A Mode-mode Coupling Scheme of Colloidal Electrolyte Friction

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The dynamics of charge-stabilized dispersions consisting of highly charged colloidal particles (macroions) dispersed in a solution of weakly charged small counter- and coions (microions) has attracted considerable interest, both experimentally and theoretically. Theoretical work on charge-stabilized colloids has been mostly based on an effective macrofluid model of dressed macroions interacting by an effective pair potential of spherical symmetry, by integrating out the microionic degrees of freedom.

A major drawback of the dressed macroion model is that it does not account for the kinetic influence of the microionic atmosphere on the colloidal dynamics. The theoretical modeling and quantification of electrokinetic effects originating from the non-instantaneous relaxation of the microionic atmosphere is a demanding task even for a single spherical macroion diffusing in an unbounded multi-component electrolyte. In this case, light scattering experiments [1] have revealed that the diffusive motion of the microions relative to the large macroion gives rise to an increase (decrease) in the friction coefficient (sedimentation velocity) of the tracer macroion. As a consequence, the long-time self-diffusion coefficient, D_T^L, of the tracer has a minimal value when the thickness of the microionic cloud, as measured by the screening length κ^{-1}, is comparable to the radius a of the macroion (cf. Fig. 1).

The mean velocity, U, of a slowly sedimenting macroion in the presence of its neutrally buoyant electrolyte atmosphere is related to the long-time self-diffusion coefficient by $D_T^L = k_BT/(6\pi\eta a + \Delta\zeta_T) = D_T^0\, U/U^0$, where U^0 and D_T^0 are the Stokesian sedimentation velocity and the diffusion coefficient, respectively, of the tracer, and η denotes the solvent viscosity. The effect of the microion relaxation is embedded in the excess friction contribution $\Delta\zeta_T$. The statistical fluctuations of the microionic atmosphere around the colloidal tracer are coupled to the corresponding hydrodynamic fluctuations through the intervening solvent. Therefore, it is necessary to treat the steric and electrostatic direct interactions, and the hydrodynamic interactions (HI) between tracer and microions on equal footing.

Based on a recently formulated mode-mode coupling scheme for Brownian systems where HI has been included [2], and where the macroion and the microions are treated, equally, as charged hard spheres immersed in an unstructured solvent, we have calculated the long-time self-diffusion coefficient and the sedimentation velocity of the tracer [4]. According to Fig. 1, our mode-mode coupling results are in good agreement with the experimental data for D_T^L. An important conclusion drawn from our theoretical analysis is that the minimum of D_T^L at $\kappa a \approx 0.5$ is due to a combined effect of hydrodynamic and direct forces acting between macroion and microions. This fact should be contrasted with earlier approaches on electrolyte friction where it has been attempted to explain the minimum of D_T^L in terms of direct forces only (cf., e.g., [5,6]). In fact, the neglect of HI gives rise to a charge-independent contribution to $\Delta\zeta_T$. This additional friction contribution, in turn, leads to a monotonic decline of D_T^L with increasing ionic strength, as seen from Fig. 1, in conflict with experimental observation. The charge-independent friction contribution arises from the excluded volume interactions between the tracer and the point-like microions. With HI, the excluded volume contribution becomes quite small, since the microparticles are advected by the hydrodynamic flow field created by the moving tracer sphere.

The theoretical results in Fig. 1 are for point-like microions described by Debye-Hückel-type pair distribution functions. For dispersions of comparably small macroions like charged globular proteins and charged micelles, which are only a few nanometers in size, one needs to account for the finite sizes of the macroions.

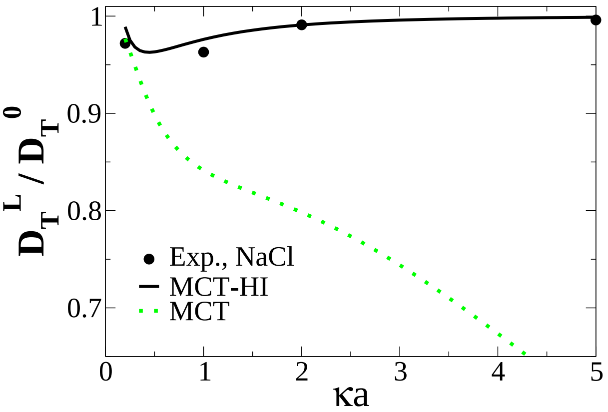

Figure 1: Mode-coupling theory (MCT) results with HI (solid line) and without HI (dotted line) for the normalized long-time self-diffusion coefficient D_T^L/D_T^0 vs. reduced screening parameter κa (from [3]). Without HI, D_T^L/D_T^0 is monotonically decreasing, in conflict with experimental observation. Experimental data points are taken from [1].

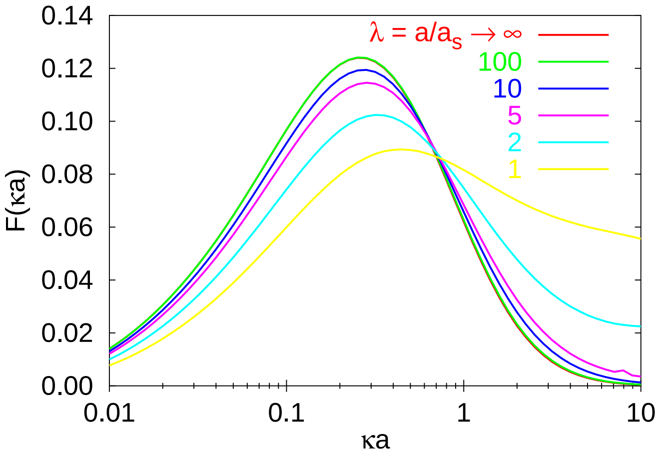

Figure 2: MCT results with HI for the reduced electrostatic part, $F(\kappa a)$, of the electrolyte friction coefficient $\Delta\zeta_T$. Various macroion-microion size ratios $\lambda = a/a_s$ are considered. From [4].

This has been achieved using mean spherical approximation expressions for the static pair correlation functions for differently sized charged spheres. Fig. 2 includes mode-mode coupling results for the reduced electrostatic part, $F(\kappa a)$, of the electrolyte friction coefficient $\Delta\zeta_T$ at various macroion-microion size ratios, $\lambda = a/a_s$, ranging from the colloidal limit $\lambda \rightarrow \infty$ to the bare electrolyte limit $\lambda \rightarrow 1$. As seen, finite size effects become significant for size asymmetries $\lambda \leq 10$.

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