Electrokinetic Effects in Charged Colloids

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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 (microionic atmosphere) has attracted considerable interest, both from the experimental and from the theoretical point of view. 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. To date, the screened Coulomb potential of Derjaguin-Landau-Vervey-Overbeek (DLVO) type is still the most widely used dressed macroion pair potential.

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 in case of 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 give 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 Debye screening length κ^{-1}, is comparable to the radius a of the macroion (cf. Fig. 1).

The sedimentation 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, D_T^L, by

$$D_T^L = \frac{k_B T}{6\pi\eta a + \Delta\zeta_T} = D_T^0 \frac{U}{U^0}$$

where U^0 and D_T^0 are the Stokesian sedimentation velocity and the diffusion coefficient, respectively, of the tracer. Furthermore η is, essentially, the solvent viscosity. The effect of the microions 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 appears to be necessary to treat the steric and electrostatic direct interactions (relaxation effect), and the hydrodynamic interactions (HI) between tracer and microions (electrophoretic effect) on equal footing for a proper treatment of the experimentally observed colloidal electrolyte friction and sedimentation effect.

Based on a recently formulated mode-coupling scheme for Brownian systems where HI has been included [2,3], and where the macroion and the microions are treated on equal footing as charged hard spheres immersed in an unstructured solvent, we have derived new analytical expressions for the (time-resolved) self-diffusion coefficient and the sedimentation velocity of the tracer [4,5]. As seen from Fig. 1, use of these expressions yields good agreement with the experimental data for D_T^L. We have further derived analytical expressions for the time-dependent generalization, $\Delta\zeta_T(t)$, of $\Delta\zeta_T$. The friction function $\Delta\zeta_T(t)$ includes the non-instantaneous memory contributions to the mean squared displacement of the tracer.

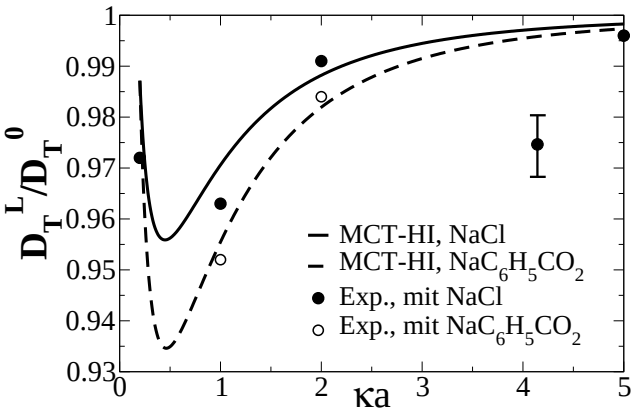

Figure 1: Normalized long-time self-diffusion coefficient D_T^L/D_T^0 versus reduced screening parameter, κa, for two different salts, NaCl and $NaC_6H_5CO_2$, respectively. Experimental data are taken from [1]. The lines are the results of our mode-coupling theory (MCT) with HI included [4,5].

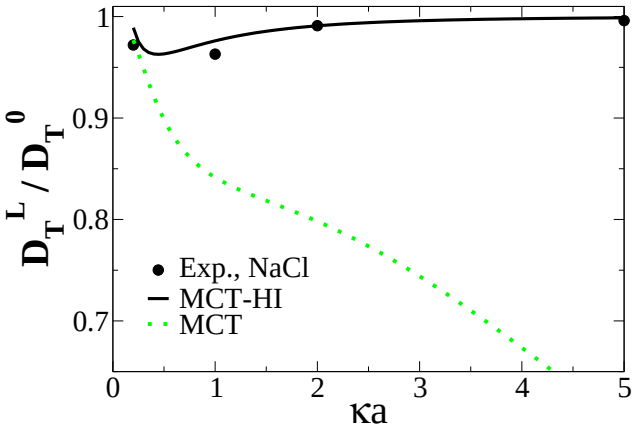

Figure 2: MCT results with HI (solid line) and without HI (dotted line) for D_T^L/D_T^0 vs. κa. Without HI, D_T^L/D_T^0 is monotonically decreasing, in conflict with experimental observation. Experimental data points are taken from [1].

An important conclusion drawn from our theoretical analysis is that the observed 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., [6,7]). 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. 2, 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 included, this excluded volume contribution becomes quite small [8] (i.e., it vanishes within the approximations made in [4,5]) since the microparticles are advected by the hydrodynamic flow field created by the moving tracer sphere (cf. Fig. 3).

Future extensions of this work will focus on electrokinetic effects in concentrated macroion dispersions with overlapping microionic atmospheres. This will allow to treat the primary and secondary electroviscous effects in a unified way.

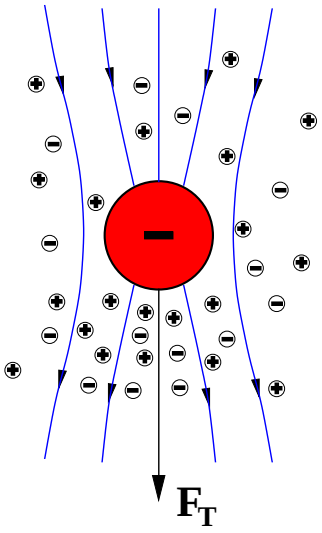

Figure 3: Sketch of the Stokesian stream lines of a negatively charged macroion with its associated microionic atmosphere of counter- and coions. The macroion sphere is acted on by a weak external force F_T.

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