Diffusion and Rheology of Charged and Neutral Colloids

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A first principle calculation of rheological and diffusional properties of suspensions of spherical colloidal particles from the knowledge of their direct and hydrodynamic interactions (HI) is a major theoretical challenge. It is important to develop an understanding for the microscopic origin of the transport properties of these systems since they can serve as model systems for more complex colloids relevant to chemical and pharmaceutical industry.

In a series of recent articles, we have formulated and employed a fully self-consistent mode coupling theory (MCT) adjusted to describe the over-damped dynamics of neutral and charged colloidal particles. For concentrated hard-sphere dispersions, we used a short-time hydrodynamic rescaling procedure to approximate the strong many-body influence of the HI on the particle dynamics. Experimentally accessible dynamical quantities determined using the (rescaled) MCT comprise the suspension viscosity η, dynamic elastic storage and viscous loss moduli $G'(\omega) = \omega\eta''(\omega)$ and $G''(\omega) = \omega\eta'(\omega)$, mean-squared displacement $W(t)$, dynamic structure factor $S(q,t)$, long-time collective and self-diffusion coefficients, and collective and self-memory functions. Comparison of our MCT results with experiment and computer simulations leads to good agreement, particularly for systems with strong particle correlations (cf. [1,2]).

Fig. 1a shows MCT results for the volume fraction (i.e. Φ-) dependence of the reduced suspension viscosity η/η_0, where η_0 is the solvent viscosity. The HI-rescaled MCT is in good accord with the experimental data for η by Segrè et al. (Phys. Rev. Lett. **75**, 958 (1995)). There is also decent qualitative agreement between the MCT result for η without HI, and Brownian dynamics (BD) simulation results of Strating (Phys. Rev. E **59**, 2175 (1999). Notice the strong hydrodynamic contribution to the viscosity at larger Φ. MCT results for the reduced dynamic viscosities $R(\omega)$ and $I(\omega)$ without HI of a concentrated hard-sphere dispersion are included in Fig. 1b and compared with BD data of Heyes and Mitchell (J. Chem. Soc. Faraday Trans. **90**, 1931 (1994)), and a non-equilibrium HNC closure scheme of Lionberger and Russel (J. Rheol. **41**, 399 (1997)). The MCT is seen to be in better agreement with the simulation data than the HNC scheme. In Fig. 1c, MCT results for the reduced mean squared displacement $W(t)/(D_0 t)$ of hard spheres are compared with BD data of Cichocki and Hinsen (Physica A **187**, 133 (1992)). The agreement between MCT and BD improves with increasing Φ, with nearly coincident results for $\Phi = 0.45$

From our MCT calculations we were further led to interesting predictions concerning the validity of certain empirically found generalized Stokes-Einstein (GSE) relations linking low-shear viscoelastic properties to diffusion coefficients. Most of these GSE relations were shown to hold fairly well for hard-sphere dispersions, whereas the violation of the same GSE relations is predicted in case of charge-stabilized suspensions with long-range interactions (cf. [1]).

For an application of the fully self-consistent MCT scheme to charge-stabilized dispersions consider Fig. 2. This figure demonstrates the damping out of density fluctuation correlations with increasing correlation time t, quantified by the dynamic structure factor $S(q,t)$. The system parameters used for the results shown in the figure are typical of deionised aqueous dispersions of highly

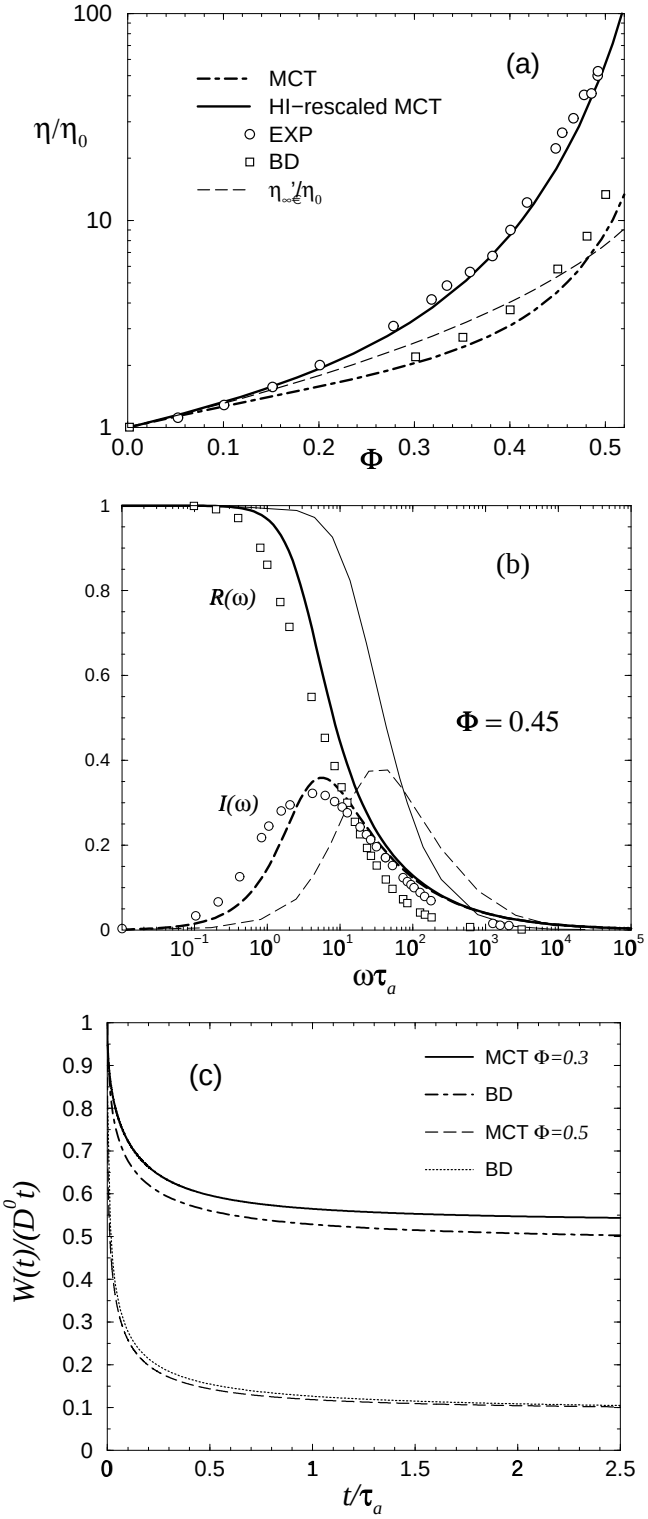

Figure 1: (a) Hard-sphere reduced viscosity η/η_0 in MCT with and without HI-rescaling vs. experimental data (Segrè et al.) and BD results without HI (Strating). Dashed line: high-frequency limiting viscosity η'_∞, normalized by η_0. (b) Real part $R(\omega) = (\eta'(\omega) - \eta'_\infty)/(\eta - \eta'_\infty)$ and imaginary part $I(\omega) = \eta''(\omega)/(\eta - \eta'_\infty)$ of the reduced dynamic viscosity for a concentrated hard-sphere suspension vs. reduced frequency $\omega\tau_a$, with $\tau_a = a^2/D_0$. Thick lines: MCT results; open symbols: BD data of Heyes and Mitchell; thin lines: non-equilibrium HNC closure scheme of Lionberger and Russel. (c) Reduced mean squared displacement for hard spheres at $\Phi = 0.3$ (upper two curves) and $\Phi = 0.5$ (lower two curves). Figures taken from [1,2].

charged colloidal spheres. Our MCT results for $S(q,t)$ are compared with BD data of Gaylor et al. (J. Phys. A **13**, 2513 (1980)), and with results of López-Esquivel et al. (J. Chem. Phys. **96**, 1651 (1992)) derived from a two-exponential approximation (SEXP) of $S(q,t)$ based on exact short-time moments. The MCT $S(q,t)$ is in excellent agreement with the BD results of Gaylor et al. even for the largest time $t = 1.6$ ms considered. The SEXP predicts a too rapid progression of structural relaxation.

It should be noted that charge-stabilized dispersions are qualitatively different from hard-sphere systems regarding the short-time and long-time transport properties, due to the combined influence of long-range electrostatic and hydrodynamic interactions. An important example is provided by the Φ-dependence of the sedimentation velocity U. For dilute suspensions of charged particles at low salinity, the reduced sedimentation velocity is well represented by the non-linear form $U/U_0 = 1 - p\,\Phi^{\alpha}$, with $\alpha = 1/3$ in case of strongly charged spheres and $\alpha = 1/2$ for weakly charged particles [3]. The exponent $1/3$ has indeed been observed in sedimentation experiments on strongly charged particles.

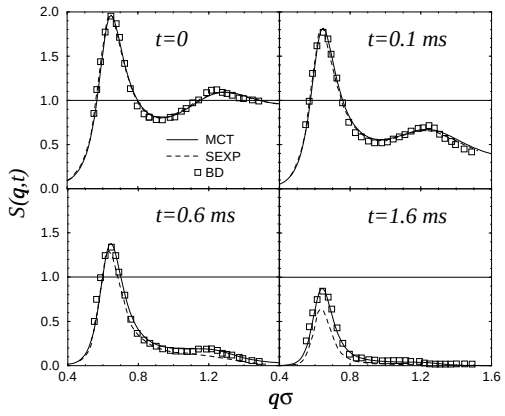

Figure 2: Dynamic structure factor of a deionized charge-stabilized dispersion. Solid lines: MCT results; dashed lines: SEXP results of López-Esquivel et al.; open squares: BD data (Gaylor et al.). Figure reproduced from [2].

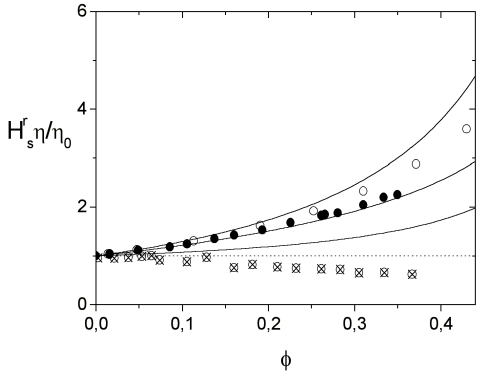

Figure 3: Experimental values for $H_s^r = D_s^r/D_0^r$ times semi-empirical results for η'_∞/η_0 at tracer/host size ratio $\lambda = 0.33$ and 1, and, for $\lambda = 10$, times the rescaled MCT result for η/η_0 (cf. Fig. 1a). Solid lines: theoretical predictions for $H_s^r\eta'_\infty/\eta_0$; the dotted line represents $H_s^r\eta'_\infty/\eta_0 = 1$. Figure taken from [4].

Aside from translational motion, colloidal spheres perform rotational Brownian motion which can be investigated experimentally by depolarized dynamic light scattering, time-resolved phosphorescence anisotropy (TPA), and NMR. So far, rotational diffusion is much less understood than translational diffusion, sedimentation and viscoelasticity. In a joint theoretical/experimental project, we have studied the (short-time) rotational diffusion of colloidal tracer spheres in a dense colloidal host fluid (cf. [4,5]). Experimental/theoretical results for the rotational diffusion coefficient, D_s^r, of a neutral tracer sphere in a hard-sphere host dispersion, normalized by its limiting value D_0^r at infinite dilution and multiplied by η'_∞/η_0 are displayed in Fig. 3. Note the approach towards a generalized Stokes-Einstein behavior $D_s^r \propto (\eta'_\infty)^{-1}$, and $D_l^r \propto \eta^{-1}$, with increasing tracer/host diameter ratio λ. The TPA data are qualitatively well described by our approximate theory, which accounts only for the asymptotically leading three-body HI, provided λ is not too different from one.

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