Dynamics of colloidal systems: time-dependent structure factors

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Abstract. The technique of Brownian dynamics is used to calculate the time and scattering vector dependence of the structuring in colloidal systems. The van Hove space–time correlation functions and the corresponding intermediate scattering functions are presented; the latter are in good qualitative agreement with those obtained experimentally.

1. Introduction

The quasi-elastic scattering of slow neutrons has been used as an extremely useful probe in the study of the dynamics of liquid systems (e.g. Larsson *et al* 1968). From the differential scattering cross-section or scattering function one is able, in principle, to obtain the space–time correlation functions which in turn represent the basic data from which many dynamic properties of the fluid may be calculated (Chen 1971, p 116). Furthermore, measurement of the incoherent and coherent scattering cross-sections allows a separation of the correlation function into distinct and self components.

On the theoretical side, the direct computer simulation of the molecular motion has considerably elucidated the complex dynamical properties of liquids. Molecular dynamics (MD) calculations have shown that such computer simulation techniques are able to predict the results of neutron scattering experiments (Rahman 1964, Harp and Berne 1970, Levesque and Verlet 1970); in fact MD can often provide much more detail than the corresponding experiment (Zwanzig 1965).

In the study of colloidal solutions, where one is usually dealing with particle diameters and interparticle spacings several orders of magnitude larger than those in simpler molecular fluids, a more appropriate probe for measuring the dynamic properties is visible light. In fact, quasi-elastic light scattering (QELS), with one-line correlation of the intensity fluctuations of the scattering light, has become widely used for investigating the dynamics of colloidal systems. From the intensity autocorrelation function measured in QELS one is able to calculate the intermediate scattering function and the space–time correlation function. For truly monodisperse systems, however, only coherent scattering is possible and the resolution into self and distinct particle correlations cannot be made. Only in the limit of dilute (non-interacting) systems, or large scattering vectors for interacting systems, can the self motion be recovered (Pusey 1978). The usefulness of neutrons in these systems, however, is not to be discounted.

Small-angle neutron scattering has been used to determine the time-averaged structure of microemulsions and concentrated dispersions of small latex particles (Dvolaitzky *et al* 1978, Cebula 1979 unpublished). In such concentrated systems, apart from the difficulties of multiple scattering, the range of available scattering vectors offered in light scattering is very limited and small-angle neutron scattering is an essential complementary technique.

Unlike the case in simple liquids, in colloidal solutions there is a large size difference between the background and dispersed particles. This would make an MD simulation, over a timescale sufficiently large to follow the dynamics of the dispersed particles, prohibitive in terms of computing time. However, an alternative approach called Brownian dynamics (BD) has recently been shown to be applicable to the study of the dynamic properties of many-particle colloidal systems. This simulation method, which essentially treats the particle–background molecule collisions by a stochastic force, has computational requirements comparable with those simulation methods usually applied to simple liquids. The present authors have reported results of calculations of some dynamical properties, such as diffusion coefficients and van Hove space–time correlation functions, for dilute dispersions of strongly interacting spheres (Gaylor *et al* 1979a, b).

In this paper, we use the BD method on the aforementioned system, to calculate the time and wavevector dependence of the intermediate scattering function and the normalised electric field autocorrelation function as measured in typical QELS experiments. Unlike the QELS experiments, however, the BD method does allow the evaluation of self and distinct components.

2. Computer simulation technique

2.1. Brownian dynamics method

In a colloidal solution of interacting particles, the motion of a given particle can be thought of as being due to the random collisions with the molecules of the background medium (normal Brownian motion), perturbed by the fact that we have a many-particle system interacting via hydrodynamic and direct particle–particle interaction forces. However, in a dilute system, such as that in this study, one can ignore the tensorial hydrodynamic effects. The sampling scheme used in this work, based on the generalised Smoluchowski equation (Ermak 1975) and fully investigated in previous studies (Gaylor *et al* 1979b), gives the following expression from which the trajectory of the *i*th colloidal particle in an *N*-particle system may be calculated:

$$r_i(t + \Delta t) = r_i(t) + R_c(\Delta t) + (D_0/kT)F_i(t)\Delta t. \tag{1}$$

In the above $R_c(\Delta t)$ is the net effect of the particle–background molecule collisions during the time interval Δt; it is sampled from a Gaussian distribution of zero mean and variance $6D_0\Delta t$. D_0 is the free particle diffusion constant. The force $F_i(t)$ is due to the interaction of the *i*th particle with the remaining particles in the system and, assuming pairwise additivity, is of the form

$$F_i(t) = \sum_{i \neq j} F(r_{ij}(t)). \tag{2}$$

The pair force is related to the pair potential U by

$$\boldsymbol{F}(r_{ij}) = -\frac{\partial U(r_{ij})}{\partial r_{ij}} \frac{\boldsymbol{r}_{ij}}{r_{ij}} \tag{3}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_i$, $r_{ij} = |\boldsymbol{r}_{ij}|$ and $r_{ij} = r_{ij}(t)$.

2.2. Computer simulation method

The particles are assumed to interact via a pairwise additive screened Coulomb potential of the form

$$U(r_{ij}) = \frac{2\pi\epsilon_0\epsilon_r \, d\psi_0^2}{r_{ij}} \exp[-\kappa d(r_{ij}-1)], \tag{4}$$

where $\epsilon_r(=80)$ is the relative permittivity of the background and ϵ_0 is the permittivity of free space. $\psi_0(=0\cdot15 \text{ V})$ is the particle surface potential and the interparticle distance r_{ij} has been expressed in units of the particle diameter $d(=4\cdot6\times10^{-8} \text{ m})$. The Debye screening length $1/\kappa$ for a monovalent electrolyte is given by

$$\frac{1}{\kappa} = \frac{1}{e}\left[\frac{\epsilon_0\epsilon_r kT}{2N_A n}\right]^{1/2} \tag{5}$$

where e is the electronic charge, N_A is Avogadro's number, k is Boltzman's constant, $n(=10^{-3} \text{ mol/m}^3)$ the bulk electrolyte concentration and $T(=300 \text{ K})$ is the absolute temperature. The quoted parameters are the same as those used in Monte Carlo studies of dilute dispersions (van Megen and Snook 1977). Indeed, the equilibrium properties calculated with the BD technique converge quite well to the Monte Carlo results (Gaylor *et al* 1979b). The calculations reported here were done for a dispersion of volume fraction $\phi = 0\cdot044\%$. The simulation uses a periodic cube containing $N = 256$ particles and a time step of $\Delta t = 10^{-5}$ s was found to be optimum. Although accurate results for dynamic properties are obtainable with a smaller number of particles, we use 256 particles here in order to facilitate the Fourier transformation of the space–time correlation functions. The particles were initially arranged on a face centred cubic lattice and the first 1000 time-steps discarded in order to minimise the effect of the starting configuration. A further 640 time-steps were then generated to give the particle trajectories used to calculate the reported dynamical properties.

3. Results and discussion

3.1. Time-dependent distribution functions

In equilibrium statical mechanics extensive use is made of the equilibrium pair distribution function or radial distribution function, $g(r)$, to describe the structure of the system and to calculate the bulk equilibrium properties. This information is also accessible experimentally via the static structure factor $S(k)$. The time dependent generalisation of $g(r)$ was first proposed for the interpretation of neutron scattering experiments (van Hove 1953). Once these van Hove space–time correlation functions are known for a particular system, many of its dynamical properties are, in principle,

accessible (Chen 1971, p 116). In the classical limit this space–time correlation function is defined by

$$G(r, t) = \frac{1}{N}\left\langle \sum_{i,j=1}^{N} \delta[r + r_i(0) - r_j(t)] \right\rangle \tag{6}$$

where, given that there is a particle at r_i at time t_1, $G(r, t)$ is the probability density for locating a particle at $r_j = r_i + r$ at a later time $t_1 + t$. For a system in equilibrium the result is independent of t_1, which is here set to zero. One can immediately separate those terms for which $i = j$ and $i \neq j$, giving the self and distinct space–time correlation functions, i.e.

$$G(r, t) = G_d(r, t) + G_s(r, t) \tag{7}$$

where

$$G_d(r, t) = \frac{1}{N}\left\langle \sum_{i \neq j} \delta[r + r_i(0) - r_j(t)] \right\rangle \tag{8}$$

and

$$G_s(r, t) = \frac{1}{N}\left\langle \sum_{i} \delta[r + r_i(0) - r_i(t)] \right\rangle. \tag{9}$$

The limiting behaviour of equations (8) and (9) is given below:

$$\lim_{t \to 0} G_s(r, t) = \delta(r) \qquad \lim_{t \to 0} G_d(r, t) = \rho g(r) \tag{10}$$

$$\lim_{t \to \infty} G_s(r, t) = \lim_{r \to \infty} G_s(r, t) = \frac{1}{V} \simeq 0 \qquad \lim_{t \to \infty} G_d(r, t) = \lim_{r \to \infty} G_d(r, t) = \rho \tag{11}$$

where ρ is the number density of the system.

The van Hove space–time functions are readily calculated from the particle trajectories discussed in the previous section, using equations (8) and (9). Figures 1 and 2 show G_s and G_d as functions of r/d for several different delay times. Since we are dealing with spherically symmetric interparticle forces $G(r, t) = G(r, t)$. It may be seen that for this system and the timescale investigated here, there is very little spatial overlap of the self and distinct correlation functions. The correlation functions can also be seen to be approaching their limiting values as defined in equations (10) and (11).

3.2. Scattering functions

The quantity usually extracted from QELS experiments is the normalised electric field autocorrelation function

$$g^{(1)}(k, \tau) = \langle E(k, 0)E^*(k, \tau) \rangle / \langle |E(k, 0)|^2 \rangle \tag{12}$$

where E^* is the complex conjugate of the electric field E and k is the scattering vector. In the absence of multiple scattering, equation (12) may be written as (Pecora 1964)

$$g^{(1)}(k, \tau) = F(k, \tau)/S(k) \tag{13}$$

where

$$F(k, \tau) = \frac{1}{N} \sum_{i,j=1}^{N} \langle \exp[ik \cdot (r_i(0) - r_j(\tau))] \rangle \tag{14}$$
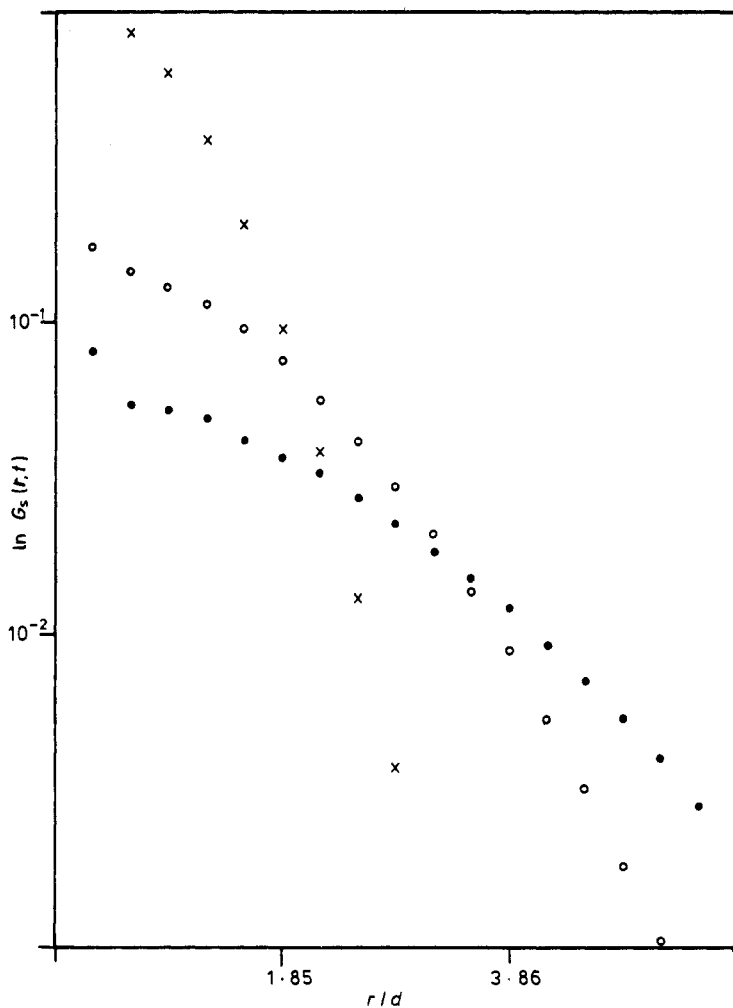
Figure 1. $\ln G_s(r, t)$ plotted against r/d at: $\times \times \times$ $t = 10^{-4}$ s; $\bigcirc \bigcirc \bigcirc$ $t = 6 \times 10^{-4}$ s; $\cdots$ $t = 1 \cdot 6 \times 10^{-3}$ s.
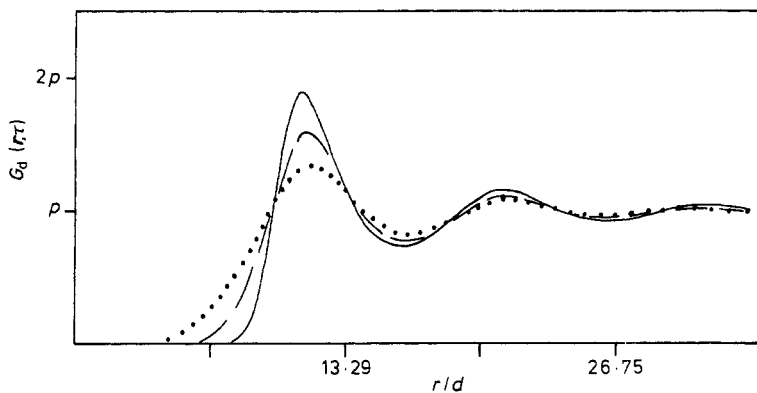

Figure 2. van Hove distinct correlation function plotted against r/d at: —— $t = 0$; ——— $t = 6 \times 10^{-4}$ s; $\cdots t = 1 \cdot 6 \times 10^{-3}$ s.

is the coherent intermediate scattering function or dynamic structure factor and

$$S(k) \equiv F(k, 0) \tag{15}$$

is the (static) structure factor. It follows that (Egelstaff 1967, p 96)

$$F(k, \tau) = \int e^{ik \cdot r}[G(r, \tau) - \rho] \, dr \tag{16}$$

$$S(k) = 1 + \rho \int e^{ik \cdot r}[g(r) - 1] \, dr. \tag{17}$$

As before, the space–time correlation function can be split into its self and distinct parts to yield the self and distinct parts of the intermediate scattering function:

$$F_s(k, \tau) = \int e^{ik \cdot r} G_s(r, \tau) \, dr \tag{18}$$

$$F_d(k, \tau) = \int e^{ik \cdot r}[G_d(r, \tau) - \rho] \, dr. \tag{19}$$

Thus from the van Hove functions of the previous section one can calculate the scattering functions. Moreover, one can investigate the relative importance of the self and distinct components in the experimentally accessible coherent intermediate scattering function.

In figure 3, F_s and F_d are plotted at different times. At large k values, where F_d is virtually zero at all times, F_s is quite pronounced at small delay times and decays quite
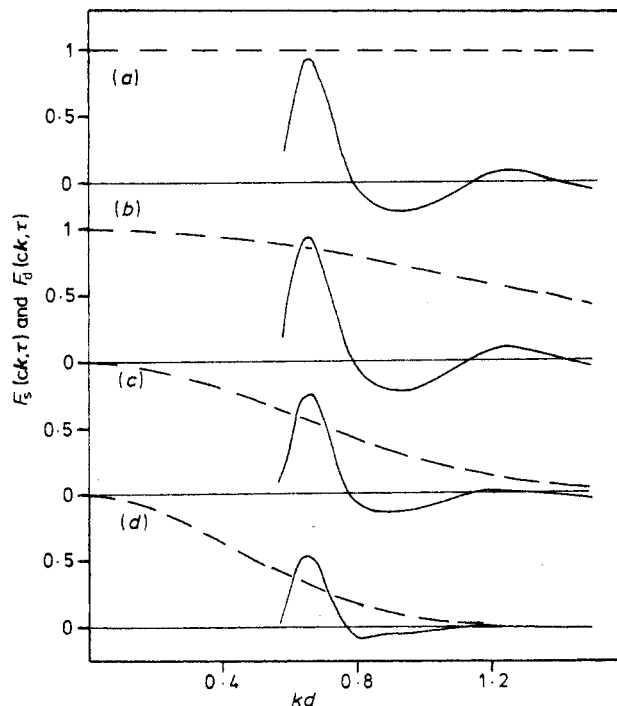

Figure 3. Self intermediate scattering function (— — —) and distinct intermediate scattering function (——) at (a) $t = 0$ s; (b) $t = 10^{-4}$ s; (c) $t = 1 \cdot 6 \times 10^{-3}$ s; (d) $t = 1 \cdot 6 \times 10^{-3}$ s.

quickly. In the previous section we saw that the self and distinct correlation functions were well separated in coordinate space. This is also reflected here in that the large-k behaviour is dominated by F_s. For these types of colloidal solutions, this is consistent with results of QELS experiments in which it has been possible to extract mean square displacements from $F(k, \tau)$ at large κ. Even around the maximum in F_d the temporal relaxation of F_d is seen to be more sluggish than that of F_s. The sum of F_s and F_d gives the coherent intermediate scattering function $F(k, \tau)$ displayed in figure 4.
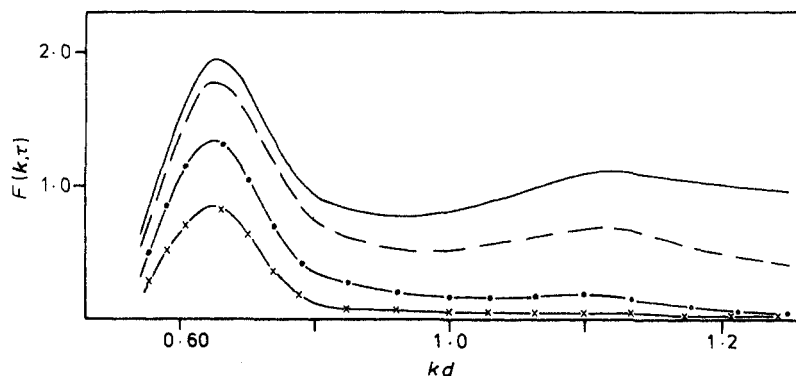

Figure 4. Total intermediate scattering function for —— $t = 0$; – – – $t = 10^{-4}$ s; – · – · – $t = 6 \times 10^{-4}$ s; – × – × – × – $t = 1 \cdot 6 \times 10^{-3}$ s.

In figure 5 we plot the logarithm of the normalised field autocorrelation function in a form in which QELS data is often presented. For an ideal (infinitely dilute, mono-disperse) colloidal solution

$$g^{(1)}(k, \tau) = \exp(-D_0 k^2 \tau) \tag{20}$$

and a plot of $\ln g^{(1)}$ against $k^2 \tau$ yields a straight line independent of k with slope D_0, the diffusion constant for a freely diffusing particle. As expected from the above results and clearly illustrated in figure 5, both the linearity of $\ln g^{(1)}$ against $k^2 \tau$ and the k independence are lost for a colloidal solution of interacting particles. The results are shown for three different values of k around the first peak in $F(k, \tau)$. These results are in qualitative agreement with QELS experiments (Pusey 1978).
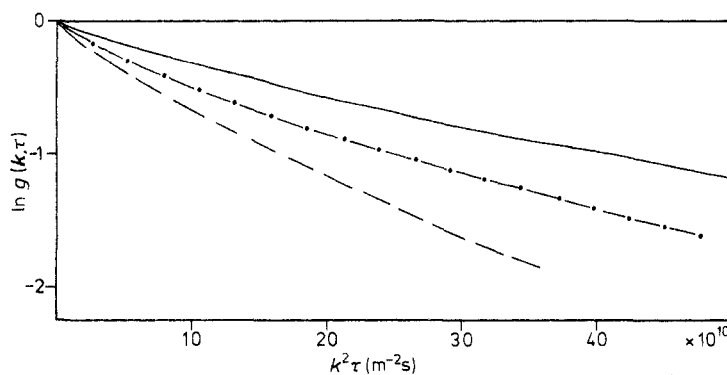

Figure 5. The normalised field autocorrelation function at three different scattering vectors: —— $k^* = 0 \cdot 65$; – – – $k^* = 0 \cdot 55$; – · – · – $k^* = 0 \cdot 75$ ($k^* = kd$).

Simulations of this type are possible only by using periodic boundary conditions in which an infinite system is replaced by cubic replicas of length L and containing at most a few hundred particles. In our case

$$L = 100\pi N/6\phi = 67\cdot3d.$$

This means, however, that the correlation functions are truncated at $r = L/2$, making the Fourier transformed results unreliable at small values of k. Methods are presently being investigated to make this region of k space accessible.

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