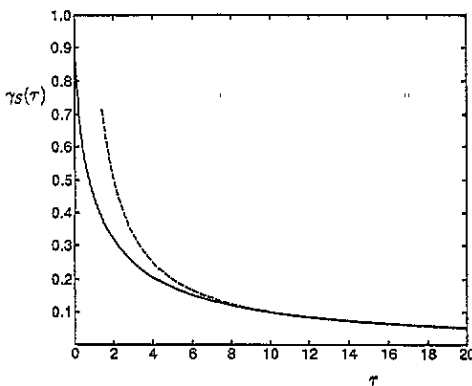

Figure 1. Reduced relaxation function $\gamma_S(\tau) = \mu_S(t)/2\phi D_0$ as a function of $\tau = D_0 t/a^2$ for a semidilute dispersion of hard discs of radius a and diffusion coefficient D_0 at area fraction ϕ. We compare the exact function (full curve) with the long-time behaviour $\gamma_S(\tau) \simeq 1/\tau$ (dashed curve).
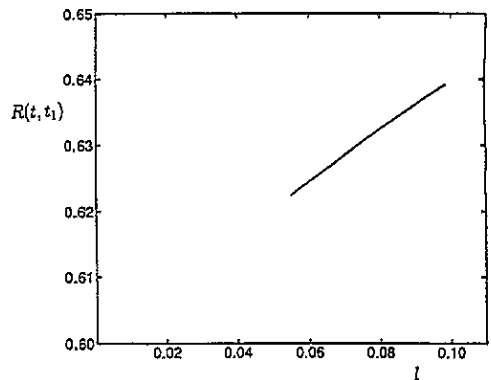
Figure 2. Plot of the ratio $R(t, t_1)$, defined in equation (10), as a function of the variable l, defined in equation (12), for a semidilute dispersion of hard discs at area fraction $\phi = 0.2$ and for $t_1 = 10\tau_0$.

in equation (21) of [4]. The fit to the simulation data for the two-dimensional Yukawa fluid should be based on equation (8), rather than the expression (22) of Löwen [4].

4. Laplace transform

In this section we indicate how the coefficient D_S^L and the time scales τ_L and τ_M are related to properties of the Laplace transform of the relaxation function. The long-time behaviour of the relaxation function corresponds to the low-frequency behaviour of its one-sided Fourier transform

$$\hat{\mu}_S(\omega) = \int_0^\infty e^{i\omega t} \mu_S(t) \, dt. \tag{15}$$

equation (8) implies the limiting behaviour

$$\lim_{t\to\infty} \int_0^{t'} \left[\mu_S(t') - (D_S^S - D_S^L)\frac{\tau_L}{t' + \tau_M} \right] dt' = 0. \tag{16}$$

Inserting a factor $\exp(i\omega t')$ with $\omega = 0+$ in the integrand, and interchanging limits we obtain

$$\lim_{\omega\to 0} \left[\hat{\mu}_S(\omega) - (D_S^S - D_S^L)\tau_L \exp(-i\omega\tau_M)E_1(-i\omega\tau_M) \right] = 0 \tag{17}$$

where $E_1(z)$ is the exponential integral [9]. This implies the low-frequency behaviour

$$\hat{\mu}_S(\omega) = -(D_S^S - D_S^L)\tau_L[\ln(-i\omega\tau_M) + \gamma] + O(1) \tag{18}$$

where γ is Euler's constant.

We write the relaxation function as

$$\mu_S(t) = (D_S^S - D_S^L)\gamma_S(t/\tau_0). \tag{19}$$

It follows from the general properties of the Smoluchowski equation that the dimensionless function $\gamma_S(\tau)$ may be expressed as

$$\gamma_S(\tau) = \int_0^\infty p_S(u)e^{-u\tau} \, du \tag{20}$$

with a positive spectral density $p_S(u)$ which has been normalized to

$$\int_0^\infty p_S(u) \, du = 1. \tag{21}$$

The relaxation function decays monotonically with time. Its Fourier transform may be expressed as

$$\hat{\mu}_S(\omega) = (D_S^S - D_S^L)\tau_0 \, \Gamma_S(z) \tag{22}$$

where $\Gamma_S(z)$ is the Laplace transform of the function $\gamma_S(\tau)$

$$\Gamma_S(z) = \int_0^\infty e^{-z\tau} \gamma_S(\tau) \, d\tau \tag{23}$$

with the variable $z = -i\omega\tau_0$. Substituting equation (20) we find that $\Gamma_S(z)$ is given by the Stieltjes integral

$$\Gamma_S(z) = \int_0^\infty \frac{p_S(u)}{u + z} \, du. \tag{24}$$

Thus $\Gamma_S(z)$ is analytic in the complex z plane with a branch cut along the negative real axis. From the normalization (21) it follows that

$$\Gamma_S(z) \simeq \frac{1}{z} \qquad \text{as } z \to \infty. \tag{25}$$

From the low-frequency behaviour (18) it follows that $\Gamma_S(z)$ behaves for small z as

$$\Gamma_S(z) \simeq -C_L \ln z \qquad \text{as } z \to 0 \tag{26}$$

where the coefficient C_L is defined by

$$\tau_L = C_L \tau_0. \tag{27}$$

Correspondingly the spectral density tends to a constant for small u

$$p_S(0+) = C_L. \tag{28}$$

Hence it follows that the coefficient C_L is always positive. From the Tauberian theorem [8] it follows that the relaxation function $\gamma_S(\tau)$ decays as C_L/τ for large τ.

More precisely, equation (18) shows that for small z

$$\Gamma_S(z) = -C_L[\ln(C_M z) + \gamma] + O(1) \tag{29}$$

with the coefficient C_M defined by $\tau_M = C_M \tau_0$. Using the identity

$$\int_0^\infty \frac{e^{-C_M u}}{u + z} \, du = e^{C_M z} E_1(C_M z) \tag{30}$$

and the expansion of the exponential integral [9], we find from equations (24) and (29) the sum rule

$$\int_0^\infty \frac{p(u) - C_L \exp(-C_M u)}{u} \, du = 0. \tag{31}$$

The expression (29) allows determination of the coefficients C_L and C_M from the behaviour of $\Gamma_S(z)$ for small z.

5. Semidilute suspension with square-well interaction

It is of interest to investigate how the coefficients D_S^L, C_L, and C_M depend on the nature of the interactions. For a semidilute suspension of discs with hard core and square-well interactions these quantities, as well as the complete spectral density $p_S(u)$, can be calculated explicitly. The calculation is quite analogous to that for spheres [10].

The general expression for the memory function is [11, 12]

$$\hat{M}_S(\omega) = \tfrac{1}{2} \langle U_1' \cdot (i\omega + \mathcal{L})^{-1} U_1' \rangle \tag{32}$$

where $\mathcal{L}$ is the adjoint of the Smoluchowski operator, and $U_1' = \mathcal{L} R_1$ is the velocity of the selected particle on the Smoluchowski time scale [13]. To first order, in density we write

$$\hat{M}_S(\omega) = D_0 \alpha_S(\omega) \phi \tag{33}$$

with a dimensionless coefficient $\alpha_S(\omega)$ which may be found from the solution of the pair Smoluchowski equation. The corresponding expression for the Laplace transform $\Gamma_S(z)$ is

$$\Gamma_S(z) = \frac{\alpha_S(\omega) - \alpha_S(0)}{i\omega \tau_0 \alpha_S(0)}. \tag{34}$$

The coefficient $\alpha_S(\omega)$ may be evaluated from a one-dimensional integral

$$\alpha_S(\omega) = \tfrac{1}{2} \int_0^\infty x g f U \, dx \tag{35}$$

where $x = r/2a$ is the dimensionless pair distance, and $g(x)$ is the low-density radial distribution function

$$g(x) = \exp[-\beta\, v(2ax)] \tag{36}$$

for interaction potential $v(r)$. Furthermore, $f(x)$ is the radial part of the perturbed pair distribution function, and $U(x)$ is a given function expressed in terms of the interactions. In the absence of hydrodynamic interactions $f(x)$ satisfies the radial differential equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(xg\,\frac{\mathrm{d}f}{\mathrm{d}x}\right) - g\,\frac{f}{x} - \alpha^2 xgf = 2x\,\frac{\mathrm{d}g}{\mathrm{d}x} \tag{37}$$

with the variable

$$\alpha^2 = -2i\omega a^2/D_0 = -2i\omega\tau_0. \tag{38}$$

For vanishing hydrodynamic interaction the function $U(x)$ is given by

$$U(x) = \frac{2}{g}\,\frac{\mathrm{d}g}{\mathrm{d}x}. \tag{39}$$

In the following we consider specifically the square-well potential

$$v(r) = \begin{cases} \infty & \text{for } 0 < r < 2a \\ v_1 & \text{for } 2a < r < 2b \\ 0 & \text{for } 2b < r. \end{cases} \tag{40}$$

The depth $-v_1$ may be positive as well as negative. We shall use the dimensionless parameters

$$\epsilon = \exp(-\beta\, v_1) \qquad x_1 = b/a. \tag{41}$$

The function $g(x)$ is constant on each of the intervals $1 < x < x_1$ and $x_1 < x < \infty$, so that the coefficient $\alpha_S(\omega)$ is given by

$$\alpha_S(\omega) = \epsilon f(1+) - (\epsilon - 1)x_1 f(x_1). \tag{42}$$

On each interval the right-hand side of equation (37) vanishes. The zero-flux condition at $r = 2a$ corresponds to the boundary condition $f'(1+) = 2$. At $x = x_1$ the function $f(x)$ must satisfy the jump conditions

$$\begin{aligned} f(x_1+) &= f(x_1-) \\ -2 + f'(x_1+) &= -2\epsilon + \epsilon f'(x_1-). \end{aligned} \tag{43}$$

Also it must tend to zero at infinity.

We consider first the case of hard discs. Then $\epsilon = 1$ and the solution is [5]

$$f(x) = 2\frac{K_1(\alpha x)}{\alpha K_1'(\alpha)} \qquad 1 < x < \infty \qquad \text{(HD)} \tag{44}$$

where $K_1(z)$ is a modified Bessel function [9]. We define α such that $\alpha = (1-i)(\omega a^2/D_0)^{1/2}$ for $\omega > 0$. The coefficient $\alpha_S(\omega)$ is

$$\alpha_S(\omega) = 2\frac{K_1(\alpha)}{\alpha K_1'(\alpha)} \qquad \text{(HD)}. \tag{45}$$

In the limit of zero frequency this yields $\alpha_S(0) = -2$. From equation (34) we find for the Laplace transform $\Gamma_S(z)$

$$\Gamma_S(z) = \frac{2K_0(\alpha)}{\alpha^2 K_0(\alpha) + \alpha K_1(\alpha)} \qquad \text{(HD)}. \tag{46}$$

At low frequency $\Gamma_S(z) \simeq -2\ln\alpha$, which confirms the value $C_L = 1$ by comparison with equation (26), since $z = \frac{1}{2}\alpha^2$. In addition we find $C_M = \frac{1}{2}\exp(\gamma) = 0.89054$. Furthermore, it is evident that $\Gamma_S(z) \simeq 2/\alpha^2$ for large z, in agreement with equation (25). The spectral density $p_S(u)$, corresponding to the Laplace transform $\Gamma_S(z)$ according to equation (24), is given by

$$p_S(u) = \frac{1}{\pi^2 u^2 |Z(v)|^2} \qquad \text{(HD)} \tag{47}$$

with the abbreviations

$$Z(v) = J_1'(v) + i\, Y_1'(v) \qquad v = \sqrt{2u} \tag{48}$$

where $J_1(v)$ and $Y_1(v)$ are Bessel functions. In figure 3 we plot the spectral density as a function of $\log_{10} u$. In the limit of zero frequency the distribution function becomes

$$f^{(0)}(x) = -\frac{2}{x} \qquad x > 1 \qquad \text{(HD)} \tag{49}$$

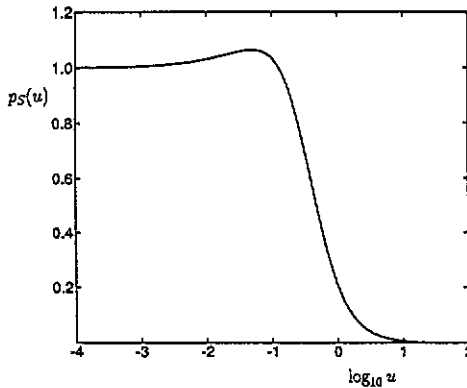which shows an extremely slow decay with distance.

Figure 3. Plot of the spectral density $p_S(u)$ as a function of $\log_{10} u$ for a semidilute dispersion of hard discs.
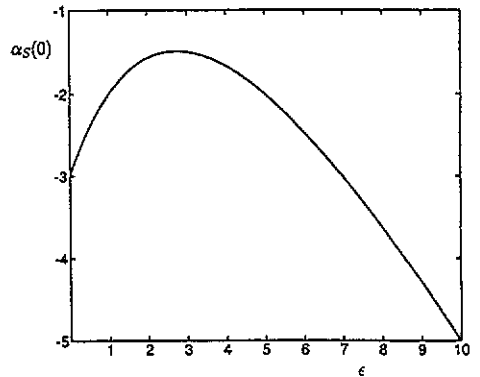
Figure 4. Plot of the coefficient $\alpha_S(0)$, as given by equation (89), for a semidilute dispersion of discs with square-well interaction. We plot $\alpha_S(0)$ as a function of the parameter ϵ for fixed $\rho = 1.5$.

In the more general case of a square-well potential with $v_1 \neq 0$ we can write the solution of equation (37) in the form

$$\begin{aligned}
f(x) &= A_1 I_1(\alpha x) + B_1 K_1(\alpha x) & \text{for } 1 < x < x_1 \\
f(x) &= B_2 K_1(\alpha x) & \text{for } x_1 < x < \infty
\end{aligned} \tag{50}$$

where $I_1(z)$ is the regular modified Bessel function. The coefficients are found from the boundary condition $f'(1+) = 2$ and the jump conditions (43). The coefficient $\alpha_S(\omega)$ is written conveniently with the parameter

$$\zeta = \frac{1}{\epsilon} - 1. \tag{51}$$

The explicit expression reads

$$\alpha_S(\omega) = 2\epsilon\, \frac{P + \zeta\, Q + \zeta^2 R}{S + \zeta\, T} \tag{52}$$

with coefficients

$$P(\alpha) = K_1(\alpha)$$

$$Q(\alpha, x_1) = 2x_1 K_1(\alpha x_1) + \alpha x_1 K_1'(\alpha x_1)[I_1(\alpha)K_1(\alpha x_1) - I_1(\alpha x_1)K_1(\alpha)]$$

$$R(\alpha, x_1) = \alpha x_1^2 K_1(\alpha x_1)[I_1'(\alpha)K_1(\alpha x_1) - I_1(\alpha x_1)K_1'(\alpha)] \tag{53}$$

$$S(\alpha) = \alpha K_1'(\alpha)$$

$$T(\alpha, x_1) = \alpha^2 x_1 K_1'(\alpha x_1)[I_1'(\alpha)K_1(\alpha x_1) - I_1(\alpha x_1)K_1'(\alpha)].$$

Hence one finds the spectral density

$$p_S(u) = \frac{-2}{\pi^2 u^2 \alpha_S(0)} \frac{[1 + \zeta Y(v, x_1)]^2}{|Z(v) + \zeta Y(v, x_1) Z(vx_1)|^2} \tag{54}$$

with the notation of equation (48) and the abbreviation

$$Y(v, x_1) = \tfrac{1}{2}\pi v x_1 [J_1(vx_1)Y_1'(v) - J_1'(v)Y_1(vx_1)]. \tag{55}$$

The coefficient $\alpha_S(0)$ is always negative. For hard discs it takes the value -2, and in the case of a square well its value can be found from equation (52). The long-time diffusion coefficient is given to first order in density by

$$D_S^L = D_0[1 + \alpha_S(0)\phi]. \tag{56}$$

In the next two sections we derive compact expressions for the coefficients $\alpha_S(0)$, C_L, and C_M.

6. Steady-state distribution

We have shown previously [14] that for semidilute suspensions of spheres the important parameters characterizing the relaxation process can be obtained from the steady-state pair distribution function. Here we show that the same is true for suspensions of discs. The method allows determination of the parameters also in dense suspensions, on the basis of an approximate calculation of the steady-state pair distribution.

The radial differential equation (37) may be written in the abbreviated form

$$[\mathcal{L}_x - \alpha^2]f = U \tag{57}$$

with the operator

$$\mathcal{L}_x = \frac{1}{xg}\left[\frac{\mathrm{d}}{\mathrm{d}x} xg \frac{\mathrm{d}}{\mathrm{d}x} - \frac{g}{x}\right]. \tag{58}$$

From equation (39) it follows that the function $U(x)$ is given by

$$U(x) = 2\mathcal{L}_x x. \tag{59}$$

Introducing the scalar product

$$(A|B) = \int_0^\infty xg A^* B \, \mathrm{d}x \tag{60}$$

we may write the coefficient $\alpha_S(\omega)$ formally as

$$\alpha_S(\omega) = \tfrac{1}{2}\left(U\Big|\frac{1}{\mathcal{L}_x - \alpha^2}\Big|U\right). \tag{61}$$

The operator $\mathcal{L}_x$ is Hermitian with respect to the scalar product (60).

The steady-state coefficient $\alpha_S(0)$ may be calculated from the solution $f^{(0)}(x)$ of the equation

$$\mathcal{L}_x f^{(0)} = U \tag{62}$$

and the corresponding integral (35). As in the three-dimensional case, equation (62) can be related to a dielectric problem [12], and the coefficient $\alpha_S(0)$ can be calculated from the corresponding electric polarizability $\alpha_p = \beta_p a^2$ according to the relation

$$\alpha_S(0) = \beta_p + J_S \tag{63}$$

where β_p is twice the coefficient of the asymptotic decay of the steady-state distribution

$$f^{(0)}(x) \simeq \frac{\beta_p}{2x} \qquad \text{as } x \to \infty \tag{64}$$

and J_S is given by the integral

$$J_S = \int_0^\infty x^2 g U \, dx = 2(x|\mathcal{L}_x|x). \tag{65}$$

It follows from the long range of the distribution function that the integral $(U|\mathcal{L}_x^{-2}|U)$ diverges. This implies that the coefficient $\alpha_S(\omega)$, as given by equation (61), is non-analytic in α^2. The explicit form equation (44) for hard discs suggests that we expand the solution $f(x, \alpha)$ of equation (37) as

$$f(x, \alpha) = f^{(0)}(x) + f^{(1)}(x)\alpha^2 \ln \alpha + f^{(2)}(x)\alpha^2 + O((\alpha^2 \ln \alpha)^2). \tag{66}$$

It follows from equation (35) that the coefficient $\alpha_S(\omega)$ has the corresponding expansion

$$\alpha_S(\omega) = \alpha_S(0) + \alpha_S^{(1)} \alpha^2 \ln \alpha + \alpha_S^{(2)} \alpha^2 + O((\alpha^2 \ln \alpha)^2). \tag{67}$$

The coefficient $\alpha_S^{(1)}$ may be related to the time τ_L, and the coefficient $\alpha_S^{(2)}$ may be related to the time τ_M. From equations (29) and (34) we find

$$C_L = \frac{\alpha_S^{(1)}}{\alpha_S(0)} \qquad C_M = 2 \exp\left[2\frac{\alpha_S^{(2)}}{\alpha_S^{(1)}} - \gamma\right]. \tag{68}$$

It follows from equation (59) that the solution $f^{(0)}(x)$ of the static equation (62) may be related to the solution $f_0(x)$ of the homogeneous equation

$$\mathcal{L}_x f_0 = 0 \tag{69}$$

according to

$$f^{(0)}(x) = f_0(x) + 2x. \tag{70}$$

In order that $f^{(0)}(x)$ vanish at infinity we must select the solution of equation (69) that tends to $-2x$ at large x. Since $g(x)$ tends to unity at large x the function $f_0(x)$ has the asymptotic behaviour

$$f_0(x) \simeq -2x + \frac{\beta_p}{2x} \qquad \text{as } x \to \infty \tag{71}$$

in agreement with equation (64).

We assume for simplicity that the radial distribution $g(x)$ equals unity beyond a cut-off distance x_c, which may be arbitrarily large. Then the solution of equation (37) takes the form

$$f(x, \alpha) = \alpha\gamma(\alpha)K_1(\alpha x) \qquad \text{for } x > x_c \tag{72}$$

with a coefficient $\gamma(\alpha)$ which has the expansion

$$\gamma(\alpha) = \gamma^{(0)} + \gamma^{(1)}\alpha^2 \ln\alpha + \gamma^{(2)}\alpha^2 + O((\alpha^2 \ln\alpha)^2). \tag{73}$$

By comparison with equation (66) we see that beyond the cut-off distance

$$f^{(0)}(x) = \frac{\gamma^{(0)}}{x} \tag{74}$$

$$f^{(1)}(x) = \tfrac{1}{2}\gamma^{(0)}x + \frac{\gamma^{(1)}}{x} \tag{75}$$

$$f^{(2)}(x) = \frac{\gamma^{(2)}}{x} + \tfrac{1}{2}\gamma^{(0)}[x\ln x + J_E x] \qquad \text{for } x > x_c \tag{76}$$

where

$$J_E = \gamma - \tfrac{1}{2} - \ln 2 = -0.61593. \tag{77}$$

By comparison of equation (74) with equation (57) we find

$$\gamma^{(0)} = \tfrac{1}{2}\beta_p. \tag{78}$$

By substitution of expansion (66) in equation (57) we find that $f^{(1)}(x)$ and $f^{(2)}(x)$ must satisfy

$$\mathcal{L}_x f^{(1)} = 0 \qquad \mathcal{L}_x f^{(2)} = f^{(0)}. \tag{79}$$

By comparison of equation (75) with equation (71) we find

$$\gamma^{(1)} = -\tfrac{1}{16}\beta_p^2. \tag{80}$$

The function $f^{(1)}(x)$ is given everywhere by

$$f^{(1)}(x) = -\tfrac{1}{8}\beta_p f_0(x). \tag{81}$$

By substitution with equation (35) and use of equations (63) and (70) we find for the coefficient $\alpha_S^{(1)}$

$$\alpha_S^{(1)} = -\tfrac{1}{8}\beta_p^2. \tag{82}$$

It follows from equations (68), (77), and (82) that the amplitude C_L of the long-time tail C_L/τ of the relaxation function is directly related to the amplitude of the long-range tail of the steady-state pair distribution.

Next we consider the coefficient $\alpha_S^{(2)}$. Let $h(x)$ be the solution of the inhomogeneous equation

$$\mathcal{L}_x h = f^{(0)} \tag{83}$$

which satisfies the boundary condition $h'(1+) = 0$ and which behaves as

$$h(x) = \tfrac{1}{2}\gamma^{(0)}x\ln x + \frac{h_1}{x} \qquad \text{for } x > x_c. \tag{84}$$

Then the solution $f^{(2)}(x)$ takes the form

$$f^{(2)}(x) = h(x) + C_0 f_0(x). \tag{85}$$

By comparison with equation (76) we find the coefficients

$$\gamma^{(2)} = h_1 + \tfrac{1}{2}\beta_p C_0$$
$$C_0 = -\tfrac{1}{4}\gamma^{(0)} J_E. \tag{86}$$

By substitution of $f^{(2)}(x)$ into equation (35) we finally find the coefficient $\alpha_S^{(2)}$.

7. Coefficients for square-well potential

The coefficients $\alpha_S(0)$, C_L, and C_M can be evaluated for the square-well potential from the explicit expression for the coefficient $\alpha_S(\omega)$ given in equations (52) and (53). However, it is simpler to use the formalism developed in the preceding section.

Thus we consider again the potential $v(r)$ given by equation (40), characterized by parameters ϵ and x_1 defined in equation (41). For the reduced electric polarizability one finds

$$\beta_p = 4\rho \frac{(\rho - 1)(\epsilon - 1) - 2}{(\rho - 1)(\epsilon - 1) + 2\rho} \tag{87}$$

where $\rho = x_1^2$. The integral defined in equation (65) is given by

$$J_S = 2 - 2(\rho - 1)(\epsilon - 1). \tag{88}$$

Hence we find for the zero-frequency coefficient $\alpha_S(0)$ by use of equation (63)

$$\alpha_S(0) = -2 \frac{(\rho - 1)^2(\epsilon - 1)^2 - (\rho - 1)(\epsilon - 1) + 2\rho}{(\rho - 1)(\epsilon - 1) + 2\rho}. \tag{89}$$

The solution $f^{(0)}(x)$ is given explicitly by

$$f^{(0)} = \begin{cases} Ax + B/x & \text{for } 1 < x < x_1 \\ \beta_p/2x & \text{for } x_1 < x \end{cases} \tag{90}$$

with coefficients

$$A = 2\frac{(\rho - 1)(\epsilon - 1)}{(\rho - 1)(\epsilon - 1) + 2\rho} \qquad B = A - 2. \tag{91}$$

The solution $f^{(1)}(x)$ is given by equations (70) and (81). By use of equation (42) one confirms the value given by equation (82) for $\alpha_S^{(1)}$.

The solution $f^{(2)}(x)$ is given by

$$f^{(2)}(x) = \begin{cases} \frac{1}{8} Ax^3 + \frac{1}{2} Bx \ln x + Cx + D/x & \text{for } 1 < x < x_1 \\ \frac{1}{4} \beta_p[x \ln x + J_E x] + E/x & \text{for } x_1 < x \end{cases} \tag{92}$$

with additional coefficients

$$C = \frac{(\epsilon - 1)F + G + H}{(\rho - 1)(\epsilon - 1) + 2\rho} \qquad D = C + F \qquad E = \rho C + D - G \tag{93}$$

where

$$\begin{aligned} F &= \tfrac{7}{8} A - 1 \\ G &= \tfrac{1}{4} \rho \left[(\beta_p - 2B)\ln x_1 + \beta_p J_E - \tfrac{1}{2}\rho A \right] \\ H &= \tfrac{1}{4}\rho \left[(\beta_p - 2\epsilon B)(1 + \ln x_1) + \beta_p J_E - \tfrac{3}{2} \epsilon\rho A \right]. \end{aligned} \tag{94}$$

The coefficient $\alpha_S^{(2)}$ is given by

$$\alpha_S^{(2)} = \epsilon(A + 2C - 1) - (\epsilon - 1)\left[\tfrac{1}{4} \beta_p \rho(J_E + \ln x_1) + E \right]. \tag{95}$$

The coefficients C_L and C_M can now be calculated from equation (68).

To give an impression of the dependence of the coefficients D_S^L, C_L, C_M on the parameters ϵ and $\rho = x_1^2$ we present several plots. In figure 4 we plot $\alpha_S(0)$ as a function of ϵ for fixed $\rho = 1.5$. In figure 5 we plot $\alpha_S(0)$ as a function of ρ for fixed $\epsilon = 0.5$. In figure 6 we plot the coefficients C_L and C_M as functions of ϵ for fixed $x_1 = 1.5$. The peculiar behaviour near $\epsilon = 2.6$ is due to the vanishing of the reduced polarizability β_p at this point.
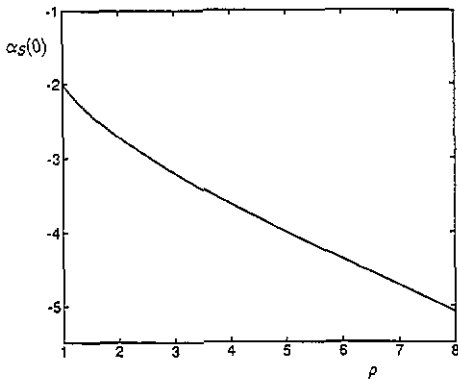
Figure 5. Plot of the coefficient $\alpha_S(0)$ as a function of ρ for a semidilute dispersion of discs with square-step interaction with height given by $\epsilon = 0.5$.
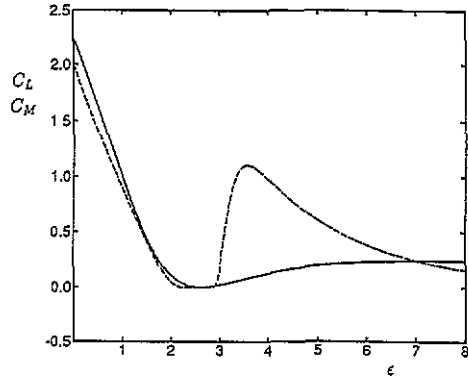
Figure 6. Plot of the coefficients C_L (full curve) and C_M (dashed curve) as functions of ϵ for fixed $x_1 = 1.5$ for a semidilute dispersion of discs with square-well interaction.
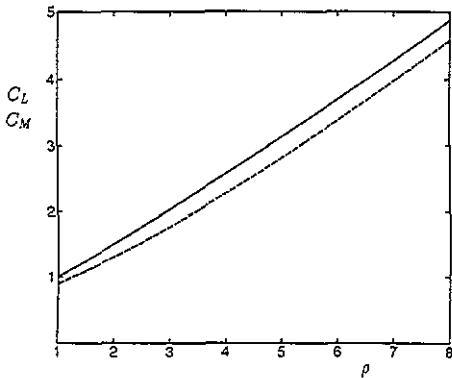

Figure 7. Plot of the coefficients C_L (full curve) and C_M (dashed curve) as functions of ρ for fixed $\epsilon = 0.5$.
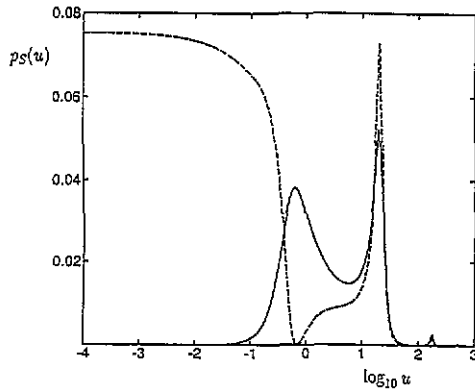
Figure 8. Plot of the spectral density $p_S(u)$ as a function of $\log_{10} u$ for $x_1 = 1.5$ and $\epsilon = 2.6$ (full curve) and $\epsilon = 3.5$ (dashed curve).

A similar resonance behaviour occurs in the case of spheres, and we have commented on it in [10]. In figure 7 we plot C_L and C_M as functions of ρ for fixed $\epsilon = 0.5$.

In figure 8 we plot the spectral density $p_S(u)$, as given by equation (54), for $x_1 = 1.5$ and the values $\epsilon = 2.6$ and $\epsilon = 3.5$, corresponding to a square well with depth near the resonance shown in figure 6. For a repulsive potential the behaviour of the spectral density is much simpler, as discussed in the next section.

8. Approximate relaxation function

The behaviour of the one-sided Fourier transform $\hat{\mu}_S(\omega)$ of the relaxation function at low frequency is given by equation (18). It is characterized by the two diffusion coefficients D_S^S and D_S^L, and by the two time scales τ_L and τ_M. The initial value of the relaxation function

is $\mu_S(0) = D_S^S - D_S^L$. Hence the limiting behaviour at high frequency is also known. We construct an approximate expression for the transform $\Gamma_S(z)$, which incorporates the behaviour both at low and at high frequency, based on the exact expression for a semidilute suspension of hard discs. We demonstrate the validity of the approximation by comparing the approximate spectral density with the exact one for a semidilute suspension of hard discs with square-step interaction.

The approximate expression for the Laplace transform $\Gamma_S(z)$ reads, in analogy to equation (46),

$$\Gamma_S(z) \simeq \frac{2C_L K_0(\mu\alpha)}{C_L\alpha^2 K_0(\mu\alpha) + \mu\alpha K_1(\mu\alpha)} \tag{96}$$

where the factor μ is related to the coefficient C_M by

$$\mu = (2C_M)^{1/2} \exp(-\tfrac{1}{2}\gamma). \tag{97}$$

This incorporates the low-frequency behaviour given by equations (18) and (22), and the high-frequency behaviour given by equation (25). The corresponding approximate expression for the spectral density is

$$p_S(u) \simeq \frac{4C_L}{\pi^2} \frac{1}{[2C_L u Y_0(\mu\, v) - \mu v Y_1(\mu\, v)]^2 + [2C_L u J_0(\mu\, v) - \mu v J_1(\mu\, v)]^2} \tag{98}$$

with $v = \sqrt{2u}$.

We compare the approximate spectral density with the exact one for a semidilute suspension of hard discs with square-step potential characterized by parameters $\epsilon = 0.5$, $x_1 = 1.5$. In figure 9 we plot the two spectra as functions of $\log_{10} u$. The values of the coefficients are $C_L = 1.6321$, $C_M = 1.4155$. The plot shows that equation (98) provides an excellent approximation to the spectral density. In figure 10 we show the relaxation function $\gamma_S(\tau)$, as calculated from the exact and approximate spectra according to equation (20). The agreement is again excellent.

We expect equation (96) to provide a good approximation to the actual relaxation function for systems of particles with repulsive potentials. The approximation is characterized by the two coefficients C_L and C_M. For systems with attractive interactions the spectral density is more complicated due to the appearance of an additional time scale, as can be shown on the example of a semidilute suspension with attractive square-well potential. The approximate expression (96) corresponds to the evolution of the pair distribution function described by the two-particle diffusion equation with an effective diffusion constant and an effective hard-core radius. Leegwater *et al* [15, 16] have argued that the two-particle diffusive evolution should provide a good model for memory effects in dense fluids or suspensions. Thus we expect that the expression (96), with appropriate values of the coefficients C_L and C_M, describes the self-diffusion process at any concentration.

9. Discussion

We have shown that the self-diffusion of interacting discs is characterized by a frequency-dependent self-diffusion coefficient with striking long-time memory effects. Correspondingly, the time-dependent mean square displacement of a selected disc behaves as shown in equation (8). The time scale τ_L of the logarithmic correction to the asymptote depends on the nature of the interactions. For a semidilute suspension the time scale τ_L is directly related to the amplitude of the long-range tail of the steady-state pair distribution function, as found from linear-response theory.
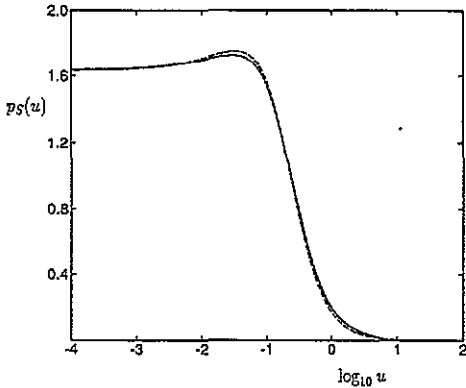
Figure 9. Plot of the spectral density $p_S(u)$ as a function of $\log_{10} u$ for a semidilute suspension of discs with square-step potential characterized by parameters $\epsilon = 0.5$ and $x_1 = 1.5$. We compare the exact spectral density given by equation (54) (full curve) with the approximate spectral density given by equation (98) (dashed curve).
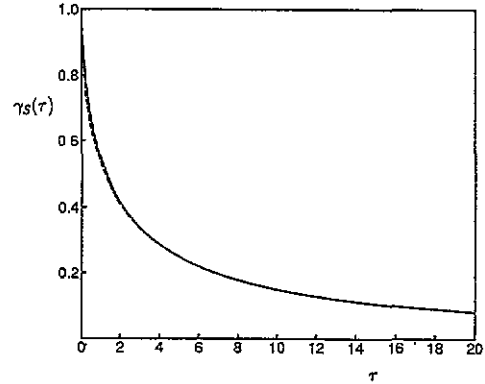
Figure 10. Plot of the relaxation function $\gamma_S(\tau)$, as a function of $\tau = t/\tau_0$, as calculated according to equation (21) from the exact spectral density (full curve) and the approximate one (dashed curve) shown in figure 9.

The long-time behaviour of the mean square displacement is characterized in more detail by a second time scale τ_M. We have shown that the time scales τ_L and τ_M may be used to construct an approximate expression for the relaxation function $\gamma_S(\tau)$ characterizing the memory effects. A comparison with an exact calculation for a semidilute suspension of hard discs interacting with an additional square potential shows that the approximation is excellent if the interaction potential is repulsive. In the approximation the mean square displacement is characterized by the short-time and long-time diffusion coefficients D_S^S and D_S^L, and by the two time scales τ_L and τ_M. We expect that the approximation provides an accurate description of the self-diffusion of particles with repulsive interactions at any concentration. The description should be valid over a wide time range, excluding only very short times. We suggest that the approximation be used to analyse computer simulations and experimental data.

The parameters of the approximation may be calculated from the steady state-distribution function, if a diffusion-type equation is assumed for the time evolution of the pair distribution [15, 16], by use of the formalism developed in section 6. The approximation should also be applicable in the presence of hydrodynamic interactions. The formalism of section 6 can be extended to include this case.

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