Cooperative Diffusion and Glassy Dynamics in Colloidal Mixtures

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Suspensions of spherical colloidal particles have a variety of interesting dynamical properties, which are of general interest both in the areas of fundamental colloid science and applied chemical engineering. Unlike simple liquids, in which the molecular motion is ballistic and determined only by the intermolecular force law, the colloid dynamics is dissipative due to the intervening solvent which gives rise to Brownian motion and to long-ranged hydrodynamic interactions (HI). The many-body HI between the colloidal particles complicates the theoretical treatment of the colloidal dynamics considerably. There is a strong need for a unifying theoretical method to describe the colloidal dynamics on the basis of a microscopic model.

In recent articles, we have developed a general mode coupling theory (MCT) for calculating both dynamical and viscoelastic properties of many-component colloidal suspensions [1-3]. The self-consistent MCT has been deviced using a projection operator formalism based on the many-particle Smoluchowski equation governing the colloidal dynamics. The MCT accounts not only for direct particle interactions, but also in an approximate way for the far-field part of the solvent-mediated HI. Due to its generality, the MCT can be used, e.g., to study polydispersity and mixing effects of concentrated colloidal suspensions. This feature of the theory is particularly intriguing since experiments have revealed that size polydispersity or the mixing of suspensions of particles with different sizes and interactions strongly influence the dynamical and rheological behaviour. Another intriguing feature of the MCT is that it predicts a dynamic glass transition scenario where long-time diffusion ceases and the zero-shear viscosity diverges. The predictions of the MCT for the glass transition of hard sphere colloids have been found to be in good accord with experimental observations.

We have applied the MCT to study long-time diffusion, glass transition and viscoelastic behaviour of dispersions of charged and neutral colloidal spheres [3-5]. For these systems, various measurable quantities where calculated: dynamic structure factors, non-exponentiallity factors, self-intermediate scattering functions, particle mean square displacements, (dynamic) viscosities, memory functions, and a variety of long-time transport coefficients. The MCT has led to interesting predictions concerning the validity of generalised Stokes-Einstein relations relating diffusion and viscoelastic properties [4], and the influence of HI on the long-time diffusion of charge-stabilised colloidal particles [5,6]. These studies have established the MCT as a powerful method for predicting the suspension dynamics.

As an example, Fig. 1 shows MCT results for the self-intermediate scattering functions $G_\alpha(k,t)$ of small ($\alpha = 1$) and large ($\alpha = 2$) spheres of a binary colloidal hard sphere mixture [3]. We focus on the temporal relaxation at wave number $k = 3.53a_2^{-1}$ corresponding to the position of the primary peak of the large spheres static structure factor. Various total volume fractions ϕ are considered. As seen, for $\phi < \phi_c \approx 0.5185$ both $G_1(k,t)$ and $G_2(k,t)$ relax completely to zero, as

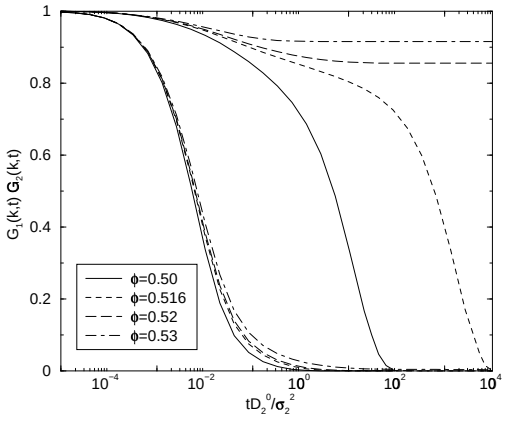

Figure 1: MCT results for the hard-sphere self-intermediate scattering functions $G_\alpha(k,t)$ for size ratio $\lambda_{21} = a_1/a_2 = 0.2$ and molar fraction $x_1 = 0.9$ at $ka_2 = 3.53$ as functions of dimensionless time for various volume fractions ϕ as labelled. Here, $\sigma_\alpha = 2a_\alpha$ and D^0_α are the diameter and Stokesean diffusion coefficient of α-type particles . From [3].

do the dynamic structure factors, indicating that the system is in a (possibly metastable) fluid state. For $\phi_c < \phi < \phi_{c2} \approx 0.53$, $G_2(k,t)$ of the large spheres shoes non-ergodic behaviour while $G_1(k,t)$ relaxes to zero. This suggests that the large spheres are localised over long times, whereas the small spheres execute interdiffusion in the matrix of structurally arrested large spheres. A localisation transition of this type has been observed experimentally by Imhof and Dhont [7] in binary colloidal hard sphere mixtures. The capability of MCT to predict such a localisation-delocalisation transition was first discovered for binary simple liquids [8].

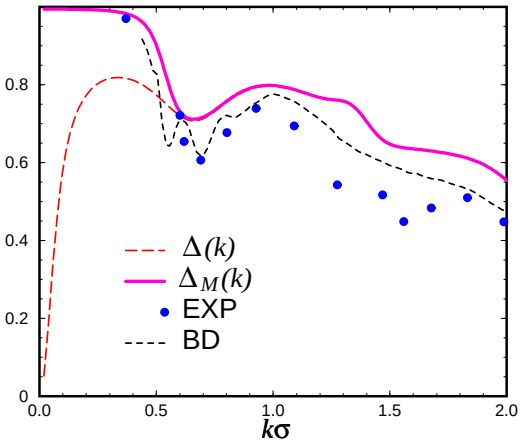

Figure 2: Measurable non-exponentiallity function $\Delta_M(k)$ of strongly correlated charged particles with 6 percent size polydispersity. Comparison between experimental data of Härtl et al. [10] (•), Brownian dynamics simulation data (short-dashed line) and MCT prediction (solid line). Also included is the MCT prediction for the non-exponentiallity function $\Delta(k)$ with zero size polydispersity (dashed line). From [5].

A measure of the non-exponential relaxation of the measurable dynamic structure factor $S_M(k,t)$ of one-component suspensions is the non-exponentiallity factor $\Delta_M(k) = 1 - \tau^S(k)/\overline{\tau}(k)$,where $\tau^S(k)$ denotes the short-time decay time of $S_M(k,t)$ and $\overline{\tau}(k) = \int_0^\infty dt S_M(k,t)/S_M(k)$ is the mean

relaxation time [5,6]. In Fig. 2, we compare MCT calculations of $\Delta_M(k)$ for a charge-stabilised suspension with experimental data and with Brownian dynamics simulation results. Considering the statistical fluctuations in the BD data, there is remarkably good agreement between theory and BD results. The small overestimation of the experimental non-exponentiallity can be attributed to the long-ranged part of HI, which is neglected both in the MCT [5] and BD calculations [9].

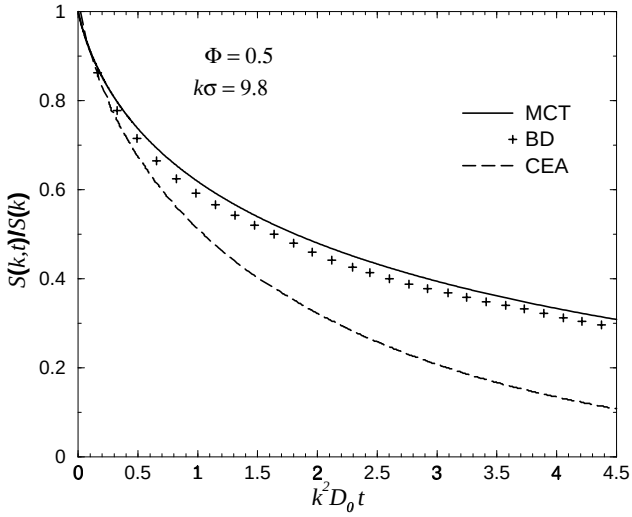

Figure 3: Dynamic structure factor of hard spheres without HI for volume fraction $\Phi = 0.5$ and reduced wave number $k\sigma = 9.8$ versus reduced time. From [5], with CEA and BD data taken from [10].

Fig. 3 includes our MCT results without HI for the hard-sphere dynamic structure factor $S(k,t)$, divided by the static structure factor $S(k)$, in comparison with Brownian Dynamics (BD) simulation data, and so-called contact Enskog approximation (CEA) results of Cichocki and Felderhof (cf. [10]). For the given large volume fraction $\Phi = 0.5$ and reduced wave number $k\sigma = 9.8$, the MCT result compares well with the BD data, whereas the relaxation of $S(k,t)$ is strongly overestimated in CEA.

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