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The role of hydrodynamic interactions in colloidal electrolyte friction and sedimentation

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Abstract. – Based on a recently formulated mode coupling scheme for Brownian systems, new analytical expressions are derived for the time-resolved tracer-diffusion, electrolyte friction coefficient and sedimentation velocity of a colloidal macroion suspended in a many-component electrolyte solution. Use of these expressions yields good agreement with experimental data and Booth's theory of macroion sedimentation. Our theoretical expressions allow for a separate assessment of the influence of hydrodynamic and potential forces on the relaxation of the electrolyte atmosphere. Inclusion of hydrodynamic interactions (HI) effects is shown to be essential for a proper description of colloidal electrolyte friction and sedimentation.

The dynamics of charge-stabilized dispersions of spherical colloidal particles has been studied for many years using various scattering techniques [1–3]. The Brownian dynamics of the colloidal macroions is commonly described in terms of an effective macrofluid model of dressed macroions interacting via an effective pair potential of spherical symmetry. The effective macroion pair potential has been determined on various levels of approximation from integrating out the degrees of freedom of the neutralising atmosphere of microions around the macroions [4, 5]. To date, the screened Coulomb potential of Derjaguin-Landau-Vervey-Overbeek (DLVO) type is still the most widely used dressed macroion pair potential. Here, the electrostatic screening effect of the microions is described in mean-field–like way by a screening parameter κ and an effective macroion charge [6].

While the effective macrofluid model has been successfully used as the basis for a theoretical description of the colloidal statics and dynamics [1–3], it is incomplete since it does not account for the effect of the non-instantaneous relaxations of the microion atmosphere on the colloidal dynamics. The theoretical modeling and quantification of these so-called electrokinetic effects originating from the microion cloud relaxation is a demanding task even in case of a single macroion diffusing in an unbounded multi-component electrolyte solution. In this case, experiments have shown that the relative motions of the microions with respect to the macroion give rise to an increase (decrease) in the friction coefficient (sedimentation velocity) of the tracer macroion [7–9]. As a consequence, the long-time self-diffusion coefficient, $D_{\mathrm{T}}^{\mathrm{L}}$, of the tracer shows a minimum when the thickness of the microion cloud, as measured by the

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Debye screening length κ^{-1}, is comparable to the radius of the macroion [9]. The fluctuations in the electrolyte ions (microions) atmosphere surrounding the macroion are coupled to the corresponding hydrodynamic fluctuations through the intervening solvent. Therefore it appears necessary to consider direct interactions (relaxation effect) and hydrodynamic interactions (electrophoretic effect) between the tracer and the microions on equal footing for a proper theoretical treatment of colloidal electrolyte friction and sedimentation.

In this letter, we derive analytical results for the (time-dependent) friction function $\Delta\zeta_{\mathrm{T}}(t)$, the long-time tracer diffusion coefficient $D_{\mathrm{T}}^{\mathrm{L}}$, and the sedimentation velocity U of a spherical macroion immersed in a multi-component electrolyte solution. The derivation is based on a unifying simplified mode-coupling scheme (MCS) for the overdamped Brownian dynamics of macroion and microions governed by the many-body Smoluchowski equation [10, 11]. The solvent-mediated HI between tracer and microions are described on a pairwise additive level using the far-field Rotne-Prager (RP) form of the hydrodynamic mobility tensors [10, 12]. The microions are considered as point-like regarding their excluded-volume interactions relative to the dimension of the macroion, but they are characterised by finite values of their free diffusion constants. To obtain analytical results, the static microion-microion and macroion-microion pair correlation functions required as input in the MCS are treated on the basis of the mean spherical approximation (MSA). For point-like microions, the MSA is identical with the Debye-Hückel (DH) approximation [13, 14].

Consider the tracer diffusion of a spherical macroion of charge number Z_{T}, radius a and free diffusion coefficient D_{T}^{0} immersed in a solvent of shear viscosity η and dielectric constant ϵ. The solvent contains further an m-component mixture of point-like microions of charge numbers $\{Z_\alpha\}$, number densities $\{n_\alpha\}$ and free diffusion coefficients $\{D_\alpha^0\}$. Within the Smoluchowski dynamics, the time evolution equation for the tracer mean-squared displacement (MSD) $W_{\mathrm{T}}(t) = \left\langle [\boldsymbol{R}_{\mathrm{T}}(t) - \boldsymbol{R}_{\mathrm{T}}(0)]^2 \right\rangle /6$ is given by [10]

$$\frac{\partial}{\partial t} W_{\mathrm{T}}(t) = D_{\mathrm{T}}^{\mathrm{S}} - \frac{1}{\zeta_{\mathrm{T}}^{\mathrm{S}}} \int_0^t \mathrm{d}u \, \Delta\zeta_{\mathrm{T}}(0, t-u) \, \frac{\partial}{\partial t} W_{\mathrm{T}}(u) \,. \tag{1}$$

Here, $\boldsymbol{R}_{\mathrm{T}}(t)$ is the position vector of the macroion centre at time t, and $D_{\mathrm{T}}^{\mathrm{S}} = k_{\mathrm{B}}T/\zeta_{\mathrm{T}}^{\mathrm{S}}$ is the short-time tracer diffusion coefficient which is equal to the initial slope of $W_{\mathrm{T}}(t)$. The integral term including the time-dependent tracer friction function $\Delta\zeta_{\mathrm{T}}(t)$ accounts for the electro-hydrodynamic retardation effects due to the non-instantaneous relaxation of the microions and the associated solvent.

The time-integrated electrolyte friction contribution $\Delta\zeta_{\mathrm{T}} = \int_0^\infty \mathrm{d}t \, \Delta\zeta_{\mathrm{T}}(t)$ is related to the final slope, $D_{\mathrm{T}}^{\mathrm{L}}$, of $W_{\mathrm{T}}(t)$ and to the sedimentation velocity, U, of a slowly sedimenting macroion in the presence of its neutrally buoyant electrolyte atmosphere by

$$D_{\mathrm{T}}^{\mathrm{L}} = \frac{k_{\mathrm{B}}T}{\zeta_{\mathrm{T}}^{\mathrm{S}} + \Delta\zeta_{\mathrm{T}}} = D_{\mathrm{T}}^{0} \frac{U}{U^0} \,, \tag{2}$$

where U^0 is the Stokesian sedimentation velocity of the tracer in the absence of electrolyte ions. While the relation between $D_{\mathrm{T}}^{\mathrm{L}}$ and U in eq. (2) is expected to hold on physical grounds, it can also be derived rigorously using linear response theory [15].

Application of the MCS to the exact microscopic expression of $\Delta\zeta_{\mathrm{T}}(t)$, using the RP form of HI, has led to the following result [10]:

$$\Delta\zeta_{\mathrm{T}}(t) = \frac{D_{\mathrm{T}}^{0}}{6\pi^2} \int \mathrm{d}k \, k^4 \, G_{\mathrm{T}}(k,t) \, \boldsymbol{v}_{\mathrm{T}}(k) \cdot \boldsymbol{S}(k,t) \cdot \boldsymbol{v}_{\mathrm{T}}(k) \,. \tag{3}$$

Within the MCS, $\Delta\zeta_{\rm T}(t)$ is thus expressed in terms of the self-intermediate scattering function $G_{\rm T}(q,t) = \langle \exp[i\boldsymbol{q}\cdot(\boldsymbol{R}_{\rm T}(t)-\boldsymbol{R}_{\rm T}(0))]\rangle$ of the tracer, and in terms of $m(m+1)/2$ partial dynamic structure factors $S_{\alpha\beta}(k,t)$, with $\alpha,\beta \in \{1,...,m\}$, the latter describing the partial density-density correlations of the bulk electrolyte. The $S_{\alpha\beta}(k,t)$ constitute the elements of the symmetric $m\times m$ dynamic structure factor matrix $\boldsymbol{S}(k,t)$. The m-component vertex vector $\boldsymbol{v}_{\rm T}(k)$ contains the partial vertex functions

$$v_{{\rm T}\alpha}(k) = n_\alpha^{1/2}\, c_{{\rm T}\alpha}(k) - \frac{1}{D_{\rm T}^0}\sum_{\gamma=1}^{m} n_\gamma^{1/2}\, h_{{\rm T}\gamma}^{\rm d}(k)\, S_{\gamma\alpha}^{-1}(k)\,, \tag{4}$$

where $c_{{\rm T}\alpha}(k)$ is the direct correlation function for the tracer and a microion of component α. Here $S_{\gamma\alpha}^{-1}(k)$ is the (γ,α)-th element of the matrix inverse of the bulk electrolyte static structure factor matrix $\boldsymbol{S}(k) = \boldsymbol{S}(k,t=0)$. The HI between macroion and point-like microions is accounted for in RP approximation through the distinct partial hydrodynamic functions $h_{{\rm T}\gamma}^{\rm d}(k)$ [10], given by

$$h_{{\rm T}\gamma}^{\rm d}(k) = D_{\rm T}^0\, V \left\langle \hat{\boldsymbol{k}}\cdot\boldsymbol{T}_{{\rm T}\gamma}^{\rm RP}(r)\cdot\hat{\boldsymbol{k}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\right\rangle = D_{\rm T}^0 \int {\rm d}^3r\, g_{{\rm T}\gamma}(r)\, \hat{\boldsymbol{k}}\cdot\boldsymbol{T}_{{\rm T}\gamma}^{\rm RP}(r)\cdot\hat{\boldsymbol{k}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \tag{5}$$

where $\boldsymbol{T}_{{\rm T}\gamma}^{\rm RP}(\boldsymbol{r}) = a\left\{3/(4\,r)\,[\boldsymbol{1}+\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}] + a^2/(4\,r^3)\,[\boldsymbol{1}-3\,\hat{\boldsymbol{r}}\hat{r}]\right\}$, with $\hat{\boldsymbol{k}} = \boldsymbol{k}/k$ and $\hat{\boldsymbol{r}} = \boldsymbol{r}/r$ is the Rotne-Prager tensor in the limit of microions of zero radius a_γ. This amounts to disregard contributions to the hydrodynamic function of order $\mathcal{O}(a_\gamma/a)$.

On the basis of the primitive model for the tracer and microions, we use next the DH/MSA approximation for the static correlation functions $c_{{\rm T}\alpha}(k)$ and $\boldsymbol{S}(k)$ entering into the vertex functions. The DH approximation for $\boldsymbol{S}(k)$ is applicable for monovalent microions of number densities in a typical range of 10^{-4}–10^{-3} mol/l. This is the concentration range where the electrolyte friction effect is most pronounced, with $\kappa a \approx 1$ and κ defined as $\kappa^2 = l_{\rm B}\sum_{\alpha=1}^m n_\alpha Z_\alpha^2$. Here $l_{\rm B} = 4\pi\, L_{\rm B}$, and $L_{\rm B} = e^2/(\epsilon\, k_{\rm B}T)$ is the Bjerrum length. The DH/MSA form of $c_{{\rm T}\alpha}(k)$ is used for analytical simplicity, however, with $Z_{\rm T}$ treated as an adjustable effective macroion charge [3].

The vertex vector is then determined as

$$\boldsymbol{v}_{\rm T}(y) = \begin{cases} -\left[A(y)\,\boldsymbol{n}^{1/2} + l_{\rm B}\, Z_{\rm T}\, D(y)\,\boldsymbol{u}\right]\,, & \text{no HI}\,,\\ w_{\rm T}(y) Z_{\rm T}\boldsymbol{u}\,, & \text{with HI}\,,\end{cases} \tag{6}$$

with m-dimensional vectors $\boldsymbol{n}^{1/2}$ and $\boldsymbol{u}$ of elements $\{n_\alpha^{1/2}\}$ and $\{n_\alpha^{1/2} Z_\alpha\}$, respectively. Moreover $A(y) = 3\,\Omega_{\rm T}\, j_1(y)/y$, $D(y) = (a^2/y)\,[j_1(y)\,\kappa a/(1+\kappa a) + \cos(y)/y]$, where $\Omega_{\rm T} = 4\pi\, a^3/3$ is the tracer volume and

$$w_{\rm T}(y) = \Omega_{\rm T}\left(1+\frac{(\kappa a)^2}{y^2}\right)\left[w^{(1)}(y) + w^{(2)}(y)\right] - l_{\rm B} D(y)\,. \tag{7}$$

Furthermore

$$\begin{aligned} w^{(1)}(y) &= -\frac{9}{2}\frac{L_{\rm B}}{a}\frac{e^{\kappa a}}{1+\kappa a}\int_1^\infty {\rm d}x\, e^{-\kappa a x}\left(j_0(xy) - \frac{j_1(xy)}{xy}\right)\,,\\ w^{(2)}(y) &= -\frac{3}{2}\frac{L_{\rm B}}{a}\frac{e^{\kappa a}}{1+\kappa a}\int_1^\infty {\rm d}x\, \frac{e^{-\kappa a x}}{x^2}\, j_2(xy)\,, \end{aligned} \tag{8}$$

and $x = r/a$ and $y = k\,a$ are reduced distances and wave numbers, respectively.

Due to modest microion correlations in the bulk, $\boldsymbol{S}(k,t)$ is expected to be only modestly perturbed form its short-time form at later times. Therefore, we approximate $\boldsymbol{S}(k,t)$ in eq. (3) by its short-time form $\boldsymbol{S}(k,t) \approx \exp[-k^2\,\boldsymbol{D}^0 \cdot \boldsymbol{S}^{-1}(k)\,t] \cdot \boldsymbol{S}(k)$, with $D^0_{\alpha\beta} = \delta_{\alpha\beta} D^0_\alpha$, neglecting the HI between the microions as compared to the strong tracer-macroion HI [3,16]. According to smart Brownian Dynamics simulations on bulk electrolyte mixtures, the influence of HI is indeed found to be small for number densities corresponding to $\kappa a \approx 1$ [17]. Since $S(k,t)$ decays much faster than $G_{\rm T}(k,t)$ due to $D^0_{\rm T} \gg D^0_\alpha$, we further approximate $G_{\rm T}(k,t)$ in eq. (3) by its short-time form $G_{\rm T}(k,t) = \exp[-k^2\,D^0_{\rm T}\,t]$, valid in the RP treatment of HI. Notice that the use of the short-time forms for $G_{\rm T}(k,t)$ and $\boldsymbol{S}(k,t)$ in the friction function $\Delta\zeta_{\rm T}(t)$ is consistent with the DH/MSA treatment of weak static particle correlations including terms up to quadratic order in the macroion charge.

The simplified MCS with static DH input, referred to as MCS-DH, leads to analytic expressions for $\Delta\zeta_{\rm T}(t)$, $D^{\rm L}_{\rm T}$ and U for the general case of differently mobile microions. For conciseness we present here results for the long-time properties $D^{\rm L}_{\rm T}$ and U only. To reveal the primordial importance of the electro-hydrodynamic coupling to electrolyte friction, we discuss the cases with and without HI separately. A lengthy calculation based on the vertex $\boldsymbol{v}_{\rm T}(k)$ without HI in eq. (6) leads to the result

$$\begin{aligned}\frac{\Delta\zeta_{\rm T}}{\zeta^0_{\rm T}} &= \frac{\Omega_{\rm T}}{3}\sum_{\alpha=1}^{m}\frac{n_\alpha}{D^*_\alpha} + 8\,\Omega_{\rm T}\,L_{\rm B}\,a^2 q_m^2 \int_0^\infty {\rm d}y\,\frac{j_1(y)}{y^2+(\kappa_m a)^2} \\ &+ \frac{16\,L_{\rm B}}{3} Z_{\rm T}\,q_m \int_0^\infty {\rm d}y\,\frac{y^2 j_1(y)}{y^2+(\kappa_m a)^2}\,D(y) \\ &+ \frac{Z_{\rm T}^2\,\kappa a}{6\,(1+\kappa a)^2}\,\frac{L_{\rm B}}{a}\,\frac{1-d^2}{d}\left[1+\exp\left[-2\kappa a\,d\right]\frac{d-1}{d+1}\right], \end{aligned} \tag{9}$$

where $D^*_\alpha = 1 + D^0_\alpha/D^0_{\rm T}$, $q_m = \sum_{\alpha=1}^m D^0_{\rm T}/(D^0_\alpha + D^0_{\rm T})\,n_\alpha\,Z_\alpha$, $\kappa_m^2 = l_{\rm B}\sum_{\alpha=1}^m n_\alpha\,Z_\alpha^2\,D^0_\alpha/(D^0_\alpha + D^0_{\rm T})$, and $d^2 = \kappa_m/\kappa$. The corresponding MCS-DH expressions for $D^{\rm L}_{\rm T}$ and U follow readily from eq. (2), and $\zeta^{\rm S}_{\rm T} = \zeta^0_{\rm T} = k_{\rm B}T/D^0_{\rm T}$ valid in the RP treatment of HI.

The MCS-DH result for $\Delta\zeta_{\rm T}$, with HI described in RP approximation, is given in terms of the integral expression

$$\frac{\Delta\zeta_{\rm T}}{\zeta^0_{\rm T}} = \frac{Z_{\rm T}^2\,(\kappa^2-\kappa_m^2)}{6\,\pi^2\,l_{\rm B}\,a^3}\int_0^\infty {\rm d}y\,\frac{y^6\,w_{\rm T}(y)^2}{(y^2+\kappa^2a^2)(y^2+\kappa_m^2a^2)}\,, \tag{10}$$

which has been derived using the vertex vector in eq. (6) with HI.

We proceed with a qualitative discussion of eqs. (9) and (10). In the limit $a \to 0$ of vanishing tracer size both equations reduce to Onsager's exact limiting expression $\Delta\zeta_{\rm T}/\zeta^0_{\rm T} = L_{\rm B}Z_{\rm T}^2(\kappa-\kappa_m)/3$ for the friction coefficient of a weakly charged multi-component electrolyte [18]. The coefficient $\Delta\zeta_{\rm T}$ vanishes in the limit $\{D^*_\alpha \to \infty\}$ of infinitely mobile microions, since the microion cloud remains then spherically symmetric with respect to the tracer at each instant of time. The friction function without HI includes, contrary to the case with HI, charge-independent contributions. The first term in eq. (9), proportional to $\Omega_{\rm T}$ and independent of $Z_{\rm T}$ and $\{Z_\alpha\}$, gives an electrolyte friction contribution originating from a neutral cloud of Brownian point-like particles interacting with the excluded volume of the tracer. Without HI this cloud is described by a non-isotropic steady-state distribution function. To leading order in the microion densities, this zero-charge friction contribution can be calculated exactly, with the exact result differing from the MCS result by a factor of 3/2 [15, 19]. For typical experimental parameters, this charge-independent contribution can overwhelm all other contributions in eq. (9), leading to monotonic increase of $\Delta\zeta_{\rm T}$ with increasing κ in conflict with

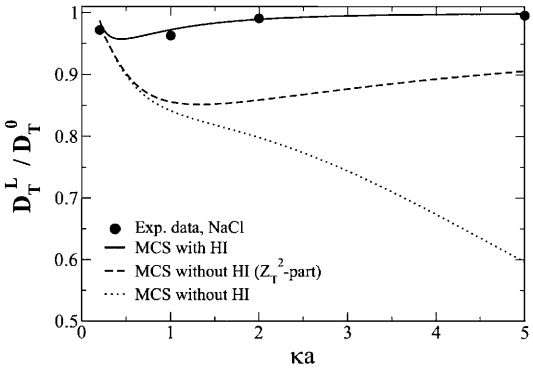

Fig. 1 – Normalised long-time tracer diffusion coefficient $D_{\mathrm{T}}^{\mathrm{L}}/D_{\mathrm{T}}^{0}$ *vs.* reduced screening parameter κa for a dilute aqueous dispersion of polystyrene spheres in NaCl solution. System parameters: tracer radius $a = 20\,\mathrm{nm}$, effective microion radii $a_{\mathrm{Na}^+} = 0.28\,\mathrm{nm}$, $a_{\mathrm{Cl}^-} = 0.18\,\mathrm{nm}$ with corresponding diffusion coefficients according to the Stokes-Einstein relation $D_\alpha = k_{\mathrm{B}}T/(4\pi\eta a_\alpha)$ for slip boundary conditions [9], effective macroion charge number $Z_{\mathrm{T}} = 145$, and $L_{\mathrm{B}} = 0.71\,\mathrm{nm}$. The number density, $n(\mathrm{NaCl})$, of added salt is small even at $\kappa a = 5$ corresponding to $n(\mathrm{NaCl}) = 6 \times 10^{-4}\,\mathrm{mol/l}$. Solid line: MCS-DH with HI according to eq. (10); dotted line: MCS-DH without HI according to eq. (9); dashed line: Coulomb part of the MCS-DH without HI proportional to Z_{T}^2; filled circles: experimental data taken from [9].

experimental results showing a maximum of $\Delta\zeta_{\mathrm{T}}$ near $\kappa a = 0.5$. The second term in eq. (9) is again independent of Z_{T}, but it depends implicitly on the $\{Z_\alpha\}$ through the parameter q_m. The MCS without HI predicts thus an extra friction contribution to $\Delta\zeta_{\mathrm{T}}$ which persists even for an uncharged tracer. It arises from differently mobile microions, dynamically coupled to each other by their Coulomb interactions. Notice that $q_m = 0$ for equally mobile microions.

It is remarkable that, according to the MCS-DH equation (10), charge-independent terms in $\Delta\zeta_{\mathrm{T}}$ are absent when the far-field part of HI is considered, since $\boldsymbol{v}_{\mathrm{T}}(k) \propto Z_{\mathrm{T}}$. The absence of charge-independent friction contributions with HI follows also from exact low-density calculations [15]. This non-existence of charge-independent friction contributions can be attributed to the advection of the point-like microparticles in the Stokesian flow field created by the moving tracer. This is in accord with the physical expectation that the microions are, concerning their short-range part of direct (*i.e.* excluded volume) interactions and HI not qualitatively different from solvent molecules. The friction effect of the solvent is included already in ζ_{T}^0. Our finding that HI are essential for a consistent physical description of electrolyte friction should be compared with earlier approaches of Schurr [20] and Medina-Noyola *et al.* [19, 21], the latter approach based on a generalised Langevin equation description, where it has been attempted to explain the observed maximum of $\Delta\zeta_{\mathrm{T}}(\kappa)$ in terms of direct forces only.

MCT results for the normalised long-time tracer diffusion coefficient $D_{\mathrm{T}}^{\mathrm{L}}/D_{\mathrm{T}}^{0}$ with HI (eq. (10)) and without HI (eq. (9)) are shown in fig. 1, plotted *vs.* the reduced screening parameter κa of added NaCl salt. As seen, the friction contribution to the tracer due to electro-hydrodynamic microion relaxation is largest when κ^{-1} is roughly equal to the tracer diameter. The monotonic decrease of the MCS-$D_{\mathrm{T}}^{\mathrm{L}}$ without HI is essentially due to the charge-independent excluded-volume term on the right-hand side of eq. (9), which gives the dominant contribution to $\Delta\zeta_{\mathrm{T}}$ at larger values of κa. The comparison with experimental data of $D_{\mathrm{T}}^{\mathrm{L}}$ for a dilute dispersion of polystyrene spheres in NaCl solution depicted in fig. 1 (cf. also fig. 2),

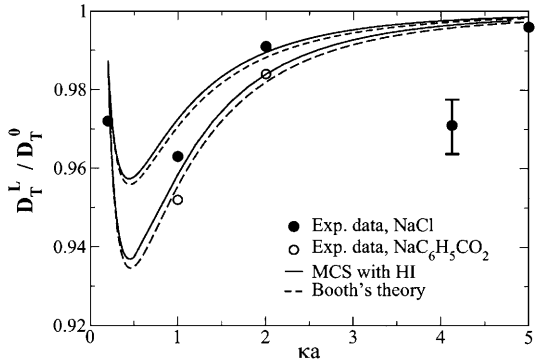

Fig. 2 – $D_{\mathrm{T}}^{\mathrm{L}}/D_{\mathrm{T}}^{0}$ *vs.* κa for two different added salts, NaCl and $\mathrm{NaC_6H_5CO_2}$, respectively. Solid lines: MCS with HI; dashed lines: Booth's theory [22, 23]; open and filled circles: experimental data for aqueous NaCl and $\mathrm{NaC_6H_5CO_2}$ electrolytes, taken from [9]. Macroion parameters Z_{T}, a, $a_{\mathrm{Na^+}}$, $a_{\mathrm{Cl^-}}$ as in fig. 1, with $a_{\mathrm{C_6H_5CO_2^-}} = 0.43\,\mathrm{nm}$.

suggests that the experimentally observed minimum in $D_{\mathrm{T}}^{\mathrm{L}}$ cannot be explained in terms of direct forces only. A minimum in $D_{\mathrm{T}}^{\mathrm{L}}(\kappa)$ without HI is found only when the second largest contribution to $\Delta\zeta_{\mathrm{T}}$ proportional to Z_{T}^2 in eq. (9) is considered alone. This term, however, gives a minimum in $D_{\mathrm{T}}^{\mathrm{L}}$ four times lower and located at κa twice as large as the minimum obtained in MCS-DH with HI (cf. fig. 1).

Figure 2 shows MCT results with HI for two added salts, NaCl and $\mathrm{NaC_6H_5CO_2}$, respectively, in comparison with corresponding experimental data [9], and results obtained from Booth's theory of colloidal electrolyte friction [22], in a corrected version given by Geigenmüller [23]. The electrolyte friction for $\mathrm{NaC_6H_5CO_2}$ is more pronounced than for NaCl due to the smaller mobility of the $\mathrm{C_6H_5CO_2^-}$ anions as compared to the $\mathrm{Cl^-}$ anions. The MCT results for $D_{\mathrm{T}}^{\mathrm{L}}$ are in good accord with the experimental data and they follow closely the results obtained from Booth's theory. In Booth's approach, HI are described on the level of the Stokes flow created by the sedimenting sphere, with the electrolyte treated as incompressible. Contrary to Booth's theory, which deals only with the long-time steady-state aspect of electrolyte friction, the present MCS leads also to analytical expressions describing transients in the microion atmosphere [15]. It allows furthermore for a separate analysis of potential and of hydrodynamic force effects.

In summary, we have presented a simple mode coupling scheme of colloidal electrolyte friction with HI included, leading to results which compare quite well with experimental data. The versatile MCS can be rather straightforwardly extended to systems with large electrostatic macroion potentials and to systems like charged micelles, where finite-size effects of the microions are important. Finally, the present MCS can be generalised to describe electrokinetic effects in concentrated macroion dispersions with strongly overlapping double layers. Work on these extensions of the MCS is in progress.

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