Dynamic Scaling and related Freezing Criteria in Two and Three Dimensions

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In this project we have analyzed the static and dynamic scaling behavior of three-dimensional and quasi-two-dimensional (Q2D) colloidal dispersions with strong and long-range particle repulsions. Typical examples of such Q2D systems are monolayers of charged colloidal spheres between two glass plates interacting by long-range screened electrostatic interactions, and super-paramagnetic colloidal spheres located at a liquid-air interface and interacting by repulsive dipolar magnetic forces induced by a perpendicularly applied external magnetic field.

We have employed a Brownian Dynamics (BD) simulation method with the dominant far-field part of the hydrodynamic interactions (HI) included, to study the statics and dynamics of these Q2D systems with its implications on related static and dynamic freezing criteria [1,2]. For this purpose, various measurable quantities are calculated like the radial distribution function $g(r)$, the static structure factor $S(q)$, the mean squared displacement $W(t)$, the dynamic structure factor $S(q,t)$, and the distinct and self van Hove space-time correlation functions $G_d(r,t)$ and $G_s(r,t)$, respectively. An analogous study for three-dimensional salt-free dispersions of charge-stabilized particles was performed using a fully self-consistent mode-coupling scheme [3].

The radial distribution functions, $g(r) = G_d(r, t = 0)/n$, of these systems reveal a pronounced principal peak located at a radial distance, r_m, which is nearly equal to the geometric mean particle distance, $r_0 = n^{-1/d}$. Here, n is the number density of particles, and d denotes the system dimension. Since r_m is the only physically relevant static length scale, different systems sharing the same principal peak height $g(r_m)$ have radial distribution functions which superimpose nearly perfectly when plotted versus reduced distance r/r_0 (cf. Fig. 1). The static scaling behavior of the $g(r)$'s implies that the corresponding static structure factors nearly coincide when plotted versus the reduced wave number q/q_0 with $q_0 = 2\pi/r_0$. Without considering HI, there is a single characteristic time scale $\tau_0 = r_0^2/D_0$ associated with r_0. As a consequence there is dynamic scaling, i.e. colloidal systems with strong and long-range particle repulsion and identical peak heights $g(r_m)$ (likewise, identical $S(q_m)$) show nearly identical dynamical properties, e.g., nearly identical $G_d(r,t)/n$, , $W(t)/r_0^2$ and $S(q,t)$ as functions of reduced time $\tau = t/\tau_0$, distance $x = r/r_0$ and wave number $y = q/q_0$ (cf. Fig. 1 displaying $G_d(r,t)/n$ at time $t/\tau_0 = 0.035$).

Hydrodynamic interactions introduce the particle radius a as another relevant length scale since the particles are in contact with the solvent. With HI, a more restricted form of dynamic scaling holds where, e.g., the master curves for $G_d(x,\tau)/n$ and $D(\tau)$, defined by $D(\tau) = W(t)/(D_0 t)$, depend on the characteristic length ratio a/r_0. Furthermore, HI cause a modest enhancement of self-diffusion which becomes stronger with increasing a/r_0. The enhancement of self-diffusion is indicative of systems with prevailing influence of the far-field part of HI (cf. Fig. 2 showing $D(\tau)$).

The dynamic scaling behavior of systems with strong and long-range repulsion implies in particular a one-to-one correspondence between $S(q_m)$ and the non-dimensionalized long-time self-diffusion

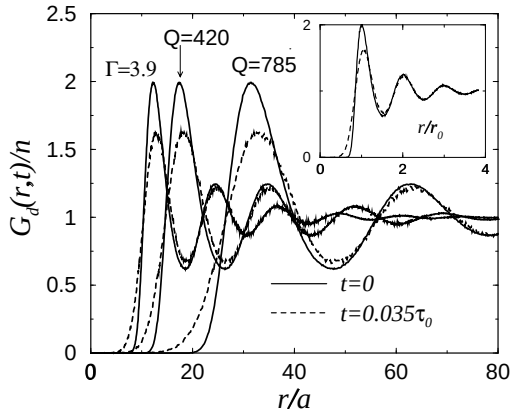

Figure 1: BD results for the distinct van Hove function $G_d(r,t)/n$ versus r/a of a magnetic dispersion with coupling parameter $\Gamma = 3.9$ and of two charge-stabilized Q2D systems of particle charge numbers $Q = 420$ and $Q = 785$, respectively. Note that $G_d(r, t = 0)/n = g(r)$ at $t = 0$. The inset exemplifies the static and dynamic scaling (from [1,2]).

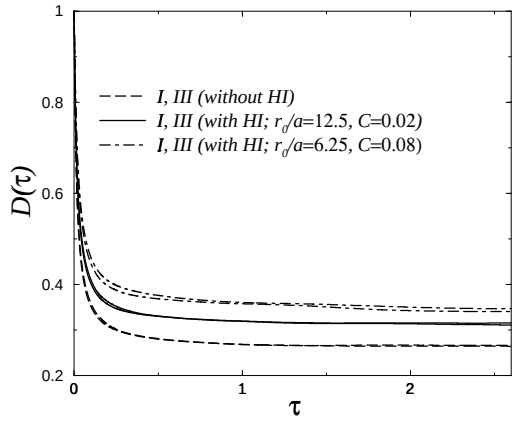

Figure 2: BD results with/without HI for the normalized self-diffusion coefficient $D(t) = W(t)/(D_0 t)$ of a magnetic systems, labeled by I, and a charged Q2D system, labeled by III, versus reduced time τ. Here, $C = \pi n a^2$ is the area fraction, and $S(q_m) = 2.2$ is constant for all systems considered in this figure (from [1,2]).

coefficient $D_S^L/D_0 = D(t \to \infty)$. Fig. 3a includes the master curve for D_S^L/D_0 vs. $S(q_m)$ as obtained for deionized three-dimensional dispersions of charge-stabilized particles using a fully self-consistent mode-coupling scheme without HI. Note that a peak height of $S(q_m) = 2.85$ corresponds to $D_S^L/D_0 = 0.1$. This result is in accord with an empirical static freezing criterion of Hansen and Verlet [4], which states that the onset of freezing in three-dimensional systems should occur when $S(q_m) \approx 2.85$, and with a dynamic criterion of Löwen, Palberg and Simon [5], which localizes the freezing line of three-dimensional Brownian systems at $D_S^L/D_0 \approx 0.1$.

Our BD results of D_S^L/D_0 vs. $S(q_m)$ for magnetic and charged Q2D dispersions with and without HI are displayed in Fig. 3b. Without HI, there is for Q2D systems again a single master curve, but now with $D_S^L/D_0 \approx 0.085$ and $S(q_m) \approx 5.5$ at freezing. This finding is in excellent accord with an empirically found dynamic criterion for two-dimensional freezing of Löwen [6] stating that $D_S^L/D_0 \approx 0.085$ at the freezing line independent of the pair potential and the nature of the

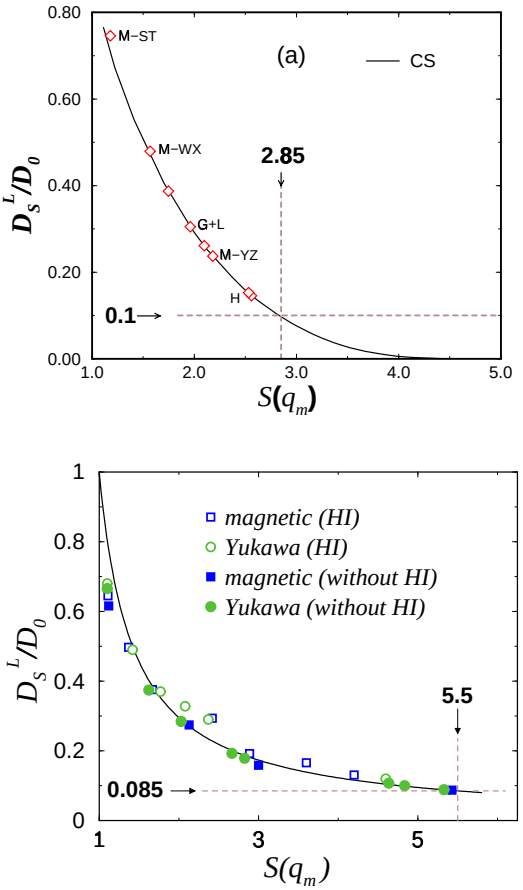

Figure 3: Reduced long-time self-diffusion coefficient D_S^L/D_0 vs. liquid static structure factor peak height $S(q_m)$. Mode-coupling results without HI (from [3]) for deionized three-dimensional bulk dispersions of charge-stabilized particles are included in (a). The particle interactions in (a) are described by a Yukawa-like screened Coulomb potential of DLVO type. BD results with/without HI for magnetic and charge-stabilized Q2D systems are shown in (b) (from [2,3]).

freezing process. Moreover, a value of $S(q_m) \approx 5.5$ at freezing was indeed found from computer simulations of Broughton et al. [7]

For three-dimensional and Q2D dispersions with strong and long-range particle repulsion we have thus shown that dynamic scaling is at the origin of the equivalence of related static and dynamic freezing criteria. According to Fig. 3b, the value of D_S^L/D_0 close to freezing is only modestly enlarged by HI, indicating that the dynamic freezing rule of Löwen et al. applies also when far-field HI are considered.

For systems with strong near-field HI and lubrication forces acting between the particles like dispersions of colloidal hard spheres, $D_S^S < D_0$, where D_S^S is the short-time self-diffusion coefficient. The dynamic freezing criterion should then be restated in terms of D_S^L/D_S^S instead of D_S^L/D_0.

Very recently, we have proposed novel dynamic freezing criteria for three- and two-dimensional colloids in terms of collective diffusion properties. A paper on these criteria has been submitted [8].

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