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## The study of Brownian motion by intensity fluctuation spectroscopy

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The principles and methods of quasielastic light scattering and intensity fluctuation spectroscopy (i.f.s.) are reviewed briefly. Their application to the study of Brownian motion is discussed with emphasis on the behaviour of the velocity autocorrelation function  $\phi(\tau)$  of a single particle. We consider: (i) The situation usually assumed where  $\phi(\tau)$  decays rapidly compared with other timescales of interest; (ii) the modification of (i) due to the  $\tau^{-\frac{3}{2}}$  'long-time tail' in  $\phi(\tau)$  including the recent i.f.s. experiment of Boon & Bouiller (1976) which confirms its existence, and finally (iii) systems of charged colloidal particles exhibiting 'liquid-like' spatial ordering due to long-range Coulombic interactions. Here  $\phi(\tau)$  has a *negative* long-time tail. We also consider the many-body dynamics in these systems by exploiting the similarity with neutron scattering by simple atomic liquids. 'Solid-like' systems are discussed briefly.

## 1. INTRODUCTION

Brownian motion, the thermally induced random movement of microscopic particles dispersed in a fluid medium, was first observed at least 150 years ago. In the first decade of this century Einstein, von Smoluchowski, Langevin and others laid the basis for a theoretical description of the phenomenon. This work, along with the subsequent experiments of Perrin, led to virtually universal acceptance of the molecular hypothesis of matter (see Brush (1976) for a discussion of this early work). Brownian motion still, 70 years later, plays a fundamental role in many dynamical theories. It comes as something of a surprise, therefore, to realize that, after all this time, there remain unsolved problems in the theory of Brownian motion and that experiments on Brownian motion *per se* are still needed as a test of and guide to the developing theories. An important experimental advance has been the development over the past 15 years of intensity fluctuation spectroscopy (i.f.s.), the electronic analysis of temporal fluctuations in the intensity of scattered laser light. The aim of this paper is to describe some recent applications of i.f.s. to the study of Brownian motion.

In § 2 we review briefly the principles and methods of i.f.s. Sections 3–5 are then devoted to the main topic. Perhaps the simplest non-trivial indicators of Brownian particle dynamics are the temporal autocorrelation function of the velocity of a single particle (the v.a.f.,  $\phi(\tau)$ ) and related quantities such as the mean-square particle displacement. It is the behaviour of these quantities that will be emphasized. In § 3 we consider *non-interacting* Brownian particles when the decay of  $\phi(\tau)$  is assumed to be rapid compared to any other time of importance in the measurement. In § 4 we show how these simple ideas are modified by a more realistic treatment which leads to a slower  $\tau^{-\frac{3}{2}}$  'long-time tail' in the decay of the v.a.f. Finally, in § 5, we discuss the Brownian motion of particles interacting through strong, repulsive, long-ranged, Coulombic forces. These forces cause strong correlations in both the positions and motions of different particles.

## 2. LIGHT SCATTERING AND INTENSITY FLUCTUATION SPECTROSCOPY

I.f.s. is one of many techniques which owe, if not their invention, at least their rapid growth to the laser (Jakeman *et al.* 1976). The technique has been reviewed extensively over the past few years (see, for example, Chu 1974; Cummins & Pike 1974, 1977; Berne & Pecora 1976; Pusey & Vaughan 1975) and here we will only provide a brief introduction.

Consider  $N$  identical, spherical Brownian particles dispersed in a fluid medium and illuminated by laser light of wavelength  $\lambda$  (in the medium). We assume that the intensity of light scattered by the medium is negligible compared to that scattered quasi-elastically by the particles. The instantaneous value of the complex amplitude of the electric field of the light single-scattered into the far field at scattering angle  $\theta$  to the laser beam can then be written

$$E(K, t) \propto \sum_{i=1}^N \exp(i\mathbf{K} \cdot \mathbf{r}_i(t)), \quad (1)$$

where  $\mathbf{K}$  is the usual scattering vector ( $K \equiv |\mathbf{K}| = (4\pi/\lambda) \sin \frac{1}{2}\theta$ ) and  $\mathbf{r}_i(t)$  is the position of the  $i$ th particle at time  $t$ . The factor  $\mathbf{K} \cdot \mathbf{r}_i(t)$  represents the phase shift in the light scattered by the  $i$ th particle relative to that scattered by a particle at the (arbitrary) origin  $\mathbf{r} = 0$ . Thus  $E(K, t)$ , considered as a function of  $\mathbf{K}$  (or detection position), describes the instantaneous random diffraction or 'speckle' pattern of the random arrangement of particles at time  $t$ . As the particle positions  $\{\mathbf{r}_i(t)\}$  change owing to Brownian motion  $E(K, t)$  fluctuates randomly in time (hence the name 'intensity fluctuation spectroscopy'). The simplest function by which a randomly fluctuating quantity can be characterized is its first order correlation function which, in normalized form, can be written

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

where the  $\langle \rangle$  indicate ensemble or time averages (since we assume the processes under study to be statistically stationary). Substitution of (1) into (2) gives

$$g^{(1)}(K, \tau) = F(K, \tau) / S(K), \quad (3)$$

where the 'intermediate scattering function' or 'dynamic structure factor'  $F(K, \tau)$  is

$$F(K, \tau) \equiv \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \langle \exp(i\mathbf{K} \cdot [\mathbf{r}_i(0) - \mathbf{r}_j(\tau)]) \rangle, \quad (4)$$

and the 'structure factor'  $S(K)$  is

$$S(K) \equiv F(K, 0). \quad (5)$$

The functional dependence of  $F(K, \tau)$  on  $K$  and  $\tau$  contains information on the Brownian motions of the particles.

The most common experimental arrangement used nowadays to process the fluctuating light intensity involves a photomultiplier operating in the photon-counting mode, followed by fast digital electronics (with resolving time down to *ca.*  $10^{-8}$  s) to construct the correlation function of the photons detected (hence the name 'photon correlation spectroscopy' p.c.s.). Detectors based on the photoelectric effect are, of course, sensitive to the intensity  $|E(K, t)|^2$  of the incident light field, and p.c.s. measures the intensity, rather than the field, correlation function. However, when, as in the experiments considered below, the number  $N$  of scatterers is large enough,  $E(K, t)$  is a (complex) Gaussian random variable, in which case there is a simple relation between the field and intensity correlation functions. P.c.s. then provides an

experimental estimate of  $C^{\frac{1}{2}}g^{(1)}(K, \tau)$  for a number (usually 50–100) of discrete values of  $\tau$  (see, for example, figure 3);  $C$  is a  $\tau$ -independent constant of order one determined by the experimental conditions.

### 3. NON-INTERACTING PARTICLES: SIMPLEST CASE

In a sufficiently dilute dispersion, particle interactions are negligible so that the positions and velocities of different particles are uncorrelated. Then cross-terms ( $i \neq j$ ) in (4) vanish,  $S(K) = 1$  and  $F(K, \tau)$  becomes the self-scattering function  $F_s(K, \tau)$ , which, with the assumption of identical particles can be written

$$F_s(K, \tau) = \langle \exp(-iK \Delta x(\tau)) \rangle, \quad (6)$$

where the particle displacement  $\Delta x(\tau)$  is given by

$$\Delta x(\tau) \equiv x(\tau) - x(0) \equiv \int_0^\tau v(t) dt, \quad (7)$$

$x(t)$  is the  $x$ -component of particle position  $\mathbf{r}(t)$ ,  $v(t)$  is the  $x$ -component of particle velocity  $\mathbf{v}(t)$ , and, without loss of generality, we have taken  $\mathbf{K}$  to be in the  $x$ -direction. In the simplest view of Brownian motion, solvent molecule – particle collisions cause the velocity  $\mathbf{v}(t)$  to fluctuate rapidly so that it can be taken to be an isotropically distributed random variable with characteristic fluctuation time  $\tau_B$  small compared to any other time of interest in the measurement. With these assumptions, (6) can be evaluated for  $\tau \gg \tau_B$  to give (see, for example, Cummins & Pusey 1977)

$$F_s(K, \tau) = \exp(-D_0 K^2 \tau), \quad (8)$$

where the diffusion constant  $D_0$  has been equated, via the fluctuation dissipation theorem, with the integral of the velocity autocorrelation function  $\phi(t)$ :

$$D_0 = \int_0^\infty \phi(t) dt, \quad (9)$$

$$\phi(t) = \langle v(0) v(t) \rangle. \quad (10)$$

Equation (8) has formed the basis of many if not most of the studies by i.f.s. of particles such as biopolymers (proteins, viruses etc.), synthetic polymers and colloids (see, for example, Cummins & Pusey 1977; Schurr 1977; for bibliographies). For spherical particles,

$$D_0 = kT/f, \quad (11)$$

$$f = 6\pi\eta R, \quad (12)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $f$  is the particle frictional coefficient,  $\eta$  is the shear viscosity of the solvent and  $R$  is the particle radius. Typically, values of  $R$  accurate to 1 or 2% can be obtained from measurements of  $g^{(1)}(K, \tau)$  (from equations (3), (8), (11) and (12)) in an experiment lasting a few seconds or minutes. The characteristic decay time,

$$T_c = (D_0 K^2)^{-1}, \quad (13)$$

is in the range between 1  $\mu$ s and 1 ms for particles smaller than 1  $\mu$ m and typical values of  $K$ .

## 4. NON-INTERACTING PARTICLES: LONG-TIME TAILS

In § 3 we obtained equation (8) by assuming that the decay time  $\tau_B$  of the particle v.a.f.,  $\phi(\tau)$ , was small compared to the decay time  $T_c$  (equation (13)) of the measured correlation function  $F_s(K, \tau)$ . In this section we explore the validity of this assumption.

The simplest expression for  $\phi(\tau)$  is obtained from the Langevin equation (Langevin 1908; see also Wax (1954) for a collection of articles on the theory of Brownian motion):

$$m (dv(t)/dt) = -fv(t) + F(t), \quad (14)$$

where  $m$  is the particle mass and  $f$  its frictional coefficient (equation (12)). The basis of this equation is the intuitive separation of the instantaneous force acting on the particle into two components, a systematic frictional part,  $-fv(t)$ , and a random part  $F(t)$  which fluctuates rapidly compared to  $v(t)$  (see, for example, Lebowitz & Rubin 1963; Fox & Uhlenbeck 1970; Nordholm & Zwanzig 1975 for more fundamental justifications of equation (14)). Integration of equation (14) and use of the equipartition theorem,

$$\langle v^2 \rangle = kT/m, \quad (15)$$

gives

$$\phi(\tau) = (kT/m) \exp(-\beta\tau), \quad (16)$$

where

$$\beta \equiv f/m \equiv \tau_B^{-1}. \quad (17)$$

From equations (11), (12), (13) and (17) the ratio  $\tau_B/T_c$  is given by

$$\tau_B/T_c = kT \rho_P R K^2 / (27 \pi \eta^2), \quad (18)$$

where  $\rho_P$  is the particle density. For particle radii  $< 10 \mu\text{m}$  and usual values for the other quantities in (18),  $\tau_B/T_c < 10^{-3}$ . These considerations, therefore, appear to justify the assumptions made in § 3.

However, despite its success in many situations, it has long been recognized that the simple Langevin equation suffers from a number of fundamental limitations. One interesting difficulty came to light in computer 'experiments' on simple liquids, which showed a much slower, long-time, decay to  $\phi(\tau)$  than that predicted by equation (16) (Alder & Wainwright 1967). This effect is thought to be due to collective motions in the fluid surrounding a particle, which effectively increase its inertia and retard the changes in velocity (Alder & Wainwright 1970). It was soon realized that the failure of the simple Langevin theory to predict these effects was due to the use of the Stokes expression (12) for  $f$  which was derived for steady motion, obviously an unreasonable approach when dealing with a randomly fluctuating velocity (Zwanzig & Bixon 1970; Widom 1971). These authors showed that the theory could be generalized by replacing the steady-flow frictional force,  $-fv(t)$ , by

$$-fv(t) - \frac{2}{3} \pi \rho R^3 \dot{v}(t) - 6R^2 (\pi \eta \rho)^{\frac{1}{2}} \int_{-\infty}^t \frac{\dot{v}(t')}{(t-t')^{\frac{3}{2}}} dt', \quad (19)$$

the result for a fluctuating motion, which is a generalization due to Boussinesq of an expression already known to Stokes in 1851 (Landau & Lifshitz 1959, p. 97). Here  $\rho$  is the fluid density.

In the last few years a large number of papers have considered the generalized Brownian motion obtained with the use of (19) (see, for example, Widom 1971; Mazo 1971; Berne 1972; Chow & Hermans 1972; Nelkin 1972; Hynes 1972; Keizer 1973; Dufty 1974; Pomeau

& Resibois 1975; Zwanzig & Bixon 1975). The results relevant to the present discussion are the following:

- (i)  $\int_0^\infty \phi(t) dt = D_0$ , the same result as for the simple theory;  
 (ii) the asymptotic decay of  $\phi(t)$  is much slower than that predicted by (16):

$$\lim_{\tau \rightarrow \infty} \phi(\tau) = \frac{1}{12} k T \rho^{\frac{1}{2}} (\pi \eta \tau)^{-\frac{3}{2}}. \quad (20)$$

A remarkable feature of this latter result is its independence of the radius and density of the Brownian particle.

Since their discovery such 'long-time tails' have assumed an important role throughout theoretical statistical physics. However, it is a curious fact that there have been very few real (as opposed to computer) experimental demonstrations of their existence. Their possible detection in Brownian motion by i.f.s. techniques has been considered by, for example, B. J. Berne (1971, private communication), Nelkin (1972), Boon & Bouiller (1976) and Harris (1975). We assume, as is frequently done in Brownian motion problems (see, for example, Dufty 1974), that the particle velocity is a Gaussian random variable. Then, from (6) and (7) we obtain (see Berne & Pecora 1976 § 5.9):

$$\ln F_s(K, \tau) = -\frac{1}{2} K^2 \langle \Delta x^2(\tau) \rangle, \quad (21)$$

where the mean-square displacement,  $\langle \Delta x^2(\tau) \rangle$ , is given by

$$\langle \Delta x^2(\tau) \rangle = 2 \int_0^\tau (\tau - t) \phi(t) dt. \quad (22)$$

For large  $\tau$ , equations (21) and (22) reduce, by use of equation (9), to equation (8). It is convenient to define a time-dependent diffusion coefficient (Harris 1975),

$$D(\tau) = \int_0^\tau \phi(t) dt, \quad (23)$$

which can be obtained from the local slope of a plot of  $\ln F_s(K, \tau)$  against  $\tau$ . From equations (9), (20) and (23) we obtain

$$D(\tau) = D_0 [1 - (\rho/\pi\eta)^{\frac{1}{2}} R\tau^{-\frac{1}{2}} + \dots]. \quad (24)$$

To date, only one i.f.s. experiment has been reported, that of Boon & Bouiller (1976) (see also Bouiller *et al.* 1978), who studied polystyrene spheres of radius *ca.* 85 nm dispersed in methanol at 30 °C. Here, equation (24) predicts that  $D(T_c)$  differs from  $D_0$  by 0.5% or less, so that the effect is small. Nevertheless, with a different approach to the data analysis, these authors were able to detect an effect of magnitude about twice the expected experimental error in the measurements. Clearly, further experiments, possibly on larger spheres, would be valuable.

## 5. INTERACTING PARTICLES

### 5.1 Introduction

Until now we have considered dilute dispersions in which the mean interparticle spacing is sufficiently large for each particle to undergo essentially free Brownian motion. We now turn to the more complicated, but interesting, situation where interactions between them cause correlations between both the positions and motions of different particles. Two classes of

interaction can be identified: *direct* interparticle interactions, and indirect *hydrodynamic* interactions where the velocity field generated in the supporting fluid by the motion of one particle affects that of other particles. Even evaluating the first order correction to free Brownian motion for the *short-ranged* hard-sphere interaction has involved considerable theoretical effort (see, for example, Altenberger & Deutch 1973; Ackerson 1976; Batchelor 1976). In this case the direct and hydrodynamic forces have opposite and roughly equal effects on the particle dynamics. However, it appears that the effect of *long-ranged* direct interactions frequently dominates that of the hydrodynamic interactions (Ackerson 1977). For simplicity, therefore, we will neglect hydrodynamic interactions and will concentrate on one particular long-ranged interaction, that due to Coulombic, or electrostatic, forces.

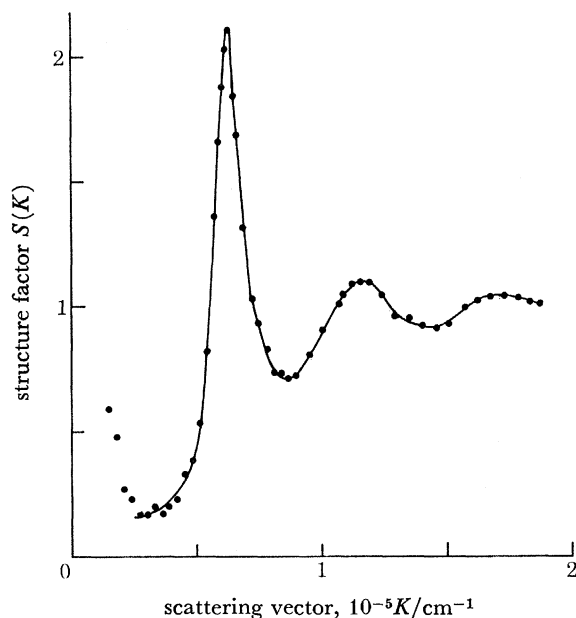


FIGURE 1. Structure factor for aqueous dispersion of polystyrene spheres of radius  $0.045 \mu\text{m}$ , showing a 'liquid-like' structure with mean interparticle spacing of about  $1.18 \mu\text{m}$ . The main peak in  $S(K)$  was at scattering angle  $\theta \approx 21^\circ$  when light of wavelength  $0.488 \mu\text{m}$  (*in vacuo*) was used.

When dispersed in a suitable liquid such as water, many types of Brownian particle, e.g. biopolymers (proteins, viruses etc.) and colloids, can carry a surface charge due to spontaneous ionization of hundreds or even thousands of surface groups. This charge will be shielded by an atmosphere or diffuse layer of small ions. At moderate to high concentrations of added electrolyte the spatial extent  $L$  of this atmosphere is small compared to the particle radius, and the particle charge is screened effectively. However, by use of ion exchange resins, it is possible to prepare aqueous systems at very low ionic strength where the small ions come largely from the particles themselves and from the intrinsic ionization of the water (Brown *et al.* 1975), and then  $L$  can reach  $1 \mu\text{m}$  or more. When  $L$  approaches in magnitude the mean interparticle spacing, any one particle will be in more or less continual interaction with several neighbours. For sufficiently strong interactions the particles can actually crystallize in a lattice with spacing of many particle diameters. With weaker interactions the particles can move through the dispersion, but a 'liquid-like' structure, exhibiting spatial correlations over two or three interparticle spacings, can persist. Since the interparticle spacing in these ordered structures can be

comparable to the light wavelength,  $\lambda$ , laser light scattering is a good technique for studying both static (§ 5.2) and dynamic (§ 5.3 and § 5.4) correlations. The most widely studied systems are aqueous dispersions of colloidal polystyrene. These spherical particles have radii in the range 20–60 nm and the charge is due to ionizable sulphate groups.

### 5.2 Static structure

When a laser beam is directed through a sample in a ‘solid-like’ state, Bragg diffraction spots are readily observed in this striking optical analogue of X-ray crystallography. Williams & Crandall (1974) have shown that there is a transition from a f.c.c. to a b.c.c. structure as the dispersion is diluted. Williams *et al.* (1976) have studied the solid–liquid ‘melting’ transition.

Figure 1 shows the structure factor  $S(K)$  (equation (5)), obtained from the angular dependence of the average intensity of the scattered light, for polystyrene spheres of radius 45 nm in a liquid-like dispersion. The form of  $S(K)$  is similar to that for atomic fluids, on a much smaller scale (by a factor of *ca.*  $10^{-3}$ ), obtained by X-ray or neutron diffraction. Particle pair correlation functions can be determined by Fourier inversion of  $S(K)$ . Previous experiments (Brown *et al.* 1975) showed significant structure in dispersions where the mean interparticle spacing was as large as 20 particle diameters (volume fraction  $< 10^{-4}$ ). Schaefer (1977) has discussed the determination of effective interparticle potentials from structure factor data.

### 5.3 Dynamics: single-particle motions

In a system of particles interacting through repulsive forces, a given particle will generally find itself in a potential well created by the instantaneous configuration of its neighbours. Insight into the particle dynamics can be obtained by considering the idealized case, soluble in terms of the Langevin equation, of a Brownian particle permanently bound in a harmonic potential:

$$m\ddot{x}(t) = F(t) - f\dot{x}(t) - m\omega^2x(t). \quad (25)$$

A similar approach has been applied by Carlson & Fraser (1974) to studies by i.f.s. of cross-linked gels. (We neglect the effect of the other terms in the Langevin equation, discussed in § 4, since they are small on the timescale of interest here.) Although, for the problem considered here, the interparticle forces are strong enough to cause spatial ordering, simple estimates show that they are still much weaker than the solvent molecule–particle ‘Brownian’ forces. Thus the motion described by (25) is strongly overdamped, i.e.

$$\beta/\omega \gg 1; \quad (\beta \equiv f/m). \quad (26)$$

In this limit the v.a.f. obtained from (25) is (Wang & Uhlenbeck 1945, equation 50 C, corrected by a factor  $\beta^2$ ),

$$\phi(\tau) = \frac{kT}{m} \left\{ \left( 1 + \frac{\omega^2}{\beta^2} \right) \exp(-\beta\tau(1 - \omega^2/\beta^2)) - \frac{\omega^2}{\beta^2} \exp(-\omega^2\tau/\beta) \right\}. \quad (27)$$

This is the sum of a term the same (to zero order in  $\omega/\beta$ ) as that applying for free Brownian motion and a *negative* small-amplitude, slowly-decaying term which reflects the effect of the potential.

This approach is obviously reasonable for a solid-like structure. However in a real ‘liquid-like’ system the potential experienced by a given particle is neither fixed nor harmonic.



Nevertheless, the general form of equation (27) suggests that a reasonable first guess for the v.a.f. in such a case would be

$$\phi(\tau) = (kT/m) \exp(-\tau/\tau_B) - A \exp(-\tau/\tau_I), \quad (28)$$

where  $\tau_B \equiv \beta^{-1}$  is the 'Brownian' velocity relaxation time.

$$A \approx (kT\omega^2/m\beta^2) \quad \text{and} \quad \tau_I < \beta/\omega^2 \quad (29)$$

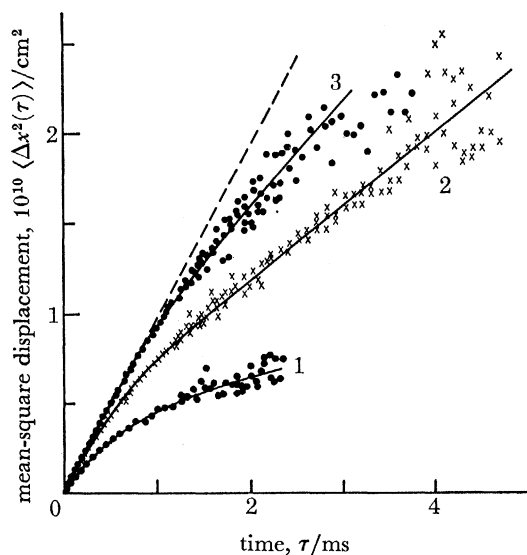


FIGURE 2. Mean-square displacement for three samples of polystyrene spheres of radius  $0.045 \mu\text{m}$ . In the most concentrated 'solid-like' sample 1, interactions strongly affect single-particle motions; in the least concentrated 'liquid-like' sample 3, the effect is much smaller. Sample 2 is the same as for figure 1. (See text for further details.) ---, Free-particle behaviour.

are parameters determined by the interaction whose 'effective angular frequency' is  $\omega$ . The time  $\tau_I$  can be identified as the typical fluctuation time of the interparticle force which, in a liquid-like dispersion, can be expected to be somewhat shorter than  $\beta/\omega^2$ , the value obtaining in a solid-like dispersion (compare equations (27) and (28)). Substitution of equation (28) into equation (22) with use of equations (17) and (9) gives, in the limit  $\tau \gg \tau_B$  to which most i.f.s. experiments are restricted (§§ 3 and 4):

$$\langle \Delta x^2(\tau) \rangle = 2D_0\tau - 2A\tau_I[\tau + \tau_I \exp(-\tau/\tau_I) - \tau_I]. \quad (30)$$

For  $\tau \ll \tau_I$  (but  $\tau \gg \tau_B$  still),

$$\langle \Delta x^2(\tau) \rangle \approx 2D_0\tau, \quad (31)$$

which indicates that, for short times, the particles diffuse essentially freely. Only at longer times,  $\tau \gtrsim \tau_I$ , is the effect of the interaction felt. For  $\tau \gg \tau_I$ ,

$$\langle \Delta x^2(\tau) \rangle = 2D_L^s\tau + 2A\tau_I^2, \quad \text{where} \quad D_L^s \equiv \int_0^\infty \phi(t) dt = D_0 - A\tau_I, \quad (32)$$

$D_L^s$  can be identified as the long-time self-diffusion coefficient of the particle in the interacting system.

Laser light scattering is intrinsically a coherent technique, so that there is no equivalent of incoherent neutron scattering for measuring single-particle motions. However, for large  $K$ , where  $S(K) \rightarrow 1$  (figure 1),  $F(K, \tau) \rightarrow F_s(K, \tau)$  so that the effects of interactions on single-particle motions can be studied by measurements of  $g^{(1)}(K, \tau)$  in this limit. Figure 2 shows

$\langle \Delta x^2(\tau) \rangle$  obtained, by use of equations (3) and (21), from such a measurement on samples of polystyrene spheres of radius = 45 nm at concentrations corresponding to mean interparticle spacings of about 8 (sample 1), 13 (sample 2) and 18 (sample 3) particle diameters. The dashed line indicates 'free-particle' behaviour (equations 8 and 21) which would obtain in the absence of interactions. At short times, all samples show the free diffusion predicted by equation (31). The observation of Bragg spots showed sample 1 to be in a solid-like state. Here, since  $\tau_I = \beta/\omega^2$ , we find from equations (27) and (32) that  $D_L^s = 0$  and that  $\langle \Delta x^2(\tau) \rangle$  levels off with increasing  $\tau$  at a value that reflects the degree of freedom of a particle to move in the neighbourhood of a lattice site from which it rarely escapes. The results in figure 2 show a tendency towards this saturation. The more dilute (and, therefore, less strongly interacting) samples 2 and 3 were in a liquid-like state still showing considerable structure in  $S(K)$  (figure 1 is for sample 2). Here the linear long-time behaviour predicted by equation (32) is evident in figure 2. For sample 2,  $D_L^s \approx \frac{1}{3}D_0$ , demonstrating how macroscopic self-diffusion is restricted by the interactions (see also Pusey 1978, figure 4).

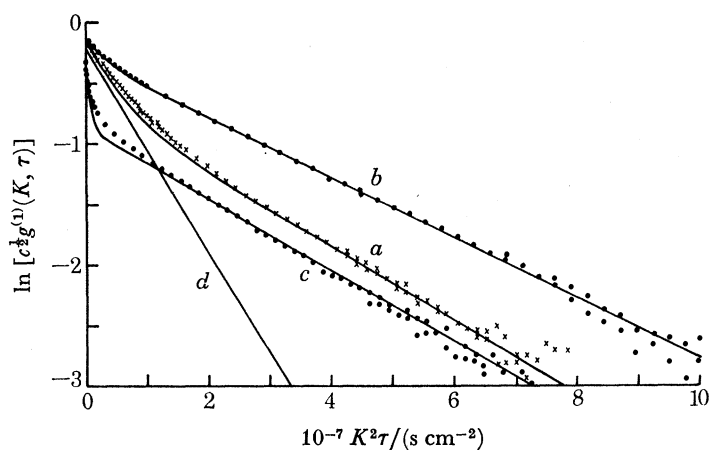


FIGURE 3. Correlation functions for polystyrene spheres (radius 25 nm) in liquid-like state for three different scattering vectors relative to the position  $K_{\max}$  of the peak of  $S(K)$ : (a)  $K > K_{\max}$ ,  $S(K) \approx 1$ ; (b)  $K \approx K_{\max}$ ,  $S(K) \approx 1.5$ ; (c)  $K \ll K_{\max}$ ,  $S(K) \approx 0.12$ ; (d) result for non-interacting particles. (Taken from Pusey 1978.)

By extending the ideas proposed in this section it should be possible to relate single-particle dynamics more quantitatively to interparticle forces in an harmonic approximation. At the very least it seems clear that the data (figure 2) require that  $\phi(\tau)$  has a weak, long-lived, negative tail. This is similar to the case of an atom in a dense atomic liquid. The particle can be viewed as temporarily trapped in the repulsive 'cage' formed by the instantaneous configuration of its neighbours (Pusey 1978).

#### 5.4 Dynamics: many-particle motions

In an i.f.s. experiment at arbitrary scattering vector  $\mathbf{K}$ , one measures the full coherent scattering function  $F(K, \tau)$  (equation (4)), which depends on the relative motions of different particles as well as on single-particle motions. A many-body problem must therefore be solved and this has not yet been done (see Ackerson (1978) for assessment of the current theoretical situation). The lack of a theory does not, of course, preclude measurements and it is still possible to provide some interpretation. Figure 3 shows measurements of  $g^{(1)}(K, \tau)$  as a function of  $\tau$  for three values of  $K$  on a sample of interacting polystyrene spheres of radius *ca.* 25 nm which

showed a main peak in  $S(K)$  at  $K_{\max} \approx 2 \times 10^5 \text{ cm}^{-1}$  ( $\theta \approx 73^\circ$ ). If the particles did not interact, the results for all three measurements should lie on curve  $d$  with slope  $D_0$  (see equations (3) and (8), noting that  $\ln g^{(1)}$  is plotted against  $K^2\tau$ ), and this was verified by adding electrolyte to the system to shield the interaction (see § 5.1). The effect of the interactions is striking. We note the following:

(i) For all  $K$ , the data show a transition from curvature at short times to a roughly linear behaviour, implying an exponential decay of  $F(K, \tau)$ , at longer times. The time at which this transition occurs is roughly the same for all  $K$ . Remembering the comments made in § 5.3, one might guess that the short-time behaviour reflects free Brownian motion but that cooperative motions of the particles determine the longer-time behaviour.

(ii) Theories based on this separation of timescales predict that in the free-particle régime,  $\tau_B \ll \tau \ll \tau_L$ , the initial decay of the coherent scattering function  $F(K, \tau)$  is given by (Pusey 1975; Ackerson 1976):

$$F(K, \tau) = S(K) - D_0 K^2 \tau + \dots, \quad (33)$$

or through equation (3),  $\ln g^{(1)}(K, \tau) = -(D_0/S(K)) K^2 \tau + \dots$  (34)

The data in figure 3 are in reasonable accord with equation (34): when  $S(K)$  is small (trace (c)) the initial decay of  $g^{(1)}$  is rapid, whereas when  $S(K)$  is large (trace (b)) the initial decay is slow (see Brown *et al.* (1975) and Pusey (1978) for more data). A similarity between the result (33) and 'de Gennes narrowing' of the quasi-elastic spectrum of neutrons scattered by a simple fluid (de Gennes 1959) was pointed out by Pusey (1975) and Ackerson (1976). The interactions enter the  $\tau$ -dependent term in equation (34) only through normalization by the static structure factor. Ackerson (1976, 1977) has obtained an expression for the next ( $\tau^2$ -dependent) term in (34) in which the interparticle potential appears explicitly.

(iii) The effective diffusion coefficients  $D_L$  obtained from the long-time slopes of the plots in figure 3 are 3–4 times smaller than  $D_0$  and show much less  $K$ -dependence than those obtained from the initial slope. Nevertheless there does seem to be a real 'slowing down' of this decay in the region of the peak of  $S(K)$  (Pusey 1978, figure 3). For  $K > K_{\max}$  where  $S(K) \approx 1$  (trace (a))  $D_L$  can be identified as the macroscopic self-diffusion coefficient  $D_L^s$  (§ 5.3). For  $K \ll K_{\max}$  (trace (c)) it describes the cooperative decay of a macroscopic concentration fluctuation of spatial extent much greater than the interparticle spacing. It is the detailed explanation of the long-time behaviour shown in figure 3 that remains the main theoretical challenge (Ackerson 1978).

### 5.5 Conclusion

The field surveyed in § 5 is young and expanding. Improvements can be expected both in the chemistry of sample preparation and characterization and in the collection and analysis of data. We conclude with a few remarks on the relevance and future direction of this research.

(i) The relevance to colloid science is obvious: improved understanding of interparticle potentials and particle dynamics should have implications in many areas including the chemical industry and biology.

(ii) The analogy with neutron scattering is close, and further exploration of the similarities and differences could lead to a better general understanding of systems with many-body interactions.

(iii) Other possibilities include investigation of particle dynamics at the solid–liquid melting transition and of dispersions of non-spherical particles which could form lyotropic liquid crystals.

(iv) Finally we remark that experiments of type outlined in § 5 lend themselves to beautiful visual demonstrations which could find a role in teaching the physics of condensed matter.

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