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Number fluctuations of interacting particles

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Abstract. The mean-square fluctuation in the number of colloidal particles (radius ~ 45 nm) in a small volume element ($\sim 8 \mu\text{m}^3$) of an aqueous dispersion was measured by photon-correlation laser light scattering. Both randomly distributed, non-interacting particles and those showing a 'liquid-like' spatial arrangement owing to long-range repulsive Coulombic interactions were studied. The magnitude of the reduced fluctuations in the latter case agreed with that predicted from the structure of the dispersion, which was determined independently from the angular dependence of the average scattered light intensity. This provides the first direct experimental verification of the fundamental Ornstein-Zernike relationship between number fluctuations and the pair distribution function $g(r)$ in a system of interacting particles. Possible extensions of the experiment, including the measurement of four-particle correlations, are discussed briefly.

1. Introduction

One of the simplest results of the grand canonical ensemble relates fluctuations $\Delta M = M - \langle M \rangle$ in the number M of interacting particles in a fixed volume V to the two-particle radial distribution function $g(r_{12})$ (see e.g. Egelstaff 1967, p 15):

$$\frac{\langle \Delta M^2 \rangle}{\langle M \rangle} = 1 + \frac{\rho}{V} \int_V d^3 r_1 \int_V d^3 r_2 (g(r_{12}) - 1), \quad (1)$$

where $\langle M \rangle$, the mean occupation number of V , is given by $\langle M \rangle = \rho V$, ρ is the number density of particles, $r_{12} \equiv |r_1 - r_2|$, r_i being the position of particle i , and the angular brackets indicate ensemble averages. (This result was first obtained by Ornstein and Zernike (1914).) If the linear dimension of V , $\sim V^{1/3}$, is much larger than the distance over which structure in $g(r_{12})$ persists, i.e. over which $g(r_{12}) - 1$ is significantly different from 0, equation (1) becomes

$$\langle \Delta M^2 \rangle / \langle M \rangle = 1 + \rho \int d^3 r (g(r) - 1). \quad (2)$$

On the other hand, thermodynamic fluctuation theory relates number fluctuations to the isothermal compressibility χ_T of the system (e.g. Egelstaff 1967, p 21):

$$\langle \Delta M^2 \rangle / \langle M \rangle = kT\rho\chi_T, \quad (3)$$

where k is Boltzmann's constant and T the absolute temperature. Combination of (2) and (3) gives

$$S(0) = kT\rho\chi_T, \quad (4)$$

where the structure factor $S(K)$ is given by

$$S(K) = 1 + \rho \int d^3r e^{i\mathbf{K}\cdot\mathbf{r}} (g(r) - 1). \quad (5)$$

$S(K)$ can be measured in scattering (neutron, x-ray or light) experiments where \mathbf{K} is the scattering vector. If χ_T is known for the system, equation (4) can be used to check the $K \rightarrow 0$ extrapolation of the data, since small- K (small-scattering-angle) measurements are notoriously prone to error.

However, there does not appear to have been any direct experimental verification of equation (1). This is not surprising if the particles are atoms or molecules, since extremely small volumes would have to be probed to obtain a measurable fluctuation. (Nevertheless, recently developed techniques of laser-induced resonance ionisation have been used to detect number fluctuations of *non-interacting* atoms (Hurst *et al* 1977).)

Here we report an experimental test of equation (1). The system studied was an aqueous dispersion of charged colloidal spheres of radius about 45 nm which interact through repulsive electrostatic forces over distances as large as 1 μm , providing a 'liquid-like' spatial arrangement of the particles. Both the static and dynamic (interacting Brownian motion) properties of these systems have been investigated over the past few years by laser light scattering (see e.g. Brown *et al* 1975, Pusey 1979 for further references). Here we also use a light-scattering technique to probe the number fluctuations: a small volume V , $\sim(2 \mu\text{m})^3$, within the sample was defined by a highly focused laser beam and a small detection aperture. Under appropriate conditions (defined in § 2) the detected intensity is simply proportional to $M(t)$, the instantaneous occupation number of V , which fluctuates as particles diffuse in and out of V . Thus processing the detector signal by standard photon-correlation techniques provides estimates of the temporal autocorrelation function $\langle M(0)M(\tau) \rangle / \langle M \rangle^2$ of the number fluctuations as well as its $\tau = 0$ value $\langle M^2 \rangle / \langle M \rangle^2$.

For repulsive interactions $S(0) < 1$ (figure 1) so that, when compared with a non-interacting system ($S(K) = 1$), equations (2) and (5) predict, not surprisingly, reduced number fluctuations. Qualitative comparison of data obtained from an interacting system with that obtained from a system in which the electrostatic interactions are suppressed by residual electrolyte (see § 3) shows a marked effect (figure 3). (Indeed, visual microscopic observation of the scattering volume showed distinctly less 'graininess' in the image of the interacting system.) Quantitatively, if we define the right-hand side of equation (1) by

$$S'(0) = 1 + \frac{\rho}{V} \int_V d^3r_1 \int_V d^3r_2 (g(r_{12}) - 1), \quad (6)$$

then the values of $\langle \Delta M^2 \rangle / \langle M \rangle = 0.218 \pm 0.021$, obtained from photon-correlation spectroscopy, and of $S'(0) = 0.182 \pm 0.022$, obtained by numerical integration of structure factor data (§ 2, equation (26)), just agree within estimated experimental error. (Note that $S'(0) \rightarrow S(0)$ for large enough V .)

In § 2.1 we outline the light-scattering theory in terms of the simple picture given above. In § 2.2 and the appendix a more complete theory is described which takes account of the fact that in the experiment the scattering volume is not uniformly illuminated and assumes instead a 'three-dimensional Gaussian' illumination profile. In § 3 the experiment is described, and in § 4 the results are analysed. Finally in § 5 we discuss some implications and possible future developments of this type of experiment.

These include investigations of systems with attractive long-range forces, e.g. reversibly aggregating colloids, and the possibility of measuring higher-order analogues of $g(r)$, e.g. four-body correlation functions.

Colloid statistics is a time-honoured subject dating back to the work of Svedberg, Westgren and others in the early 1900s (see Chandrasekhar 1943 for a review). Light-scattering techniques were first applied to these studies in 1972 by Schaefer and Berne (see Pusey 1977 for a review, also Weissman *et al* 1976, Webb 1976 for other applications). However, all these experiments involved *non-interacting* particles, and the present experiment seems to be the first to measure the effect of interactions on number fluctuations. Nevertheless, some aspects of the theory have been considered by Berne (1977), including a derivation of equation (26).

2. Theory

2.1. Uniform illumination profile

The basic elements of the theory are most simply illustrated by assuming that the scattered light originates from a uniformly illuminated scattering volume V which is much smaller than the total sample volume V_T . The treatment proceeds on similar lines to that already given for non-interacting particles (Schaefer and Berne 1972, Pusey 1977). The complex amplitude of the scattered electric field can be written

$$E(t) = \sum_{i=1}^N b_i(t) e^{i\mathbf{K}\cdot\mathbf{r}_i(t)}, \quad (7)$$

where N is the (large) number of particles in V_T , $\mathbf{r}_i(t)$ is the position of particle i at time t , \mathbf{K} is the usual scattering vector, $K \equiv |\mathbf{K}| = (4\pi/\lambda) \sin(\theta/2)$, θ being the scattering angle and λ the wavelength of the light *in the medium*, and b_i is a 'counting' variable:

$$b_i(t) = \begin{cases} 1 & \text{if } \mathbf{r}_i \text{ is in } V, \\ 0 & \text{otherwise.} \end{cases} \quad (8)$$

(Since the results will ultimately be normalised, we have set the constant of proportionality in (7) equal to one.) Then, since the intensity is $I \equiv |E|^2$, the mean intensity is given by

$$\langle I \rangle = \sum_{i=1}^N \sum_{j=1}^N \langle b_i b_j e^{i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \rangle.$$

Although b_i is a function of \mathbf{r}_i , provided $V^{1/3} \gg K^{-1}$ it is a good approximation to regard b_i and $\exp(i\mathbf{K}\cdot\mathbf{r}_i)$ as uncorrelated (e.g. Pusey 1977, p 137), so that

$$\langle I \rangle = \sum_{i=1}^N \sum_{j=1}^N \langle b_i b_j \rangle \langle e^{i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \rangle. \quad (9)$$

In the presence of particle interactions \mathbf{r}_i and \mathbf{r}_j are correlated. However, for large enough K (where $S(K) = 1$), $\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)$ can, for $i \neq j$, be taken to be effectively uniformly distributed over intervals of 2π radians, so that only the $i = j$ terms survive in (9). Since $b_i^2 = b_i$ (equation (8)),

$$\langle I \rangle = \sum_{i=1}^N \langle b_i \rangle = N \langle b \rangle.$$

For a homogeneous system

$$\langle b \rangle = V/V_T, \quad NV/V_T = \langle M \rangle \quad (10)$$

and

$$\langle I \rangle = \langle M \rangle, \quad (11)$$

where

$$M(t) = \sum_{i=1}^N b_i(t) \quad (12)$$

is the instantaneous number of particles in V .

The intensity correlation function is

$$\langle I(0)I(\tau) \rangle = \sum_i \sum_j \sum_k \langle b_i(0)b_j(0)b_k(\tau)b_l(\tau) e^{i\mathbf{K} \cdot (\mathbf{r}_i(0) - \mathbf{r}_j(0) + \mathbf{r}_k(\tau) - \mathbf{r}_l(\tau))} \rangle. \quad (13a)$$

As before, we separate the phase and amplitude averages and assume large K . Then contributions arise only for $i = j, k = l$, including $i = j = k = l$ and $i = l \neq j = k$, so that the normalised intensity correlation function $g^{(2)}(\tau)$ is given by

$$g^{(2)}(\tau) \equiv \frac{\langle I(0)I(\tau) \rangle}{\langle I \rangle^2} = \frac{\langle M(0)M(\tau) \rangle}{\langle M \rangle^2} + \frac{1}{\langle M \rangle^2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \langle b_i(0)b_i(\tau)b_j(0)b_j(\tau) \rangle |F_S(\mathbf{K}, \tau)|^2, \quad (13b)$$

where (11) and (12) have been used. The first term in (13b) is the number fluctuation term, and the second term arises from interference between the (coherent) fields scattered by different particles; $F_S(\mathbf{K}, \tau)$ is the self-intermediate scattering function

$$F_S(\mathbf{K}, \tau) = \langle e^{i\mathbf{K} \cdot (\mathbf{r}(0) - \mathbf{r}(\tau))} \rangle. \quad (14)$$

If $V^{1/3} \gg K^{-1}$, $F_S(\mathbf{K}, \tau)$ decays rapidly compared with the factor containing the b 's, so that the latter can be taken to have its zero-time value. Then

$$g^{(2)}(\tau) = 1 + \frac{\langle \Delta M(0)\Delta M(\tau) \rangle}{\langle M \rangle^2} + \beta \frac{\langle M(M-1) \rangle}{\langle M \rangle^2} |F_S(\mathbf{K}, \tau)|^2, \quad (15a)$$

a form which clearly shows how number fluctuations can be measured by dynamic light scattering. At this stage we have inserted a spatial coherence factor β (≤ 1) which affects only the interference term and takes account of the finite size of the detector photocathode. It is convenient to define the number fluctuation part of (15a) by

$$g_{\text{NF}}^{(2)}(\tau) \equiv \langle \Delta M(0)\Delta M(\tau) \rangle / \langle M \rangle^2. \quad (15b)$$

Since $F_S(\mathbf{K}, \tau)$ decays rapidly compared with $g_{\text{NF}}^{(2)}(\tau)$, it is permissible to regard the intensity averaged over the (rapid) interference fluctuations as being simply proportional to the instantaneous occupation number $M(t)$ (see § 1).

As an illustration of equation (15a) we consider its $\tau = 0$ limit for three situations (see Pusey *et al* 1974):

(i) If M is Poisson-distributed (non-interacting particles), $\langle \Delta M^2 \rangle = \langle M \rangle$, so that

$$g^{(2)}(0) = 1 + 1/\langle M \rangle + \beta. \quad (16)$$

(ii) If M is constant (extreme repulsive interactions),

$$g^{(2)}(0) = 1 + \beta(1 - 1/\langle M \rangle). \tag{17}$$

(iii) If $\langle M \rangle \rightarrow \infty$,

$$g^{(2)}(0) = 1 + \beta. \tag{18}$$

For coherent detection, $\beta = 1$, equation (18) gives $g^{(2)}(0) = 2$, corresponding to a light field having Gaussian statistics; in (16) the intensity fluctuations are enhanced above Gaussian by the particle number fluctuations; in (17) number fluctuations are absent and interference fluctuations are reduced (see § 5).

In the case of arbitrary interactions we have, from (10) and (12),

$$\langle M^2 \rangle = \left\langle \sum_{i=1}^N b_i \sum_{j=1}^N b_j \right\rangle = N(N-1)\langle b_1 b_2 \rangle + \langle M \rangle. \tag{19}$$

Now

$$\langle b_1 b_2 \rangle = \frac{1}{V_T^2} \int_V d^3 r_1 \int_V d^3 r_2 g(|r_1 - r_2|) = \frac{V^2}{V_T^2} + \frac{1}{V_T^2} \int_V d^3 r_1 \int_V d^3 r_2 (g(r_{12}) - 1), \tag{20}$$

where $g(r_{12})$ is, as before, the pair distribution function. Thus, for large N ($V_T \gg V$), equations (10), (19) and (20) give the result of equation (1),

$$\langle \Delta M^2 \rangle / \langle M \rangle = S'(0), \tag{21}$$

where $S'(0)$ is defined by equation (6). We finally obtain, from (15a) and (21),

$$g^{(2)}(0) = 1 + S'(0)/\langle M \rangle + \beta(1 + S'(0)/\langle M \rangle - 1/\langle M \rangle). \tag{22}$$

It should be emphasised that equations (11), (13b), (15a) and (22) are only valid for large K , i.e. for scattering angles much greater than the position of the main peak in the structure factor $S(K)$, where $S(K) \approx 1$. The more complicated situation, where this inequality does not hold, is discussed briefly in § 5. (Of course, the value of equation (9) for arbitrary K is, when normalised by its large- K value, simply the structure factor.)

2.2. 3D Gaussian illumination profile

Because of diffraction it is impossible to produce a small, uniformly illuminated scattering volume. An illumination profile which has the advantage of providing theoretically tractable results and approximating the experiment (see § 4) is the ‘three-dimensional Gaussian’ (Schaefer 1973, Berne 1977, Pusey 1977), for which (cf equation (7))

$$E(t) = \sum_{i=1}^N e^{-r_i^2(t)/\sigma^2} e^{i\mathbf{K} \cdot \mathbf{r}_i(t)}, \tag{23}$$

where r_i is now measured from the centre of the scattering volume, and σ is the radius at which the illuminating intensity falls to e^{-2} of its maximum value ($\sigma \ll V_T^{1/3}$). The treatment is outlined in the appendix and, perhaps surprisingly, gives the same result as in § 2.1 (equation (22)) if we take $\langle M \rangle = \rho V$, where

$$V = (\pi\sigma^2)^{3/2} \tag{24}$$

and

$$S'(0) = 1 + \rho \int d^3r e^{-r^2/\sigma^2} (g(r) - 1) \quad (25)$$

(cf equation (6)). Using the transform of equation (5) (e.g. Brown *et al* 1975, equation (9)) gives

$$S'(0) = \frac{\sigma^3}{2\sqrt{\pi}} \int_0^\infty K^2 dK e^{-K^2\sigma^2/4} S(K), \quad (26)$$

whence $S'(0) = S(0)$ for large σ (large V). Equation (26) was first derived by Berne (1977), who also determined the time dependence of the number fluctuations; then $S(K)$ is replaced by $F(K, \tau)$, the coherent intermediate scattering function for the interacting system.

3. The experiment

Samples were prepared from a 10% (volume fraction) aqueous dispersion of polystyrene latex spheres supplied by the Dow Chemical Co. The nominal particle radius was 45 nm, and standard photon-correlation measurements gave a radius of 45 ± 2 nm. A dilution by a factor of approximately 640, corresponding to a particle number density $\rho \approx 4.09 \times 10^{11} \text{ cm}^{-3}$, provided the two samples to be discussed here. The 'interacting' sample, A, was filtered through a $0.22 \mu\text{m}$ pore Millipore filter into a clean quartz cell of dimensions $0.1 \text{ cm} \times 1 \text{ cm} \times \sim 4 \text{ cm}$ which contained a few grains of mixed acid-base ion-exchange resin. The 'non-interacting' sample, B, was prepared without ion-exchange resin in a Pyrex cell of similar dimensions. The samples stood for several weeks to allow the ion-exchange resin to remove residual electrolyte from sample A, so that the range of the interaction became comparable with the interparticle spacing.

Measurements of the time-averaged light-scattering intensity $\langle I(K) \rangle$ as a function of scattering angle θ were made with equipment described previously (Brown *et al* 1975, Pusey 1978) using a large scattering volume. Figure 1 shows the data, corrected only for

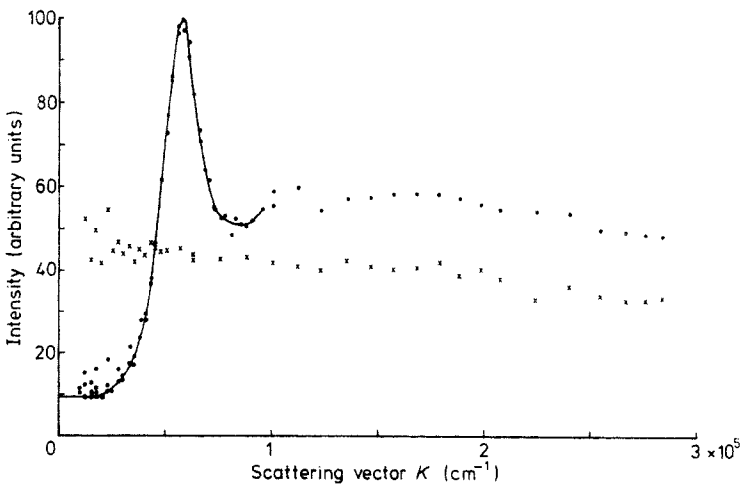


Figure 1. Time-averaged intensity (corrected for $\sin \theta$ dependence of scattering volume) as function of scattering vector K for 'interacting' sample A (full points) and 'non-interacting' sample B (crosses).

the $\sin \theta$ dependence of the scattering volume, as a function of the scattering vector K . Sample A shows the usual 'liquid-like' structure factor, implying considerable short-range ordering of the particles under the influence of the Coulombic interaction. Sample B, however, shows no obvious structure owing, presumably, to the shielding of the particle charges by the electrolyte both initially present and leached from the Pyrex cell walls. The slight fall-off in intensity for $K \geq 0.5 \times 10^5 \text{ cm}^{-1}$ is caused by intraparticle interference. At large enough K the interactions are unimportant, $S(K) \rightarrow 1$, and the ratio 1.47 ± 0.03 , of the intensities scattered by samples A and B can be taken as a measure of their relative concentrations. This difference, for samples of nominally the same concentration, is probably caused by dilution errors and possible partial retention of the latex by the filters. At small angles, $\theta \leq 15^\circ$, particulate contaminants of undetermined origin cause increased scatter in the data (figure 1) (see also Brown *et al* 1975, Pusey 1978). Occasionally the scattering volume was free of such contaminants and 'good' data were obtained for a few seconds. The full curve in figure 1 is a guessed 'best fit' which attempts to take account of this distortion. Extrapolation to $K = 0$ for sample B gave $\langle I_B(0) \rangle = 44.5 \pm 1.5$ so that, in the absence of interactions, $\langle I_A(0) \rangle$ would be $44.5 \times 1.47 = 65.4 \pm 2.6$. This value can then be used to normalise the intensity data for sample A to obtain $S(K)$. In particular, since $\langle I_A(0) \rangle = 9.5 \pm 1.0$, $S_A(0) = 0.145 \pm 0.016$.

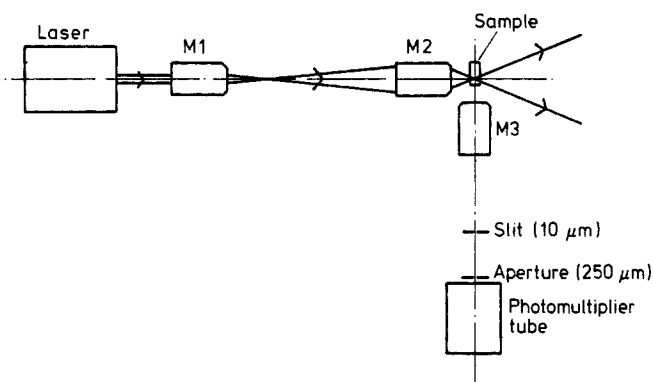


Figure 2. Layout of the optics (M1, M2 and M3 are microscope objectives).

Figure 2 shows the apparatus used to measure number fluctuations. The laser was a Spectra Physics Model 120 which, after attenuation by a factor 10, gave a power of about 0.8 mW at wavelength 633 nm *in vacuo*. The first microscope objective M1 ($\times 10$, numerical aperture (NA) 0.25) expanded the beam so that the second objective M2 ($\times 10$, NA = 0.25) was filled with more or less uniform illumination. This combination should give a focal spot diameter of order $1.22\lambda/2 \times \text{NA} \approx 1.5 \mu\text{m}$. The sample cell was placed with its short dimension parallel to the beam. Using microscope objective M3 (NA = 0.28) a magnified image (about $\times 20$) of the focal volume was cast on a vertical slit of width $10 \mu\text{m}$. Because of diffraction this arrangement will collect light from a region of length about $1.5 \mu\text{m}$ parallel to the beam. The slit was mounted on the front of the housing of an ITT FW 130 photomultiplier tube (PMT) whose photocathode (effective diameter 0.025 cm) was about 10 cm behind the slit. The PMT housing was itself mounted on an X-Y-Z micrometer positioning device, thus allowing the slit to be placed precisely in the centre of the image of the focal region of the laser beam to

provide the smallest scattering volume. The scattering angle was 90° , corresponding to a scattering vector $K = 1.87 \times 10^5 \text{ cm}^{-1}$. This is well above the structure in $S(K)$ for sample A (figure 1), so that the theory of § 2 applies.

The sample (along with objectives M2 and M3) was covered by a box to minimise air currents and consequent convection. Observation of the illuminated scattering volume with a microscope immediately after insertion of the sample showed residual cooperative streaming motions. However, after standing for an hour or two before making measurements, no convection or cooperative motion was evident. Room temperature remained in the range $22 \pm 1^\circ\text{C}$.

The photomultiplier tube was operated in the photon-counting mode. The dark count was less than 10^2 s^{-1} , which is negligible compared with the typical counting rates of 10^4 s^{-1} . Photon-correlation functions were constructed by a 'one-bit' 96-channel Malvern Instruments correlator, the duration of an experiment being typically 10^3 s . The correlator was used in the single-scaled mode to provide experimental estimates of the normalised intensity correlation function $g^{(2)}(\tau)$ (equation (13*b*)) (see Cummins and Pike 1974, 1977, for articles on the theory and practice of photon correlation).

Fine alignment of the slit-PMT combination was accomplished by adjusting its position until the number-fluctuation term in $g^{(2)}(0)$ attained its highest value (implying smallest $\langle M \rangle$ and V). Adjustment tolerance was found to be about 0.2 cm parallel to the scattering direction (i.e. in and out of focus) and about $50 \mu\text{m}$ perpendicular to this direction (i.e. along the incident beam). Taking account of the $\times 20$ magnification of the imaging system, this latter figure implies a tolerance of about $2.5 \mu\text{m}$ in the sample.

4. Data and analysis

Figure 3 shows the results of several measurements on both samples A (lower trace) and B (upper trace). Note that a wide range of times is spanned. Both samples show a rapid initial decay, virtually complete in 2 ms, owing to the interference fluctuations. The slower decays, extending to 1 s, reflect number fluctuations. The qualitative effect of the particle interactions is immediately obvious: although sample A is only slightly more concentrated than B, the amplitude of the number-fluctuation term is greatly reduced.

These amplitudes were determined by extrapolation to $\tau = 0$ after subtracting the interference contributions, measured in a separate large-scattering-volume experiment (where number fluctuations are negligible). The actual values, 0.037 ± 0.002 for sample A and 0.25 ± 0.02 for sample B, are indicated in figure 3(*b*). For the non-interacting sample B, $g(r) = S(0) = S'(0) = 1$, so that, from equation (22), $\langle M_B \rangle^{-1} = 0.25 \pm 0.02$ and $\langle M_B \rangle = 4.00 \pm 0.32$. For sample A, by use of the concentration ratio 1.47 (§ 3), $\langle M_A \rangle = 5.88 \pm 0.48$.

The optical arrangement used in this experiment (§ 3) obviously does not provide the 3D Gaussian scattering volume assumed in § 2.2. Nevertheless, diffraction probably causes the illumination to decrease as $1 - \alpha r^2 + \dots$ (where r is the distance from the centre of the scattering volume, and α is a constant), a feature it shares with the 3D Gaussian volume. Thus, for want of a better approach, we will assume that the treatment of § 2.2 applies. The validity of this assumption can be checked by the time dependence of the number fluctuations: for *non-interacting* particles in a 3D Gaussian volume, $g_{\text{NF}}^{(2)}(\tau)$, the number-fluctuation part of $g^{(2)}$ (equation (15*b*)), is given by (Pusey

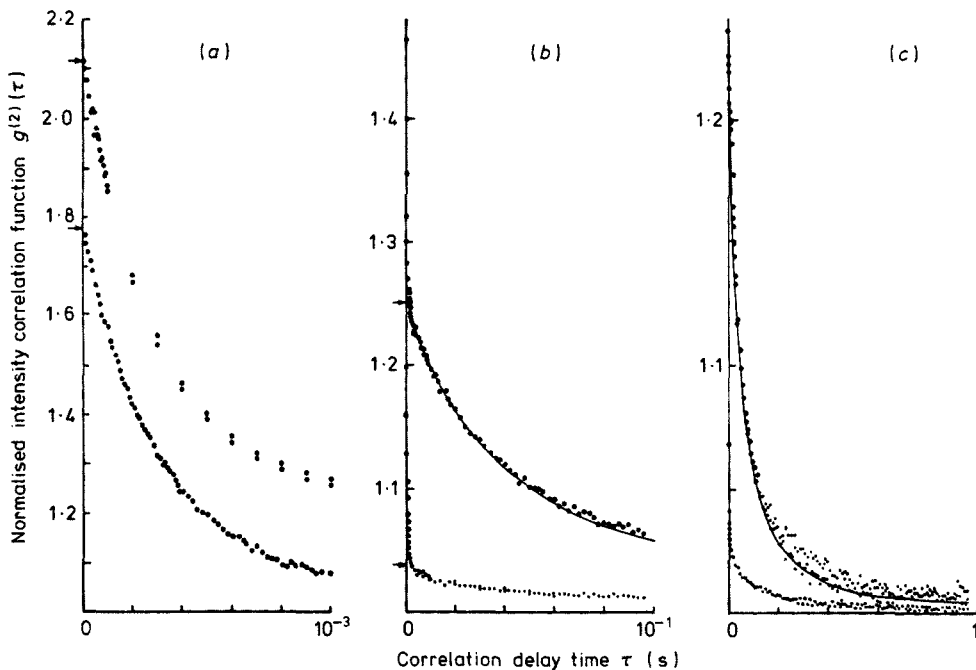


Figure 3. Composite correlation functions for sample A (lower traces) and sample B (upper traces). Note changing vertical and horizontal scales and wide range of delay times spanned. Arrows in (a) indicate zero-time intercepts $g^{(2)}(0)$ of full correlation functions (§ 5 and table 1). Arrows in (b) indicate zero-time intercepts $g_{NF}^{(2)}(0)$ of number-fluctuation parts of correlation functions. The full curve in (b) and (c) is a fit of the number-fluctuation term for sample B to the theoretical expression, equation (27).

1977, equation (4.29))

$$g_{NF}^{(2)}(\tau) = \langle M \rangle^{-1} (1 + 4D\tau/\sigma^2)^{-3/2}, \tag{27}$$

where D is the particle diffusion coefficient, and σ the radius of V (§ 2.2). The full curve in figures 3(b) and 3(c) is (27) with $\langle M \rangle = 4$, $D = 5.025 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (the expected value at 22 °C) and $\sigma = 1.1 \text{ }\mu\text{m}$ (chosen to give a ‘good fit’ as judged by eye). Thus equation (27) provides a good description of the data except in the tail of the correlation function. This value of σ is not too different from the rough estimate, $0.75 \text{ }\mu\text{m}$, given in § 3.

Using the structure-factor data taken from the full curve of figure 1, and taking $\sigma = 1.1 \pm 0.05 \text{ }\mu\text{m}$, we obtain, by numerical integration (with step $dK = 2 \times 10^3 \text{ cm}^{-1}$) of equation (26), $S'(0) = 0.182 \pm 0.022$. As mentioned in § 1, this compares favourably with $\langle \Delta M_A^2 \rangle / \langle M_A \rangle = 0.218 \pm 0.021$, obtained from $g_{NF}^{(2)}(0) = 0.037 \pm 0.002$ and $\langle M_A \rangle = 5.88 \pm 0.48$ (see above). Note that $S'(0)/S(0) = 1.26$ (§ 3), so that, for the small scattering volume used in this experiment, the approximation leading to equation (2) (which is frequently quoted without qualification) is in error by more than 25%. Values of various measured and derived quantities are collected in table 1.

Finally, we can check the internal consistency of the data by comparing the particle number densities for sample A determined in three different ways: (i) from the dilution factor (§ 3); (ii) from the intercept of the number fluctuation term (above); (iii) from the position K_{max} of the main peak in $S(K)$. In this last method we use the results of

Table 1. Summary of numerical results (see text for further explanation).

Quantity		Sample A	Sample B
$g_{\text{NF}}^{(2)}(0)$	$(=\langle \Delta M^2 \rangle / \langle M \rangle^2)$	0.037 ± 0.002	0.25 ± 0.02
$\langle M \rangle^\dagger$		5.88 ± 0.48	4.00 ± 0.32
$\langle \Delta M^2 \rangle / \langle M \rangle$	$(= \langle M \rangle g_{\text{NF}}^{(2)}(0))$	0.218 ± 0.021	
$S'(0)$	(from measured $S(K)$)	0.182 ± 0.022	
$g^{(2)}(0)$		1.775 ± 0.010	2.114 ± 0.015
$S'(0)$	(from magnitude of interference fluctuations)	0.142 ± 0.169	
$\langle M \rangle$	(nominal, from dilution factor)	3.03	
$\langle M \rangle$	(from peak in $S(K)$)	4.07 ± 0.59	

† For (non-interacting) sample B, $\langle M_B \rangle = (g_{\text{NF}}^{(2)}(0))^{-1}$; for sample A, $\langle M_A \rangle$ is obtained from $\langle M_B \rangle$ and the concentration ratio (see § 3).

previous measurements (Brown *et al* 1975) which showed that, for ordered colloidal samples of the type used here,

$$K_{\text{max}} r_{\text{max}} / 2\pi = 1.18 \pm 0.02, \quad (28)$$

where r_{max} is the position of the main peak in $g(r)$. We then use the result for the 'packing fraction' f ,

$$f = \pi \rho r_{\text{max}}^3 / 6, \quad (29)$$

to obtain ρ . Previous measurements gave $f = 0.50 \pm 0.02$, although for 'random close packing', characteristic of atomic liquids, one expects $f = 0.64$ (e.g. Bernal and King 1968). Here we take $f = 0.57 \pm 0.07$ which, combined with $K_{\text{max}} = 0.59 \pm 0.01 \times 10^5 \text{ cm}^{-1}$ (figure 1) in (28) and (29), gives $\rho = 5.49 \pm 0.68 \times 10^{11} \text{ cm}^{-3}$. We take $V = 7.41 \pm 0.58 \text{ } \mu\text{m}^3$ (obtained from (24) with $\sigma = 1.10 \pm 0.05 \text{ } \mu\text{m}$) to give $\langle M_A \rangle = 4.07 \pm 0.59$. The three values of $\langle M_A \rangle$ are listed in table 1.

The low value of the nominal concentration is not serious, since the dilution factor could be in error by as much as 100%. However, the difference between the results of methods (ii) and (iii) is significant, and we mention two possible explanations. Firstly, as mentioned above, the scattering volume is not exactly 3D Gaussian as was assumed when calculating V . For example, if we take $\sigma = 1.2 \text{ } \mu\text{m}$, which would give a better fit in the tail of the correlation function (figure 3(b)), we obtain $\langle M_A \rangle = 5.28 \pm 0.74$ by method (iii). Secondly, the detection of any 'stray signal' (e.g. dark count, parasitic scattering by the cell walls, multiply scattered light arising from outside the primary scattering volume) will cause a reduction in $g_{\text{NF}}^{(2)}(0)$ and a consequent overestimate of $\langle M_A \rangle$ by method (ii). For example, 10% stray signal will cause a 21% reduction in $g_{\text{NF}}^{(2)}(0)$. Note, however, that both these possibilities should have much the same relative effect on the values of $g_{\text{NF}}^{(2)}(0)$ for samples A and B. Thus $\langle \Delta M_A^2 \rangle / \langle M_A \rangle$, the quantity of interest in this experiment, should be largely unaffected, since it is determined from the ratio of the $g_{\text{NF}}^{(2)}(0)$ values.

5. Discussion

The experiment described above provides what appears to be the first experimental verification of equation (1), which relates number fluctuations of interacting particles to

their radial distribution function. It seems likely that future experimental refinements could significantly reduce the error, at present about 10%, in the measurement of both $\langle \Delta M^2 \rangle / \langle M \rangle$ and $S'(0)$, thus providing a more stringent test.

Such tests of fundamental relationships are obviously important in their own right. On the other hand, if such relationships are taken as proven, experiments of the type described here can be used to provide information about the systems not easily obtained by other means. For example, consider equation (3): for a colloidal dispersion χ_T is the 'osmotic compressibility'

$$\chi_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \pi} \right)_T, \quad (30)$$

where π is the osmotic pressure of the particle system. Thus a measurement by light scattering of the number fluctuations $\langle \Delta M^2 \rangle / \langle M \rangle$ can provide an estimate of χ_T . As the dispersion is diluted, measurement of number fluctuations becomes easier (because the relative fluctuations are larger), whereas measurement of osmotic pressure or $S(0)$ by conventional means becomes more difficult. Number-fluctuation data obtained over a range of concentrations could then be integrated numerically to provide the osmotic pressures of extremely dilute dispersions of interacting particles. Such measurements could also be made on systems with significant attractive parts to the interparticle potential. An example is charged particles at higher ionic strengths than those considered here, where reversible aggregation can occur in the secondary minimum of the potential which arises from non-negligible dispersion (or van der Waals) forces (e.g. Long *et al* 1973). Here number fluctuations would be greater than for non-interacting particles.

Another extension of the experiment could provide correlation functions of higher order than the pair distribution function $g(r_{12})$. Consider equation (13a). By taking the scattering vector K to be much larger than the position K_{\max} of the main peak in $S(K)$, it was possible to separate the exponential into two terms as indicated in § 2. However, for $K \approx K_{\max}$ such a treatment is not possible, and the measured value of $g^{(2)}(0)$ will depend on the fourth-order distribution function $g_4(r_{12}, r_{23}, r_{34})$. (Note that the term containing g_4 will only be important if $V^{1/3}$ is not much larger than the range of the interparticle interaction (e.g. Pusey 1977, p 121).) It should also be possible to cross-correlate the outputs of two or more detectors placed at different angles corresponding to scattering vectors $K_1, K_2, \dots \approx K_{\max}$. Although higher-order correlation functions are harder to visualise than the pair functions and are difficult to obtain from experiment, they play an important role in the theory of liquids. An experiment of the type outlined above could be used, for example, to check the validity of the superposition approximation in which higher-order correlation functions are written in terms of products of the pair functions (e.g. Egelstaff 1967).

We conclude with two further comments:

(i) By using higher-power lenses it should be possible to obtain even smaller scattering volumes V than those used here. In fact, the trial use of objectives of numerical aperture 0.45 (instead of 0.25) did not provide a smaller V because of significant spherical aberrations caused by the plane air-glass and glass-water interfaces. However, special aberration-corrected lenses would circumvent this problem. It should be realised, however, that, because of diffraction, smaller scattering volumes will come at the expense of increased spread in scattering angle (and in scattering vector). In addition, experiments which involve varying the scattering angles of several detectors

will become difficult simply because of the physical bulk of lenses of high numerical aperture.

(ii) It can be seen from equation (22) that repulsive interactions ($S'(0) < 1$), in addition to causing a reduction in the number fluctuations, also reduce the amplitude of the interference fluctuation term (the last term in (22)). Thus a measurement of this amplitude provides, in principle, an independent estimate of $S'(0)$. The experimental values of $g^{(2)}(0)$ were found by extrapolation of several measurements with correlation sample times of 1 or 2 μs and are indicated in figure 3(a). For sample B, $g^{(2)}(0) = 2.114 \pm 0.015$, so that, from (16) with $g_{\text{NF}}^{(2)}(0) = 0.25$ (table 1), we obtain

$$\beta = 0.864 \pm 0.025. \quad (31)$$

For sample A, $g^{(2)}(0) = 1.775 \pm 0.010$; from (22), with $g_{\text{NF}}^{(2)}(0) = 0.037$, we obtain

$$\beta[1 - (1 - S'(0))/\langle M_A \rangle] = 0.738 \pm 0.01,$$

which, taking $\langle M_A \rangle = 5.88$ (table 1) and β from (31), gives

$$S'(0) = 0.142 \pm 0.169.$$

This value of $S'(0)$ is consistent with those determined by other means (table 1), but the error is much larger. Finally, we note that this is not far from the extreme case, considered in equation (17), of a *small fixed* number of scatterers giving rise to a light field showing 'less-than-Gaussian' fluctuations. This situation was discussed some years ago by Pusey *et al* (1974), but has (at least in light scattering) remained a theoretical curiosity until now.

Appendix. Light scattering with 3D Gaussian illumination profile

In this case the average intensity and intensity correlation function are given by equations (9) and (13a), with

$$b_i(t) = e^{-r_i^2(t)/\sigma^2}, \quad (A1)$$

where r_i and σ are defined in § 2.2. By the same arguments as those leading to (11) and (15) we obtain, for $K \gg K_{\text{max}}$,

$$\langle I \rangle = N \langle e^{-2r^2/\sigma^2} \rangle_{V_T} \quad (A2)$$

and

$$\begin{aligned} \langle I^2 \rangle &= \sum_{i=1}^N \sum_{j=1}^N \langle e^{2r_i^2/\sigma^2} e^{-2r_j^2/\sigma^2} \rangle_{V_T} + \beta \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \langle \exp^{-2r_i^2/\sigma^2} e^{-2r_j^2/\sigma^2} \rangle_{V_T} \\ &= N \langle e^{-4r^2/\sigma^2} \rangle_{V_T} + (1 + \beta) N(N-1) \langle e^{-2r_1^2/\sigma^2} e^{-2r_2^2/\sigma^2} \rangle_{V_T}, \end{aligned} \quad (A3)$$

where

$$\langle e^{-2r^2/\sigma^2} \rangle_{V_T} = \frac{1}{V_T} \int_{V_T} d^3r e^{-2r^2/\sigma^2}, \text{ etc.} \quad (A4)$$

and

$$\langle e^{-2r_1^2/\sigma^2} e^{-2r_2^2/\sigma^2} \rangle_{V_T} = \frac{1}{V_T^2} \int_{V_T} d^3r_1 \int_{V_T} d^3r_2 e^{-(2/\sigma^2)(r_1^2+r_2^2)} g(r_{12}). \quad (A5)$$

Thus, for $V_T^{1/3} \gg \sigma$,

$$\langle I \rangle = \frac{N}{V_T} \left(\frac{\pi\sigma^2}{2} \right)^{3/2}. \quad (\text{A6})$$

By transforming to sum and difference coordinates in (A5) and assuming $N \gg 1$, we obtain

$$\langle I^2 \rangle = \frac{N}{V_T} \left(\frac{\pi\sigma^2}{4} \right)^{3/2} + (1 + \beta) \frac{N^2}{V_T^2} \left[\left(\frac{\pi\sigma^2}{2} \right)^3 + \left(\frac{\pi\sigma^2}{4} \right)^{3/2} \int d^3r e^{-r^2/\sigma^2} (g(r) - 1) \right]. \quad (\text{A7})$$

Normalisation of (A7) using (A6) gives

$$g^{(2)}(0) \equiv \frac{\langle I^2 \rangle}{\langle I \rangle^2} = \frac{1}{(N/V_T)(\pi\sigma^2)^{3/2}} + (1 + \beta) \left(1 + \frac{1}{(\pi\sigma^2)^{3/2}} \int d^3r e^{-r^2/\sigma^2} (g(r) - 1) \right). \quad (\text{A8})$$

If we now take the scattering volume V to be

$$V = (\pi\sigma^2)^{3/2}, \quad (\text{A9})$$

so that the mean occupation number $\langle M \rangle$ is

$$\langle M \rangle = NV/V_T,$$

then

$$g^{(2)}(0) = 1 + S'(0)/\langle M \rangle + \beta(1 + S'(0)/\langle M \rangle - 1/\langle M \rangle), \quad (\text{A10})$$

where

$$S'(0) = 1 + \frac{\langle M \rangle}{V} \int d^3r e^{-r^2/\sigma^2} (g(r) - 1), \quad (\text{A11})$$

which are the results quoted in § 2.2. Finally, we note that, using (A6) and the definition of V given by (A9), we obtain

$$\langle I \rangle = \langle M \rangle / 2^{3/2},$$

not simply $\langle I \rangle = \langle M \rangle$ as one might naively expect.

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