The dynamics of interacting Brownian particles

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Abstract. The dynamics of Brownian particles in dilute dispersions interacting through a long-range repulsive potential are considered. Emphasis is on interpretation of recent light scattering photon correlation measurements on such a system. It is shown that the *initial* decay of the temporal correlation function $F(K, \tau)$ of the Kth spatial Fourier component of particle number density is determined largely by free-particle Brownian motion. The initial decay rate of the *normalized* correlation function is given by $D_0 K^2 S(K)^{-1}$ (D_0 is the free-particle diffusion constant and $S(K)$ the static structure factor). The behaviour of $F(K, \tau)$ at larger correlation delay time τ is discussed briefly.

1. Introduction

Recent light scattering experiments (Brown *et al* 1975) have revealed some interesting dynamical effects in a system of Brownian particles interacting through a strong, repulsive, shielded Coulombic potential. The experiments were performed under conditions where the mean interparticle spacing was comparable to the wavelength of light. The static structure factor $S(K)$, determined from measurements of the angular dependence of the mean scattered intensity, showed peaks indicating considerable spatial ordering of the particles due to the interaction. From photon correlation measurements it was found that the effective diffusion coefficient, obtained from the *initial* decay of the *normalized* temporal correlation function of the Kth spatial Fourier component of the particle concentration, mirrored the behaviour of $S(K)$. That is, in the regions of the peaks of $S(K)$ the effective diffusion coefficient, and hence the initial decay rate of the concentration correlation function, was small whereas at small K, where $S(K) < 1$, the effective diffusion coefficient was large. The primary aim of this paper is to give a theoretical explanation of these observations.

We start by introducing the necessary notation and providing a more quantitative description of the experimental observations (for further details, see Brown *et al* 1975). Photon correlation spectroscopy provides a measurement of the modulus of the temporal autocorrelation function $G(K, \tau)$ of the scattered electrical field. Here τ is the correlation delay time and $K (\equiv (4\pi/\lambda) \sin(\theta/2))$ is the magnitude of the scattering vector K, λ being the wavelength of light in the system of interest and θ the scattering angle. For N identical spherical particles $|G(K, \tau)|$ is given by

$$|G(K, \tau)| = NM^2 BP(K)F(K, \tau) \tag{1}$$

where M is the particle mass, B is a constant for a given experiment, $P(K)$ is the single particle scattering factor and $F(K, \tau)$ is the correlation function of the Kth spatial

Fourier component of the concentration or particle number density:

$$F(K, \tau) \equiv N^{-1} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \exp[i\mathbf{K} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(t + \tau))] \rangle. \tag{2}$$

Here $\mathbf{r}_i(t)$ is the position of the centre of particle i at time t, and the angular brackets indicate an ensemble average. (In the neutron scattering literature $F(K, \tau)$ is frequently called the coherent intermediate scattering function.) From equation (1) it is seen that the normalized field correlation function $|g^{(1)}(K, \tau)|$, the quantity most easily obtained from photon correlation measurements, is equal to the normalized concentration correlation function:

$$|g^{(1)}(K, \tau)| \equiv \frac{|G(K, \tau)|}{G(K, 0)} = \frac{F(K, \tau)}{S(K)} \tag{3}$$

where we have used the definition of the static structure factor:

$$S(K) \equiv F(K, 0). \tag{4}$$

For non-interacting systems, $S(K) = 1$ and

$$F(K, \tau) = \exp(-D_0 K^2 \tau) \tag{5}$$

where, for spherical particles, the translational diffusion coefficient D_0 is given by the Stokes–Einstein relation:

$$D_0 = \frac{kT}{f} = \frac{kT}{6\pi\eta R}. \tag{6}$$

Here k is the Boltzmann constant, T the absolute temperature, f ($\equiv 6\pi\eta R$) the particle frictional coefficient, η the solvent viscosity and R the particle radius. The experimental observations of Brown *et al* for an interacting system are summarized in the equations:

$$\left. \frac{d|g^{(1)}(K, \tau)|}{d\tau} \right|_{\text{small } \tau} = -\bar{D}_{\text{eff}} K^2 \tag{7}$$

$$\bar{D}_{\text{eff}} \simeq \frac{D_0}{S(K)} \tag{8}$$

Here $\bar{D}_{\text{eff}}$ is the effective diffusion coefficient referred to above. The quantitative meaning of 'small τ' will be given in § 2.

In § 2, by making several apparently reasonable assumptions, the result of equations (7) and (8) is derived from equation (2). In particular it is assumed that the instantaneous velocity of a particle can be written as the sum of two components, a rapidly fluctuating Brownian component arising from particle–solvent molecule interactions, and a slowly fluctuating 'drift velocity' component due to the interparticle interactions. It is then shown that, to a good approximation, the initial decay of $F(K, \tau)$ is determined solely by the Brownian components of particle velocities. In § 3 the result is discussed. The relationship between this work and the phenomenon of 'de Gennes narrowing', familiar in the field of coherent quasi-elastic neutron scattering by simple fluids, is briefly explored. A brief discussion is also given of the expected behaviour of $F(K, \tau)$ at longer correlation delay times.

At points in § 2 it will be useful to base the discussion on specific numerical values for certain quantities. For convenience we will take these values to be roughly those of the experiments of Brown *et al*. These are listed in table 1. The relevance of the various quantities will become apparent.

Table 1. Typical values of parameters for dispersion of Brownian particles (Brown *et al* 1975).

Parameter	Symbol	Value
Particle radius	R	250 Å
Particle mass	M	$\sim 6.9 \times 10^{-17}$ g
Volume fraction		$< 10^{-3}$
Mean interparticle separation		~ 5000 Å
Frictional coefficient	$f\ (\equiv 6\pi\eta R)$	$\sim 4.7 \times 10^{-7}$ g s^{-1} [a]
Velocity relaxation time	$\tau_B\ (\equiv M/f)$ [b]	$\sim 1.5 \times 10^{-10}$ s
Particle diffusion coefficient	$D_0 \equiv (kT/f)$	$\sim 8.6 \times 10^{-8}$ cm^2 s^{-1} [c]

a Viscosity of water at 20 °C $\simeq$ 1 cP.
b From Langevin theory of Brownian motion (see various articles in Wax 1954).
c $T = 20$ °C.

It should be emphasized that in this paper we consider only a two-component system, that is a system of interacting particles dispersed in a fluid medium. Of course, for charged particles, a third component, the counter ions, is present and it is possible that counter ion motions may affect the particle motions. This has been discussed elsewhere (Brown *et al* 1975, § 5.3.2) and will not be further pursued here. In this work it is assumed that the dominant role of the counter ions is in determining the form of the interparticle potential.

2. Theory

Starting from equation (2) we will derive the results of equations (7) and (8). Without loss of generality the scattering vector K may be assumed to be in the x direction. Since we are interested in the initial time dependence of $F(K, \tau)$, we differentiate equation (2) with respect to delay time τ:

$$\frac{\mathrm{d}F(K, \tau)}{\mathrm{d}\tau} = -\mathrm{i}KN^{-1} \sum_i \sum_j \langle V_j(t+\tau) \exp[\mathrm{i}K(x_i(t) - x_j(t+\tau))]\rangle \tag{9}$$

where $x_j(t)$ is the x component of $r_j(t)$ and $V_j(t) \equiv \mathrm{d}x_j(t)/\mathrm{d}t$ is the x component of the instantaneous velocity of particle j. Equation (9) is re-arranged using the stationarity condition (see eg Egelstaff 1967, p 134),

$$\frac{\mathrm{d}F(K, \tau)}{\mathrm{d}t} \equiv 0 = \mathrm{i}KN^{-1} \sum_i \sum_j \langle (V_i(t) - V_j(t+\tau)) \exp[\mathrm{i}K(x_i(t) - x_j(t+\tau))]\rangle$$

to give

$$\frac{\mathrm{d}F(K, \tau)}{\mathrm{d}\tau} = -\mathrm{i}KN^{-1} \sum_i \sum_j \langle V_i(t) \exp[\mathrm{i}K(x_i(t) - x_j(t+\tau))]\rangle.$$

The identity

$$x_j(t+\tau) = x_j(t) + \int_t^{t+\tau} V_j(t')\,dt'$$

leads to

$$\frac{dF(K,\tau)}{d\tau} = -iKN^{-1}\sum_i\sum_j\langle V_i(t)\exp[iK(x_i(t)-x_j(t))]\exp(-iK\int_t^{t+\tau}V_j(t')\,dt')\rangle. \tag{10}$$

For delay times τ short enough that

$$K\int_0^\tau V_j(t')\,dt' \ll 1, \tag{11}$$

we keep only the first two terms in an expansion of the last exponential in equation (10). Thus

$$\left.\frac{dF(K,\tau)}{d\tau}\right|_{\text{small}\,\tau} = -K^2N^{-1}\sum_i\sum_j\int_0^\tau dt'\langle V_i(0)V_j(t')\exp[iK(x_i(0)-x_j(0))]\rangle \tag{12}$$

where, because of stationarity, the explicit dependence on t has been dropped from the notation. In obtaining equation (12) we have also used the fact that particle positions and velocities are uncorrelated when taken at the same time.

To proceed further we must consider the physics of the situation of current interest. Consider first a dilute dispersion of spherical particles (volume fraction $<10^{-3}$, say) in the absence of interactions other than the hard-sphere interaction. Aside from the small excluded-volume effect, a particle can take up any spatial position without interference from other particles. Due to collisions with the solvent molecules the particles will execute virtually independent Brownian motions, the average kinetic energy of each particle being given by equipartition:

$$\tfrac{3}{2}M\langle V^2\rangle = \tfrac{3}{2}kT. \tag{13}$$

Consider now 'turning on' a repulsive interaction between the particles. Little effect will be felt until the typical energy of interaction between a pair of particles becomes comparable to the thermal energy kT. For interaction energies much greater than kT a given particle will tend to keep as far away as possible from other particles leading to spatial ordering and consequent peaks in the radial distribution function $g(r)$ and the structure factor $S(K)$. In this situation the particle will tend to 'sit' within a few kT of the minimum of the instantaneous potential well created by its neighbours. Two types of force will thus act on a particle.

(i) A rapidly fluctuating 'Brownian' force due to collisions with the solvent molecules.

(ii) An 'interaction' force F_I, the resultant force on a particle due to the instantaneous configuration of its neighbours. This force will have a much longer characteristic fluctuation time τ_I, roughly the time taken for the relative positions of a particle and its neighbours to change by a significant fraction of the mean interparticle spacing. For the typical parameters given in table 1 we calculate this latter time to be of the order of the time taken by a particle to diffuse, say, 1000 Å, ie $\tau_I \simeq (10^{-5})^2/6D_0 \simeq 200\,\mu s$.

The particle velocity may similarly be considered to be composed of a Brownian component V_B arising from the Brownian force and an interaction component V_I. Since the fluctuation time τ_I of the interaction force is much greater than the velocity relaxation time $\tau_B(\equiv M/f) \simeq 1.5\times10^{-10}$ s (table 1), V_I will be related to F_I through the

'drift velocity' equation

$$V_I(t) = F_I(t)/f.$$

The order of magnitude of $\langle V_I^2 \rangle$ can be estimated by assuming that the potential felt by a particle typically changes by kT in, say, 500 Å. Thus

$$\langle V_I^2 \rangle \simeq (kT/5 \times 10^{-6} f)^2 \simeq 3 \times 10^{-4} \, \text{cm}^2 \, \text{s}^{-2}.$$

By equipartition of energy (equation (13)), however, the total velocity has mean-square value $kT/M \simeq 6 \times 10^2 \, \text{cm}^2 \, \text{s}^{-2}$. Thus

$$\langle V_B^2 \rangle \gg \langle V_I^2 \rangle. \tag{14}$$

(The preceding discussion is very similar to that given by Ermak and Yeh (1974), when considering the effects, not considered here, of counter ion motions on macro-ion motion.)

The last two paragraphs may be summarized by writing the particle velocity as the sum of two components:

$$V_i(t) = V_{Bi}(t) + V_{Ii}(t). \tag{15}$$

The Brownian component $V_{Bi}(t)$ has a large mean-square value and fluctuates rapidly with characteristic time τ_B. The interaction component has a small mean-square value and fluctuates relatively slowly. Two further properties of these velocity components are assumed. (i) Since the Brownian components are determined by solvent–particle interactions, it is expected that in dilute dispersions

$$\langle V_{Bi}(0) V_{Bj}(\tau) \rangle = \delta_{ij} \langle V_{Bi}(0) V_{Bi}(\tau) \rangle. \tag{16}$$

(ii) It is also expected that there will be no correlation between V_{Bi} and V_{Ij}, ie

$$\langle V_{Bi}(0) V_{Ij}(\tau) \rangle = 0 \qquad \text{for all } i, j \text{ and } \tau. \tag{17}$$

Substituting equation (15) into equation (12), using equations (16) and (17),

$$\frac{dF(K, \tau)}{d\tau} \bigg|_{\text{small } \tau}$$

$$= -K^2 \int_0^\tau \langle V_B(0) V_B(t') \rangle dt' - K^2 N^{-1} \sum_i \sum_j \int_0^\tau dt' \langle V_{Ii}(0) V_{Ij}(t')$$

$$\times \exp[iK(x_i(0) - x_j(0))] \rangle. \tag{18}$$

Now photon correlation spectroscopy is at present limited by instrumental considerations to delay times greater than 10^{-8} s, much greater than τ_B but still considerably smaller than τ_I. We therefore evaluate equation (18) for $\tau_B \ll \tau \ll \tau_I$, where, by virtue of equation (14), the second term can be neglected. The initial decay of $F(K, \tau)$, as measured by photon correlation spectroscopy, is thus given by

$$\frac{dF(K, \tau)}{d\tau} \bigg|_{\tau_B \ll \tau \ll \tau_I} \simeq -K^2 \int_0^\tau \langle V_B(0) V_B(t') \rangle \, dt'. \tag{19}$$

The final step in the analysis comes from noting that the integral in equation (19) is, at least for dilute dispersions, equal to the free-particle translational diffusion coefficient D_0 (see eg Kubo 1966, equation (2.5)). Thus

$$\frac{dF(K, \tau)}{d\tau} \bigg|_{\tau_B \ll \tau \ll \tau_I} \simeq -K^2 D_0. \tag{20}$$

Using equation (3), equation (20) can be written in normalized form:

$$\frac{d|g^{(1)}(K,\tau)|}{d\tau}\bigg|_{\tau_B \ll \tau \ll \tau_I} \simeq -\frac{K^2 D_0}{S(K)} \tag{21}$$

which is the result of equations (7) and (8) (see also equation (30) of Brown *et al* 1975). Note that τ is still subject to the restriction of equation (11).

3. Discussion

Equation (20) shows that the *initial* decay rates of the Fourier components of the concentration fluctuations are determined by the independent Brownian diffusion of the particles, regardless of the magnitude $S(K)$ of the Fourier component in question. This initial decay is thus independent of any interaction. However, the typical time taken for a Fourier component to decay to a given fraction of its initial value is given by the decay rate of the *normalized* correlation function (equation (21)). Here the interaction enters through normalization by the static structure factor $S(K)$, and large fluctuations, for values of K corresponding to the peaks of $S(K)$, will take longer to decay than small fluctuations.

The result of equation (21) is reminiscent of the so called 'de Gennes narrowing' of the quasi-elastic energy spectrum (the temporal Fourier transform of $F(K,\tau)$) of neutrons coherently scattered by simple fluids in the region of the peaks of $S(K)$ (de Gennes 1959, see also Sköld 1967, Venkataraman *et al* 1967). Both de Gennes narrowing and the phenomenon described in this paper are due to the fact that the *initial* decay of $F(K,\tau)$ for a system of interacting particles is determined by free-particle motion. Neutron scattering is sensitive to motions on timescales down to about 10^{-13} s, shorter than the relaxation time τ_B of the velocity autocorrelation function, and the short-time free-particle motion is thus the rectilinear motion of a perfect gas. As pointed out in §2, photon correlation spectroscopy is limited to times long compared to τ_B and the free-particle motion is Brownian diffusion. The result of de Gennes,

$$S(K)^{-1}\frac{d^2 F(K,\tau)}{d\tau^2}\bigg|_{\tau \to 0} = \frac{kTK^2}{S(K)M}$$

follows from evaluating equation (12) as $\tau \to 0$ and applying equipartition of energy (equation (13)).

In this paper, as in the experimental work of Brown *et al*, emphasis has been on the initial decay of $F(K,\tau)$. We now make a few tentative comments concerning its expected behaviour at larger τ. The derivative of $F(K,\tau)$ can be expressed by the non-local relationship,

$$\frac{dF(K,\tau)}{d\tau} = -\int_0^\tau M(K,\tau-t)F(K,t)\,dt, \tag{22}$$

where the 'memory function' $M(K,t)$ is related to the correlation function of the flux of particles and hence to the particle velocities (see eg Zwanzig 1961, Mori 1965, Berne *et al* 1966, equations (20) and (21), Pike 1974, equations (84) and (72)). From the discussion given in §2, we can expect $M(K,t)$ to have components decaying on the widely differing timescales τ_B and τ_I (see, also, Mountain 1974). For correlation delay times $\tau \gg \tau_I$, $M(K,\tau-t)$ is essentially local in time, and equation (22) predicts a single-exponential decay for $F(K,\tau)$. (Although not explicitly stated in their paper, this appears

to be the regime considered by Schaefer and Berne (1974).) This prediction is fulfilled by the experimental observations (Brown *et al* 1975, figure 7). In this regime, the decay rate of the exponential will be a complicated function of the interaction. For correlation delay times in the range $\tau_B \ll \tau \lesssim \tau_I$, the exact structure of the interaction component of $M(K, t)$ will be important in determining the (non-single-exponential) shape of $F(K, \tau)$. When further experimental data become available it should be possible to construct an empirical expression for $M(K, t)$. Ideally one would like to calculate $M(K, t)$ from first principles, though, as pointed out by Schaefer and Berne, theoretical complications are discouraging.

It is seen from inspection of equation (2) that, whatever the structure of $F(K, \tau)$, its characteristic decay time T_c is roughly the time taken for the distance between a pair of particles to change by $1/K$. For large enough K, T_c will be small compared to τ_I and $F(K, \tau)$ should have the free diffusional structure of equation (5). The data of Brown *et al* did not extend fully into this region of K, though a tendency towards the single-exponential behaviour of equation (5) was noted for large K. For small enough K where $T_c \gg \tau_I$, $F(K, t)$ should have predominantly the single-exponential behaviour discussed in the previous paragraph and it may be difficult to observe the initial decay predicted by equation (21).

It should be mentioned that the treatment given above can also be applied to the self-correlation function $F_s(K, \tau)$, the diagonal $(i = j)$ part of $F(K, \tau)$ (equation (2)), which describes single-particle motions. Thus the *initial* decay of $F_s(K, \tau)$ is given by equation (20). However, since $F_s(K, 0) \equiv 1$, there should, for the self-term, be no 'narrowing' effect in the region of the peaks of $S(K)$. For large τ the interaction components $V_i(t)$ of velocity will contribute to the decay of $F_s(K, \tau)$. Thus we can expect interacting Brownian particles to show two *self*-diffusion coefficients: a free-particle coefficient D_0 at short times $\tau_B \ll \tau \ll \tau_I$, and, at longer times $\tau \gg \tau_I$, a coefficient dependent on the interaction. Unfortunately it is not easy to measure $F_s(K, \tau)$ for an interacting system by light scattering.

In conclusion, we have considered the dynamics of Brownian motion of a dilute dispersion of particles interacting through a long-range repulsive potential. It seems likely that the ideas put forward in this paper will apply to Brownian motion in a wider class of interacting systems, including, perhaps, solutions of simple electrolytes and certain macromolecular solutions.

Acknowledgments

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