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Self-diffusion and hydrodynamic interactions in highly charged colloids

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Abstract. Colloidal systems with a Yukawa interaction potential have been investigated by static and dynamic light scattering. By simultaneously measuring the dynamic and static properties of the colloidal systems we obtained the hydrodynamic function $H(Q)$ at different concentrations. Further the self-diffusion coefficient of highly ordered colloids was determined by tracer and FRAP measurements and compared with BD simulation and theoretical predictions.

1. Introduction

The diffusion coefficients in charged colloidal systems have been investigated very thoroughly in the last decade. Whereas the influence of direct interactions is now well understood, the influence of hydrodynamic interactions (HI) is much less studied and most theories are limited to the short time behaviour [1]. In a recent theoretical approach of Klein and Nägele it was shown that even at low concentrations the effective diffusion coefficient is altered by hydrodynamic interactions [2, 3]. To prove HI in the experiment it is necessary to measure the static and dynamic behaviour of ordered colloidal systems. For standard colloidal particles which have a high index of refraction these investigations involved multiple light scattering. To circumvent these problems, new model systems with a low index of refraction have been synthesized [4, 5]. With these new systems it is now possible to investigate the static and dynamic properties at high concentrations and still observe only single light scattering.

2. Theory

To obtain the interparticular structure factor $S(Q)$ from the experimental scattering intensity $I(Q)$ one has to use the following expression:

$$I(Q) \propto S(Q)P(Q). \quad (1)$$

The single particle form factor can be obtained from a dilute reference sample with screened electrostatic interactions. A cumulant expansion of the correlation function results in an effective Q -dependent diffusion coefficient $D_{eff}(Q)$. The hydrodynamic function $H(Q)$ is connected to $D_{eff}(Q)$ by:

$$H(Q) = D_{eff}(Q)S(Q)/D_0 \quad (2)$$

where D_0 is the diffusion coefficient of a dilute system without hydrodynamic and direct interactions. The hydrodynamic function is connected to the diffusion tensor D_{ij} by the following relation [2]:

$$H(Q) = \left\langle \frac{1}{ND_0} \sum_{l,j=1}^N \hat{Q} \cdot D_{lj}(\mathbf{R}^N) \cdot \hat{Q} \cdot \exp(i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)) \right\rangle. \quad (3)$$

In the limit of high Q -values the hydrodynamic function is identical with the short time self-diffusion coefficient. To calculate the hydrodynamic function it is necessary to have an expression for the diffusion tensor D_{ij} for collective diffusion on the one hand and D_{jj} for self-diffusion on the other hand. The two body problem is completely solved and the diffusion tensors can be written as a series in powers of R/r_{lj} [1], but for higher concentrations one has to include higher body contributions. A general expression for hard spheres, which is also valid at higher concentrations, has been derived by Beenakker and Mazur [6]. In the case of charged colloidal particles, where interparticle distances are much larger, it is possible to use the simplified approach of Klein and Nägele [2]. Concerning the influence of the hydrodynamic interactions on the long time diffusion coefficients there is some evidence from experiments and theory that for charged systems an increase by HI can be observed [2, 7]. For the reduced long time self-diffusion $D^* = D_s^L/D_0$ the following relation has been derived [8]:

$$D^* = \left(1 + \frac{1}{6\pi^2 n_p} \int_0^\infty dQ Q^2 \frac{[S(Q) - 1]^2}{1 + FS(Q)} \right)^{-1} \quad (4)$$

where in the earlier version $F = 1$ was used and later it was modified to $F = D^*$.

The long time diffusion coefficient can be experimentally determined by different techniques such as field gradient NMR, dynamic light scattering or by FRAP (fluorescence recovery after photobleaching). The first two methods have the disadvantage that one cannot follow the whole time dependence of the self-diffusion coefficient and only the long time limit is accessible. Under the assumption that the interaction potentials of tracer and host particles are identical, the dynamic light scattering of the tracer particles gives the complete time dependence of the self-diffusion coefficient. The resulting self-intermediate scattering function can be written as:

$$F_S(Q, t) = \exp[-Q^2 w(t)] \{1 + \alpha_2 [Q^2 w(t)]^2 / 2! + (3\alpha_2 - \alpha_3) [Q^2 w(t)]^3 / 3! + \dots\} \quad (5)$$

where the α_n terms in the expansion contain non-Gaussian contributions, which can be neglected at low Q -values.

The function $w(t)$ is connected to the mean squared displacement by

$$w(t) = \langle [r_i(t) - r_i(0)]^2 \rangle / 6 \quad (6)$$

and the time dependent self-diffusion coefficient is defined as the slope of the mean squared displacement

$$D_S(t) = \frac{d}{dt} w(t). \quad (7)$$

3. Synthesis of charged colloidal particles

The perfluorocolloids were prepared by emulsion polymerization using a persulphate/bisulphate iron initiator as a radical starter. The details of the preparation procedure have been described previously [9]. As starting material for the perfluorocolloids we used 1H,1H,7H-dodecafluoro-1-heptylmethacrylate as monomer, which was polymerized in

a water–isopropanol mixture. To obtain large particles with a radius of 300 nm we had to perform a second polymerization starting from colloid particles of a radius of 80 nm.

The particle radius was determined by static and dynamic light scattering. As a second model system we used highly charged silica particles, which were prepared according to the Stöber synthesis [10]. The remaining hydroxyl groups of the silica particles were reacted with a functionalized silane, which was provided by Wacker Chemicals, Germany. The details of the synthesis and characterization were described recently [11].

For the FRAP measurements we attached cyanine dye YOYO-1 (purchased from Molecular Probes, USA) to the perfluorocolloids.

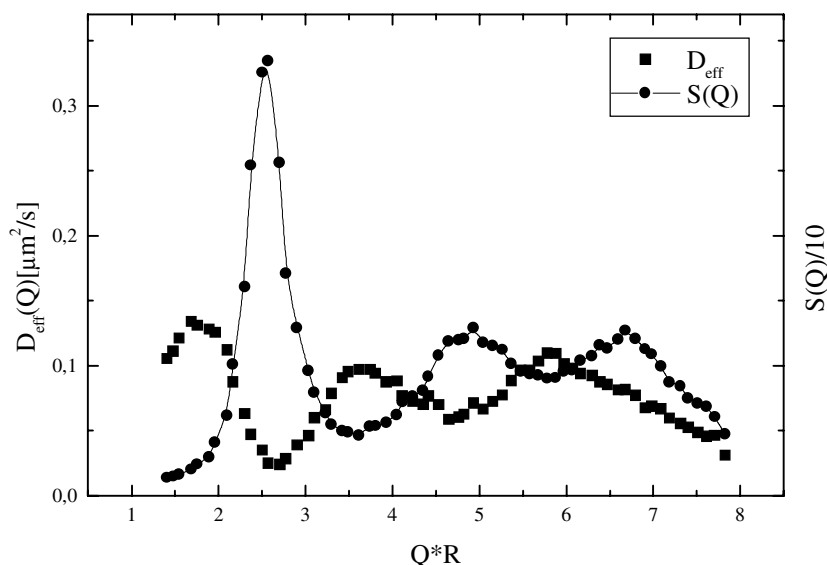


Figure 1. Structure factor $S(Q)$ and effective diffusion coefficient $D_{eff}(Q)$ for perfluorocolloids at a volume fraction of $\Phi = 0.24$ and a radius of 300 nm.

4. Results and discussion

4.1. Hydrodynamic function $H(Q)$ of highly charged systems

In a recent publication we have investigated the hydrodynamic function $H(Q)$ of highly charged silica colloids at low volume fractions [12]. The resulting experimental data are in excellent agreement to the theoretical predictions of Klein and Nägele [2]. An interesting question is now up to what concentration it is possible to use this theoretical approach which contains only two body hydrodynamic interactions. Therefore we prepared a sample of perfluorinated charged particles with a radius of 300 nm. The volume fraction of the sample is 0.24 and the corresponding structure factor and the effective diffusion coefficient are shown in figure 1. The experimental hydrodynamic function can now be obtained from equation (2) and the result is displayed in figure 2, where the Q -values are now multiplied by an effective radius to obtain an overlap between the experimental data and the hard sphere result of Beenakker and Mazur. The experimental $H(Q)$ function is much sharper than the theoretical one and the agreement is rather poor. The two body hydrodynamic approach predicts for our sample an $H(Q)$ function which should have a first maximum around 1.6, which shows that this theory cannot be applied

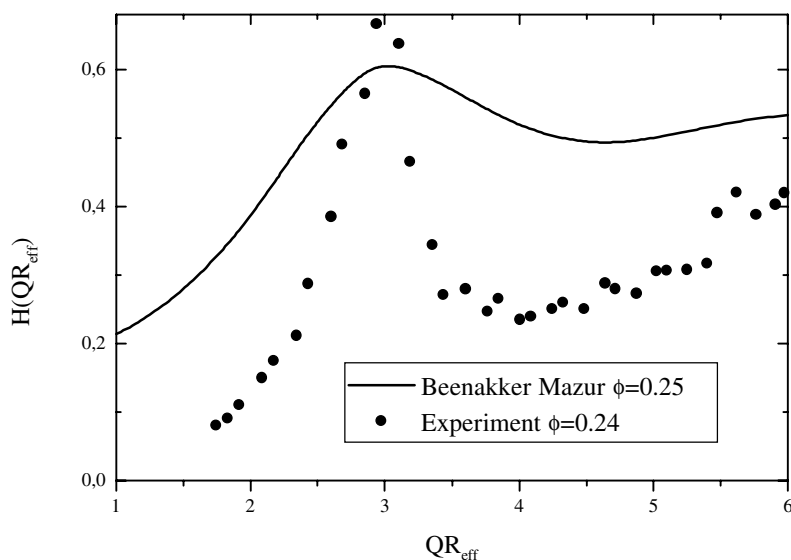


Figure 2. Experimental hydrodynamic function and hard sphere prediction of Beenakker and Mazur.

to concentrated systems; for such systems also the hard sphere theory fails even if one defines an effective particle radius.

4.2. Tracer diffusion and self-diffusion

In this section we want to treat the long time diffusion in highly charged colloids. The tracer diffusion measurements were done with perfluorocolloids as matrix particles and polystyrene as tracer particles with very similar sizes and interaction potentials. Two different samples were investigated and the ideal, corrected structure factors without the incoherent part, which contributes more than 90% to the total intensity, are displayed in figure 3, where the solid lines are the results of BD simulations.

For these simulations we used 432 particles interacting via a Yukawa potential in a cubic box with periodic boundary conditions. After equilibration of the system we performed 300 000 steps which correspond to a maximum time of 0.6 s to obtain good statistics in the range of several tens of milliseconds. The intention was now to compare the experimental $D_s(t)$ functions with the results of the simulation. Whereas the real systems are influenced by HI, the simulation was done without taking HI into account. Deviations between simulation and experiment at higher concentrations should give therefore some hints for HI. The results for the $D_s(t)$ -functions are given in figure 4 in reduced units for the two different samples: the higher concentrated sample shows a faster self-diffusion than predicted by the simulation, whereas for the dilute sample experiment and simulation agree well. This could be interpreted as an enhancement of the $D_s(t)$ -function by HI. Further evidence for this behaviour comes from our FRAP experiments. The experimental setup is nearly identical to the one described recently [13]. First we measured the structure factor of a completely deionized colloidal system with fluorescence dye by static light scattering and determined the parameters of the Yukawa potential by a BD simulation. Then with the same sample we determined the long time self-diffusion coefficient from FRAP measurements. Next a defined amount of salt was added and

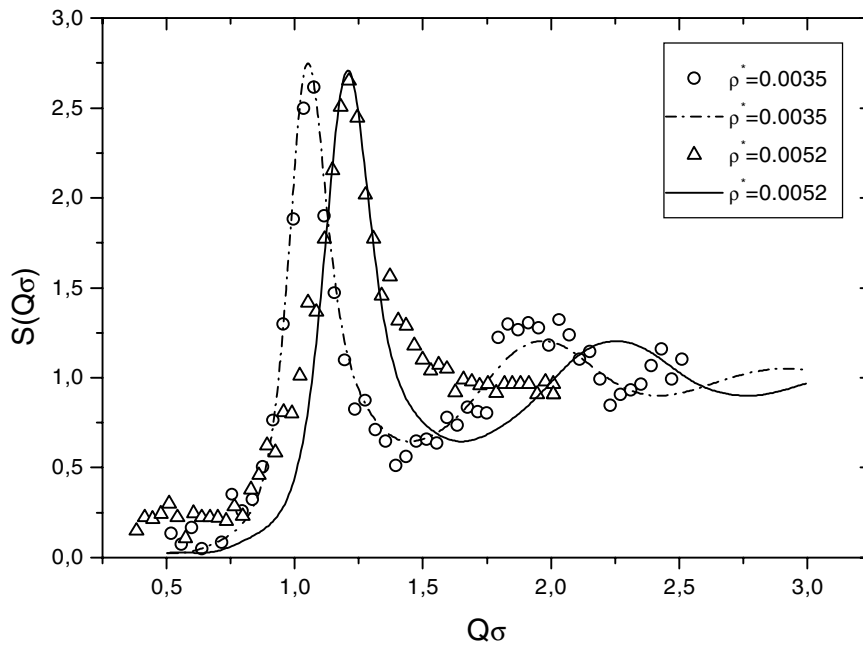


Figure 3. The incoherent scattering corrected structure factors and BD simulations for tracer systems. Here the symbols are experimental data and the lines are the BD results.

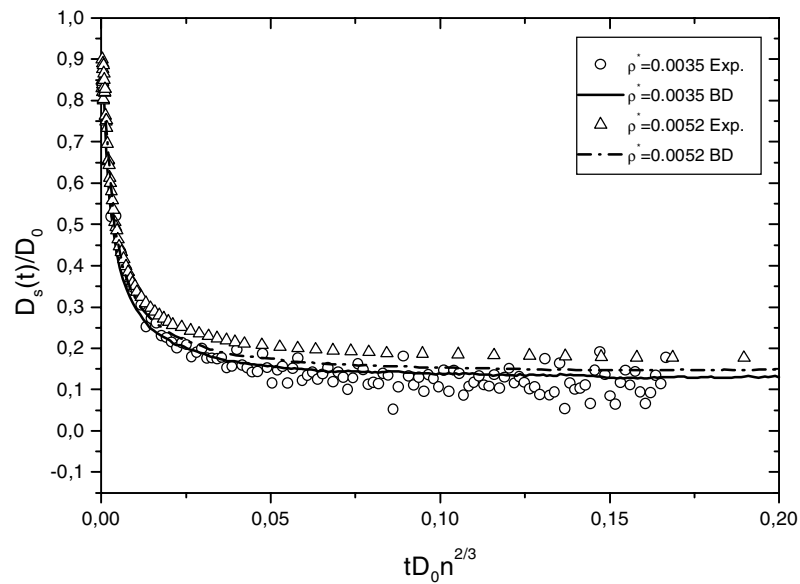


Figure 4. Same as figure 3, but now for the time dependent self-diffusion coefficient.

the static light scattering and FRAP measurements were repeated. The results for the D_s^L at different salt concentrations is shown in figure 5, together with the BD simulation and the theoretical predictions according to equation (4). Again the experimental values are above

the simulation results at all salt concentrations, but the differences decrease with increasing salt concentrations. If one compares the experimental data with the theoretical calculations the agreement seems to be much better. It has been shown previously from BD simulations by Löwen and Szamel that the above mentioned theories are not reliable for highly charged systems close to a phase transition [14].

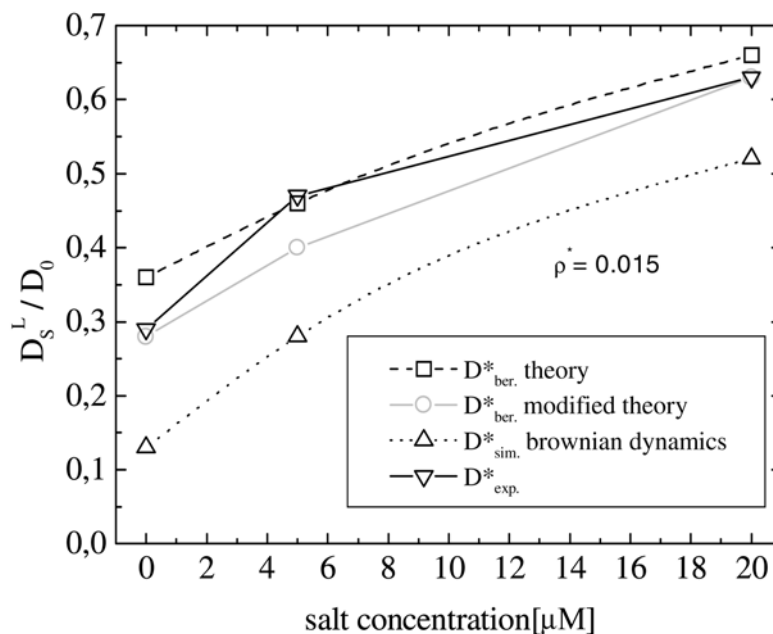


Figure 5. Experimental, simulated and theoretical long time self-diffusion coefficients at different salt concentrations.

5. Conclusions

Our present and recent [12] investigations show that HI influence the dynamic properties of highly charged colloids. Whereas in the low concentration limit the two body hydrodynamic approximation describes our experimental data well, it completely fails at higher concentrations, where many body interactions have to be taken into account. But also the more general approach of Beenakker and Mazur, which was developed for hard sphere systems, is not appropriate to model our data. Concerning the long time dynamics in our systems we have some evidence that the diffusion coefficients exhibit an enhancement induced by HI. This result is in accordance with recent experimental and theoretical investigations [7, 3]. We plan to extend our investigations to a larger concentration range and to incorporate the HI into our simulation procedure.

Acknowledgments

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