Structure and dynamics of colloidal systems

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Abstract. Structural and dynamic properties of suspensions of colloidal particles have been studied extensively by static and dynamic scattering experiments. The theoretical analysis has been performed by applying and extending equilibrium and non-equilibrium theories of simple liquids to the case of interacting Brownian particles. A fairly well developed understanding of monodisperse systems has emerged for highly charged colloids and for systems with very short-range interactions. In this contribution two extensions will be discussed: (i) static scattering from polydisperse charge-stabilized systems, and (ii) the collective diffusion of weakly charged monodisperse particles, for which hydrodynamic as well as electrostatic interactions are of importance.

1. Introduction

The determination of structural and dynamical properties of suspensions of colloidal particles provides interesting and important applications and extensions of methods developed for simple liquids. Since colloidal suspensions and similar systems such as solutions of macromolecules and polymers, micellar solutions and microemulsions are of considerable importance in basic research as well as for technological applications, a wealth of experimental data is available. Among the experimental methods scattering experiments play an important role, as in other areas of condensed matter physics. Information about the structure is obtained from the angle dependence of the total scattered intensity, $I(k)$, whereas the dynamics of the scattering centres gives rise to fluctuations in the scattered radiation. Since the macroparticles scatter much more strongly then the solvent, the latter can be treated as an inert background and the time-dependent correlation function obtained by a dynamic scattering experiment can be expressed as

$$I(k,t) = nf^2 P(k)S(k,t). \tag{1}$$

Here it is assumed that all macroparticles are identical (monodisperse system); their number density is denoted by $n = N/V$, f is proportional to the volume of the particles and $P(k)$ is the form factor. For spheres, $P(k) = [6j_1(k\sigma/2)/k\sigma]^2$, where σ is the diameter and $j_1(x)$ the spherical Bessel function. Besides these single-particle

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properties, $I(k,t)$ depends on the correlations between the macroparticles, described by the dynamic structure factor

$$S(k,t) = \frac{1}{N} \sum_{i,j=1}^{N} \left\langle \exp\{\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{r}_i(t) - \boldsymbol{r}_j(0))\} \right\rangle. \tag{2}$$

Here, $\boldsymbol{r}_i(t)$ is the position of particle i at time t and the angle brackets denote an ensemble average. If in equation (1) $t = 0$, one obtains the result of the static scattering experiment, and $S(k, t = 0) = S(k)$ is the static structure factor. Since $S(k)$ is essentially the Fourier transform of the radial distribution function $g(r)$, the integral equation methods of liquid state theory can be used to calculate $g(r)$ from the interaction potential $V(r)$. Using the effective temperature- and density-dependent interaction potential (the DLVO potential), the results of the static experiments are related, by this procedure, to the functional form and to the parameters on which the effective potential depends. This method has been used to determine the effective charge on colloidal particles [1] or on micelles [2], assuming that the interaction potential is of the screened Coulomb type and that the system is monodisperse. The latter assumption is, however, often not fulfilled; instead there will be a distribution of sizes and of charges, and in the next section we will present results for the static scattering intensity of polydisperse systems. It will be shown in section 2 that several essential features of $S(k)$ are substantially changed as a function of the width of the size and charge distribution.

With regard to the dynamics the calculation of $S(k,t)$ requires an appropriate transport equation. Since the dynamics of typical colloidal particles is much slower than that of the solvent molecules, the separation of time scales can be used to simplify the Liouville equation to the level where only the momenta and coordinates of the macroparticles remain as dynamical variables; the resulting fluid of macroparticles is then described by a many-particle Fokker–Planck equation [3]. Because of the frequent collisions between macroparticles and solvent molecules the momentum of the macrofluid is not conserved, so that for most purposes the description can be further simplified to the level of the Smoluchowski equation [3], where the coordinates of the macroparticles are the only dynamical variables. The dynamics of the colloidal suspension is thus described as a fluid of interacting Brownian particles within the fluid of the solvent molecules. The main difference compared with a simple fluid arises from the presence of the solvent; it provides a friction coefficient, ζ_0, for each particle and it gives rise to a hydrodynamic interaction between macroparticles in addition to the potential $V(r)$ of direct interaction.

From the measurement of the dynamic structure factor $S(k,t)$ one deduces directly a generalized diffusion function

$$D(k,t) = -k^{-2}\partial \ln S(k,t)/\partial t \tag{3}$$

which reduces to the collective diffusion coefficient D_c in the hydrodynamic limit. For arbitrary times, $D(k,t)$ is a rather complicated object, since it incorporates all the rearrangements and relaxation mechanisms of the macroparticles. These memory effects have so far been calculated only for strong electrostatic interactions, where hydrodynamic interactions can be neglected [4]. If hydrodynamic interactions become very important, as in the case of hard-sphere systems, results for $D(k,t)$ are available only for short times [5]. For systems such as weakly charged colloidal particles and

ionic micelles, however, it is necessary to take both types of interactions, the repulsive screened Coulomb and the hydrodynamic interactions, into account [6,7]. In section 3 of this paper we will present results for the collective diffusion coefficient of such systems.

2. Structural properties of polydisperse suspensions

If there is a distribution of sizes and charges of macroparticles, equation (1) has to be generalized, since f and $P(k)$ depend on the size, and in equation (2) particles i and j will in general belong to different parts of the distribution. Representing the continuous size distribution by a mixture of p components, the scattered intensity can be written as [8]

$$I(k) = n\overline{f^2}\ \overline{P(k)}S^{\mathrm{M}}(k) \tag{4}$$

where $\overline{f^2}$ and $\overline{P(k)}$ are averages of f_α and $P_\alpha(k)$, $\alpha = 1,\dots,p$, over the size distribution and

$$S^{\mathrm{M}}(k) = \frac{1}{\overline{f^2}\ \overline{P(k)}} \sum_{\alpha,\beta=1}^{p} f_\alpha f_\beta B_\alpha(k) B_\beta(k) S_{\alpha\beta}(k) . \tag{5}$$

Here, $B_\alpha^2(k) = P_\alpha(k)$ and $S_{\alpha\beta}(k)$ are partial structure factors

$$S_{\alpha\beta}(k) = x_\alpha \delta_{\alpha\beta} + n x_\alpha x_\beta \tilde{h}_{\alpha\beta}(k) \tag{6}$$

where x_α denotes the mole fraction of species α and $\tilde{h}_{\alpha\beta}(k)$ the Fourier transform of the partial total correlation function $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$. The function $g_{\alpha\beta}(r)$ is related to the probability of finding a particle of species β at r given that there is a particle of species α at the origin.

   In a polydisperse system there are two competing mechanisms which determine the scattered intensity $I(k)$ as compared to the monodisperse case. On the one hand the larger particles of the distribution will contribute to $S^{\mathrm{M}}(k)$ more strongly due to the presence of $f_\alpha \sim V_\alpha \sim \sigma_\alpha^3$ in equation (5). On the other hand, the density fluctuations, contained by $S_{\alpha\beta}(k)$ at the lower end of the distribution, are expected to be stronger [9]. To settle this problem we solved numerically the coupled Ornstein–Zernike equations for the p-component system (with $p \leq 10$) with the thermodynamically consistent Rogers–Young (RY) closure scheme [10]. For the interaction potential we took the screened Coulomb potential between spheres of diameters and charges σ_α, z_α and σ_β, z_β. In figure 1 we present results for $S^{\mathrm{M}}(k)$ for systems with a fixed total volume fraction ϕ but different widths, s, of the size distribution. It should be noted that the condition of constant ϕ is different from keeping the number density constant. We assumed a continuous Schulz distribution for the particle size and we replaced it by a p-component histogram. The mean particle diameter $\langle\sigma\rangle$ is the same for all systems and the charge $z_{\langle\sigma\rangle}$ on the particles of size $\langle\sigma\rangle$ is also fixed. For the particles with $\sigma_\alpha \neq \langle\sigma\rangle$ we made the assumption that the charges scale as the surface areas of the particles, $z_\alpha \sim \sigma_\alpha^2$. There are three features to be noted: (i) the height of the principal peak of $S^{\mathrm{M}}(k)$ is reduced, its position is shifted to lower values of k

and the peak is broadened; (ii) the oscillations following the first peak are progressively washed out; (iii) for small k values $S^M(k)$ increases with s. In contrast to the monodisperse case, the peak position of $S^M(k)$ for $s \neq 0$ is no longer proportional to $n^{-1/3}$, the peak height is no longer a simple measure of the order in the system and $S^M(0)$ is not simply related to the compressibility K_T of the system. With regard to the last point, we have calculated K_T from the $S_{\alpha\beta}(0)$ and found that for a distribution with a standard deviation of only 10% $S^M(0)$ is already increased by a factor of three compared with the monodisperse case, whereas K_T is practically unchanged. There is a slight decrease of K_T with increasing s, indicating that the system becomes somewhat stiffer with polydispersity. These results show that thermodynamic data cannot directly be deduced from the scattered intensity at $k = 0$ for polydisperse systems. Further studies [11] have shown that experimental data for $S^M(k)$ can often be better described by allowing for some polydispersity, as compared to an interpretation in terms of a monodisperse suspension.
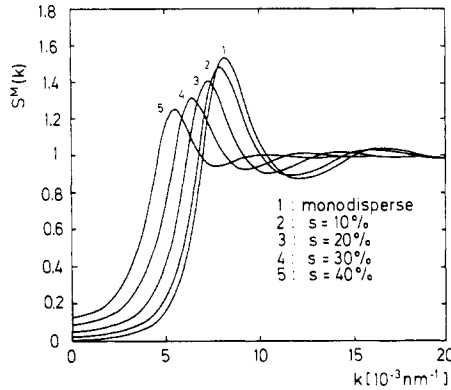
Figure 1. Static structure factor $S^M(k)$ as determined from the RY scheme for different degrees of polydispersity. The system is specified by a fixed volume fraction $\langle\phi\rangle = 1.1 \times 10^{-4}$, a mean particle diameter $\langle\sigma\rangle = 50$ nm, a charge on the particle of diameter $\langle\sigma\rangle$ of $z_{\langle\sigma\rangle} = 220\ e$ and by a Bjerrum length of 6.961 Å.

## 3. Collective diffusion in the presence of hydrodynamic interactions

The effects of hydrodynamic interactions have so far been extensively studied for hard-sphere systems. Precise results are known for the diffusion coefficients to linear order in the volume fraction ϕ for monodisperse systems [12]. At higher orders in ϕ it is necessary to consider many-body hydrodynamics [13]. In order to avoid the calculation of the complicated memory effects, which depend on both the direct and the hydrodynamic interactions, we consider the short-time limit of the diffusion function, equation (3). This quantity, which is essentially the initial decay of the experimentally determined correlation function, can be expressed as

$$D(k,0) =: D(k) = D_0 H(k)/S(k) \qquad (7)$$

where

$$H(k) = \frac{k_B T}{D_0 N k^2} \sum_{i,j=1}^{N} \left\langle \mathbf{k} \cdot \boldsymbol{\mu}_{ij}(\{\mathbf{r}_n\}) \cdot \mathbf{k} \exp[\mathrm{i}\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)]\right\rangle . \tag{8}$$

Here, $D_0 = k_B T/\zeta_0$ is the diffusion coefficient at infinite dilution and $\boldsymbol{\mu}_{ij}$ are mobility tensors which provide the relation between a force on particle j and the resulting velocity of particle i. These functions depend on the positions $\{\mathbf{r}_n\}$ of all particles. Using expressions for the mobility tensors for many-particle hydrodynamic interactions, Beenakker has derived [5,14] an expression for $H(k)$, which still depends on the structure of the suspension through the presence of the radial distribution function $g(r)$ or the static structure factor $S(k)$. We have used this expression together with the Ornstein–Zernike–RY scheme for $S(k)$ to calculate $H(k)$ and therefore $D(k)$. Good agreement has been found with experimental data on weakly charged colloids [7].
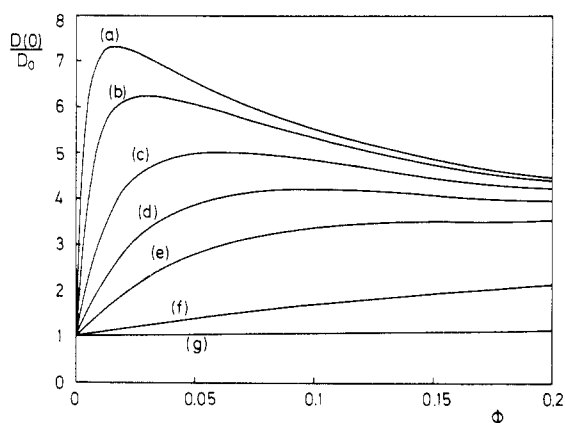
Figure 2. Dependence of the collective diffusion on the volume fraction. Particles have a diameter of 50 Å and a charge of 20 e. The different curves refer to the following concentrations of an additional 1:1 electrolyte: curve (a), 0.001 M; curve (b), 0.002 M; curve (c), 0.005 M; curve (d), 0.01 M; curve (e), 0.02 M; curve (f), 0.1 M. Curve (g) shows, for comparison, the corresponding hard-sphere results.

Another important case is provided by ionic micelles [6,15]. Their collective diffusion has been studied by light scattering at moderate volume fractions and as a function of salt added to the solution. By changing the salt content the repulsive interaction is changed, and therefore a variation of the diffusion is expected, whereas the hydrodynamic interactions remain the same. Since typical length scales in micellar systems are much smaller than the wavelength of light, it is sufficient to consider the limit $k = 0$ in equation (7). Figure 2 shows the results for the diffusion coefficient for a typical micellar system as a function of volume fraction ϕ for different amounts of added salt. As can be seen, the dependence of $D(0)$ on ϕ does not show a unique behaviour, but depends strongly on the system parameters. This can be traced back [16] to the interplay between an enhancement of diffusion by the lowered compressibility (the denominator $S(0)$ in equation (7) decreases with increasing ϕ) and an inhibition of diffusion due to hydrodynamic interactions (the numerator $H(0)$ decreases with increasing ϕ). In the case of weak screening of the electrostatic repulsion (curve (a) of figure 2) the compressibility decreases more strongly with increasing ϕ at low volume fractions than the hydrodynamic function $H(0)$, thus causing the strong increase of

$D(0)$. At higher volume fractions the further decrease of $S(0)$ is only weak and the hydrodynamic effects slow down the diffusion. As a result a maximum in $D(0)$ versus ϕ occurs. Such kind of behaviour has been observed experimentally [6, 15]. At higher salt concentrations the decreases of $S(0)$ and $H(0)$ become nearly comparable, but the decrease of $S(0)$ remains somewhat stronger, thus always leading to an enhancement of collective diffusion, as long as the direct interaction is repulsive.

There are clearly some limitations to the application of these results to real ionic micelles. We have assumed that the shape and the effective charge of the micelles are independent of volume fraction and of the amount of added salt. Furthermore, the counter-ions and salt ions have not been treated explicitly but only through the Debye screening parameter of the direct interactions. Whereas a more realistic treatment of ionic micelles is still missing, we have shown that the simplified model is sufficient to reproduce the main characteristic features of the experimental data.

Acknowledgment

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