Rotational and Translational Short-time Diffusion and Sedimentation

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The short-time diffusional motion of interacting colloidal particles has been experimentally studied extensively in the past. With regard to short-time dynamics, only correlation times are considered much shorter than the time required for a particle to diffuse its own diameter. The experimentally accessible short-time transport coefficients characterising the particle dynamics, like the translational and rotational self-diffusion coefficients D_S^S and $D_S^{S,rot}$, respectively, and the sedimentation velocity U depend both on the solvent mediated hydrodynamic interaction (HI) and on the average spatial distribution of particles. The latter is determined by potential forces arising from the steric repulsion between hard-sphere-like particles and from electrostatic repulsion of overlapping counter-ion double layers for charged particles. HI leads in general to a retardation of short-time diffusional motion. For suspensions of hard spheres, it is well known that the short-time transport coefficients are expressible by a regular virial expansion in terms of the particle volume fraction ϕ with non-vanishing linear coefficient.

In extensive theoretical studies, we have shown that the dynamics of charge-stabilised colloidal suspensions is qualitatively different from that of hard sphere suspensions. In particular, the usual virial expansion in ϕ does not apply for the short-time transport coefficients of highly charged particles. Instead, we have theoretically predicted the following non-linear volume fraction dependencies of the transport coefficients, normalised by their values at infinite dilution [1]:

$$U/U_0 = 1 - 1.8\phi^{1/3} \quad (1)$$

$$D_S^S/D_0 = 1 - 2.5\phi^{4/3} \quad (2)$$

$$D_S^{S,rot}/D_0^{rot} = 1 - 1.2\phi^2 \quad (3)$$

Eqs. (1-3) hold for dilute suspensions of highly charged spherical particles with low salt content. The prefactors are nearly independent of the particle charge as long as the charge is sufficiently high to mask the steric repulsion. The $\phi^{1/3}$-dependence of the sedimentation velocity has been confirmed experimentally in sedimentation experiments. This dependence quantifies the strongly hindered settling of charged particles with long-range repulsion. As discussed in [2], $U/U_0 - 1$ exhibits a $\phi^{1/2}$-dependence under very restrictive conditions of low density and low particle charge. Recent dynamic light scattering (DLS) measurements of the short-time translational diffusion coefficient D_S^S have qualitatively confirmed the $\phi^{4/3}$-dependence [3].

Fig. 1 shows a comparison between our theoretical prediction for the normalised short-time rotational self-diffusion coefficient and depolarised DLS results [4] on highly charged particles. The theoretical hard sphere prediction is also included in Fig. 1. As seen, the predicted ϕ^2-dependence is in qualitative agreement with the experimental data. Meanwhile, Eq. (3) for $D_S^{S,rot}(\phi)$ has been

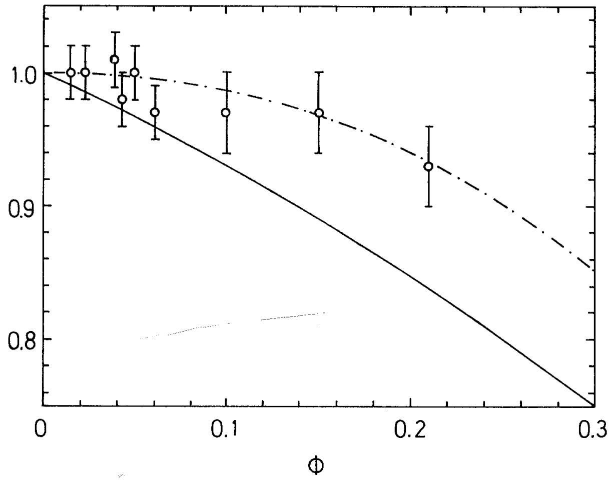

Figure 1: Dashed-dotted line: normalised short-time rotational diffusion coefficient vs volume fraction ϕ according to Eq. (3). Open circles: experimental data [4] for deionised suspensions of fluorinated polymer particles. Solid line: theoretical hard sphere result [6].

quantitatively confirmed up to volume fraction $\phi = 0.3$ using lattice-Boltzmann computer simulations [5].

Very recently, we have also considered short-time translational and rotational diffusion for a charged or neutral tracer sphere in a colloidal matrix of different particles [6,7].

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