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A unifying mode-coupling theory for transport properties of electrolyte solutions. I. General scheme and limiting laws

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We develop a general method for calculating conduction-diffusion transport properties of strong electrolyte mixtures, including specific conductivities, steady-state electrophoretic mobilities, and self-diffusion coefficients. The ions are described as charged Brownian spheres, and the solvent-mediated hydrodynamic interactions (HIs) are also accounted for in the non-instantaneous ion atmosphere relaxation effect. A linear response expression relating long-time partial mobilities to associated dynamic structure factors is employed in our derivation of a general mode coupling theory (MCT) method for the conduction-diffusion properties. A simplified solution scheme for the MCT method is discussed. Analytic results are obtained for transport coefficients of pointlike ions which, for very low ion concentrations, reduce to the Deby-Falkenhagen-Onsager-Fuoss limiting law expressions. As an application, an unusual non-monotonic concentration dependence of the polion electrophoretic mobility in a mixture of two binary electrolytes is discussed. In addition, leading-order extensions of the limiting law results are derived with HIs included. The present method complements a related MCT method by the authors for the electrolyte viscosity and shear relaxation function [C. Contreras-Aburto and G. Nägele, J. Phys.: Condens. Matter 24, 464108 (2012)], so that a unifying scheme for conduction-diffusion and viscoelastic properties is obtained. We present here the general framework of the method, illustrating its versatility for conditions where fully analytic results are obtainable. Numerical results for conduction-diffusion properties and the viscosity of concentrated electrolytes are presented in Paper II [C. Contreras Aburto and G. Nägele, J. Chem. Phys. 139, 134110 (2013)]. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4822297]

I. INTRODUCTION

Electrolyte solutions are of considerable importance in industrial applications involving electrochemical processes, such as waste water treatment and ion exchange. There is thus a need for theoretical-analytic methods, which allow to predict linear conduction-diffusion transport properties such as ion conductivity, electrophoretic mobilities, and self- and collective diffusion coefficients in non-dilute solutions. The interest in analytic methods has been further boosted by the increasing amount of research made on suspensions of charge-stabilized colloidal particles, and charged protein solutions. As a matter of fact, the transport of small microions in an electrolyte solution, and of large charged colloidal particles suspended in an electrolyte solution, are strongly inter-related research areas in colloid science and physical chemistry.

The theoretical description of the ion dynamics in electrolytes is demanding and far from being complete, owing to the long-range nature both of the Coulomb interactions, and the inter-ion hydrodynamic interactions (HIs) mediated by the intervening solvent. The interplay of these interactions gives rise to unusual features in the ionic transport coefficients. In addition to these generic interactions, which can be treated theoretically using a continuum model for the solvent, ion specific interactions may play a role, which has been addressed using concepts such as ion hydration and solvent polarization.

The electrolytes considered in this work are strong electrolyte solutions where the salt solute is fully dissociated. At concentrations less than about 0.01 M, the electrolyte ions (microions) can be treated as pointlike, and their Coulomb interactions give rise to the peculiar square-root in concentration dependence of the electrolyte transport properties. This concentration dependence is the hallmark of the celebrated Debye-Falkenhagen-Onsager-Fuoss (DFOF) limiting law expressions for the transport coefficients characterizing electrolyte conductivity and electrophoresis, self-diffusion, and viscosity. The limiting law expressions have been derived using a continuum model for the solvent, with the ions treated as pointlike Brownian particles whose equilibrium pair correlations are described by the linear Debye-Hückel (DH) theory.

The ion transport in electrolyte solutions is influenced by two major mechanisms which tend to slow the diffusive-convective motion of the ions. The first one is the relaxation effect, which describes the relaxation of the ion atmosphere around each ion as a non-instantaneous response to any perturbation of the spherical cloud symmetry. The ion cloud perturbation is counteracted by the electrostatic interactions, which tend to restore local electroneutrality, and by the Brownian motion of the ions. Additionally to the electro-steric interactions, the cloud relaxation is influenced by the HIs, since ions in motion drag the surrounding solvent along.
The second mechanism is the electrophoretic effect which is of hydrodynamic origin and becomes operative when an electric field is applied (electrophoresis). It describes the slowing influence on ion migration due to the instantaneous hydrodynamic coupling of the ionic motions.

Statistical mechanical transport theories of electrolyte mixtures are commonly based on the multicomponent primitive model (PM), where the (hydrated) electrolyte ions are treated as uniformly charged spheres interacting by Coulomb forces. The spheres are embedded in a structureless Newtonian fluid characterized by the shear viscosity, $\eta_0$, and the static dielectric constant $\epsilon$. No dielectric mismatch effects between spheres and solvent are considered in this model. A PM system is overall electroneutral, and in equilibrium certain moment conditions must be fulfilled by its static pair distribution functions. Most notable here is the local electroneutrality condition, commanding each ion to be surrounded by a cloud of ions bearing a net equal and opposite charge.8, 9

In most theoretical approaches, the Brownian dynamics of the ions is taken to be overdamped, with the configurational distribution function described by the many-particle generalized Smoluchowski equation (GSE) in combination with the stationary Stokes equation of low-Reynolds number solvent flow. We refer to this overdamped dynamics, for short, as the Smoluchowski dynamics.

The PM-based Smoluchowski dynamics has been applied, incidentally, also to dispersions of globular charged colloids and proteins, by treating them as large and slowly diffusing polymers.1 This application has allowed for the exploration of electrokinetic phenomena on the colloid level, including the study of the electrolyte friction effect (i.e., the self-correlation part of the relaxation effect) on colloidal self-diffusion in dilute10, 11 and concentrated12, 13 suspensions. When the electrophoresis of colloidal polyions in a high-dielectric constant fluid such as water is considered, one needs to account for the effect of the (colloid configuration-dependent) induced polarization electric field generated by the low-dielectric colloidal particles. This field influences the microion migrations in addition to the applied electric field. The microion cloud relaxation effect is negligible in an ultrathin double layer. Thus, when the double layer around a colloidal particle is very thin, the decrease in the colloidal electrophoretic mobility is entirely due to the electrophoretic effect, i.e., to the electro-osmotic cross-streaming of countercations plus dragged along fluid relative to the surface of the colloidal particle.

Various routes have been followed in the past to develop theoretical methods suitable for calculating conduction-diffusion transport properties for electrolyte concentrations surpassing the limiting law regime, where the excluded volume of the ions needs to be considered. We mention here, in particular, the work by Falkenhagen3 and Ebeling et al.14, 15 where the DFOF continuity equations approach has been extended to finite ion sizes. The relaxation effect contribution to the conductivity is deduced in their approach from averaging the electrostatic force experienced by a central ion using the perturbed ionic pair distribution functions.

Considerable progress along this line of research has been made in the works of Bernard, Turq, Blum, Dufreche, and collaborators. In a series of papers,16–20 these researchers extended the DFOF approach to finite ion sizes by using mostly the analytic mean-spherical approximation (MSA) expressions for the ion-ion equilibrium pair correlation functions. They obtained results, in particular, for the steady-state ion conductivity,16, 18, 20 the ion self-diffusion coefficients,21 and the mutual (chemical) diffusion coefficient22, 23 (on this subject, we refer also to Felderhof24, 25). However, to our knowledge the contribution of the HIs to the relaxation effect has not been included in these works, except for the special case of self-diffusion.26 Chandra, Bagchi, and collaborators have combined mode-coupling theory (MCT) and dynamic density functional theory (DDFT) arguments to obtain expressions for the ion conductivity19, 27, 28 and the electrolyte viscosity29 of electrolyte solutions. The excluded volumes of the ions are incorporated in their hybrid method using Attard’s generalization8 of the DH pair distribution functions. The effect of the ion-ion HIs on the relaxation effect part of the conductivity, and on the viscosity have been disregarded in their treatment. In related work, Dufreche et al.20 have combined MCT and DDFT arguments with Kirkwood’s friction formula for electrolyte friction to calculate the ion self-diffusion coefficients, and velocity autocorrelation functions, in a binary electrolyte solution. The finite ion sizes in this approach to self-diffusion are accounted for in a MSA, and the inter-ion HIs are treated on the point-particle (Oseen) level of description. In those works, the effect of (hydro-) dynamic cross correlations in the intermediate scattering functions has been disregarded.

In the present paper, we present a versatile multicomponent MCT scheme which allows for the calculation of conduction-diffusion linear transport properties of strong electrolyte mixtures within a unifying framework. Our MCT scheme is based on the Smoluchowski dynamics applied to the PM. The influence of the ion-ion HIs is accounted for both in the (short-time) electrophoretic and relaxation effect contributions. We derive MCT expressions for the steady-state molar conductivity and the ion electrophoretic mobilities in an external field, and for the long-time ionic self-diffusion coefficients. The present scheme for calculating linear conduction-diffusion properties complements recent work by the present authors where a related MCT theory with HIs has been developed for the shear viscosity, and the linear shear-stress correlation function of electrolyte mixtures.30 The MCT expressions for conduction-diffusion properties derived here are based on a linear response relation between long-time partial ion mobilities and associated equilibrium dynamic structure factors, and on the fact that conduction-diffusion transport properties are expressible as linear combinations of the long-time partial mobilities. In addition, we build on earlier work by Nägele and collaborators where a general MCT for the dynamic structure factor of Brownian particle mixtures with HIs has been developed.31–33

The ion-ion HIs are accounted for on the Rotne-Prager (RP) far-field level of description, both in the electrophoretic and relaxation effects. This is a fair approximation of the HIs for moderately concentrated electrolytes. It allows for an analytic treatment, and most importantly, it preserves the positive definiteness of the exact matrix of diffusivity tensors. The
only input required in the MCT scheme is the equilibrium pair correlation functions. We refer to the multicomponent MCT method presented here for short as the MCT-HIs scheme.

The objective of this paper (referred to as Paper I) is to provide a self-contained description of the general framework of the MCT-HIs method, serving as the basis for later applications and further developments, and to illustrate its versatility for conditions (low ion concentrations) where fully analytic expression for the diffusion-conduction transport properties are obtained. To this end, the ions are treated as pointlike, and the analytic DH pair distribution functions are used as the static input. We show that the DFOF limiting laws are correctly, and straightforwardly, recovered from the MCT scheme when the latter is specialized to the low-concentration regime. We demonstrate this for mixtures of ions with equal individual diffusion coefficients, binary electrolytes, and for the significantly more complex situation of a four-component electrolyte system including a polyion component which, as we are going to show, reveals an unusual non-monotonic concentration dependence of the polyion electrophoretic mobility. In going beyond the limiting law regime, we derive analytic MCT-HIs expressions for leading-order HIs contributions to the relaxation parts of the transport coefficients.

At larger electrolyte concentration where HIs become significantly strong, also the finite ion sizes must be considered. We therefore give the essentials of a simplified MCT-HIs solution scheme applicable to intermediately concentrated solutions, which accounts both for the excluded volumes of the ions and their HIs. In a closely related forthcoming article by the present authors of same title (Paper II84), the simplified MCT-HIs is used to derive semi-analytic expressions for the conduction-diffusion transport coefficients in moderately concentrated electrolyte solutions. Moreover, the concentration dependence of these expressions is investigated in comparison with experimental data, and against the MCT-DDFT method of Chandra and Bagchi.

The paper is organized as follows: Sec. II summarizes the considered conduction-diffusion transport properties, and relates them to specific combinations of the long-time partial mobilities. Using linear response theory, in Sec. III the partial mobilities are expressed in the form of a Green-Kubo (GK) relation. The GK relation is used subsequently in Sec. IV A to derive a useful relation between the partial mobilities and associated partial dynamic structure factors, with the latter being evaluated using a multicomponent MCT. The essentials of the MCT-HIs scheme are given in Sec. IV B. A simplified solution method is discussed in Sec. IV C. In Sec. V, analytic MCT-HIs results for the transport properties of point-ion solutions are presented, and leading-order HIs contributions are discussed. Section VI contains a summary and outlook.

II. PARTIAL MOBILITIES AND CONDUCTION-DIFFUSION PROPERTIES

We describe strong electrolyte mixtures on the PM level, including the HIs between the ions. The hydrated electrolyte ions of components \( \alpha = 1, \ldots, m \), partial numbers \( N_\alpha \), and partial number densities \( n_\alpha = N_\alpha / V \) (where \( V \) is here the macroscopic system volume) are treated as uniformly charged hard spheres interacting statically by Coulomb forces. The solvent is modeled as a structureless dielectric continuum and as an incompressible Newtonian fluid, characterized statically by the Bjerrum length \( L_B = e^2/(\epsilon k_B T) \) (in Gaussian units) with the static dielectric constant \( \epsilon \) at solvent temperature \( T \) and the proton elementary charge \( e \), and dynamically by the shear viscosity \( \eta_0 \). The dynamics of the electrolyte ions (microions) is taken to be overdamped, governed by the many-component generalized Smoluchowski equation. The ions of component \( \alpha \) are characterized by their excluded volume radius \( a_\alpha \), charge \( z_\alpha e \), and single-ion translational diffusion coefficient \( D_\alpha^0 \).

Consider now an \( m \)-component, homogeneous dispersion of spherical Brownian particles at constant solvent chemical potential and temperature. The dispersion is assumed to be weakly perturbed away from its isotropic, fluid-like equilibrium state by the application of a constant force field \([ \mathbf{F}_\alpha = F_\alpha \mathbf{q} \), acting at the centers of particles of the same component \( \alpha \). After a short transition period, the particles acquire steady-state mean velocities, \( \langle \mathbf{V}_\alpha \rangle_{st} \), collinear with the unit vector \( \mathbf{q} \). The mean velocities are linearly related to the external forces according to

\[
n_\alpha \langle \mathbf{V}_\alpha \rangle_{st} = \sum_{\gamma=1}^m (n_\alpha n_\gamma)^{1/2} \mu_{\alpha \gamma} L_{\alpha \gamma} F_\gamma.
\]

The configurational average, \( \langle \ldots \rangle_{st} \), is taken using the linearly perturbed, stationary configurational distribution function (see later).

It is important to note that the mean velocities are considered in the reference frame where the mean volume flow velocity of particles plus fluid is zero, i.e., where the suspension as a whole is at rest.24, 34–36 This is related to the fact that during the electrophoresis or sedimentation of particles in a spatially homogeneous, macroscopic system, where on average the particles drift collinear to the constant force field, volume conservation (i.e., incompressibility) of fluid and particles, and the long-range nature of the HIs, give rise to a uniform mean fluid backflow opposing the mean volume flow of the particles. The backflow is most pronounced in the case of sedimentation, where all particles drift in the same direction along the gravitational field. The sedimentation backflow is driven by a macroscopic pressure gradient originating from the buoyancy-corrected force transmitted to the fluid by the settling particles. In an electrophoresis experiment, where all ions are subject to a constant electric field of strength \( E \), so that \( F_\gamma = z_\gamma e E \), there is no macroscopic pressure gradient, since due to total charge neutrality,

\[
\sum_{\gamma=1}^m n_\gamma z_\gamma = 0,
\]

the total force transmitted to the fluid by the ions is zero. However, there is still a non-zero macroscopic backflow, except for highly symmetric situations such as for a symmetric binary electrolyte. As discussed in detail, e.g., by Batchelor and others,36–40 in spite of the long-range nature of the HIs, unambiguous finite values for the steady-state sedimentation and other mobility coefficient characteristic of a homogeneous suspension are obtained, provided the calculations (involving...
configurational averaging and the thermodynamic limit) are performed in the zero average suspension volume velocity reference frame.

The kinetic coefficients, $\mu^{L}_{\alpha\beta}$, are intrinsic properties of the system and are referred to as the long-time partial mobilities. Their scalar nature reflects the isotropy of the unperturbed system. The $\mu^{L}_{\alpha\alpha}$ constitute the elements of a symmetric and positive definite $m \times m$ mobility matrix $\mu^{L}$. This matrix is the central quantity dealt with in this work, since the transport coefficients characterizing conduction-diffusion processes can be expressed in terms of its elements. The partial mobilities are directly related to the symmetric Onsager coefficients of irreversible thermodynamics, $L_{\alpha\beta} = (n_{\alpha}n_{\beta})^{1/2}\mu^{L}_{\alpha\beta}$, likewise defined with respect to the average suspension volume velocity rest frame.

Consider now an electrophoresis experiment on a strong electrolyte solution in a constant, weak electric field $E$, where

$$\langle V_{\alpha} \rangle_{st} = \mu^{el}_{\alpha} E$$

(3)

is the steady-state mean electrophoretic drift velocity of $\alpha$-type ions in the zero average suspension velocity frame. The steady-state electrophoretic mobility of $\alpha$-type ions,

$$\mu^{el}_{\alpha} = \sum_{\gamma=1}^{m} \left( \frac{n_{\gamma}}{n_{\alpha}} \right)^{1/2} \frac{z_{\gamma} e}{\mu^{L}_{\alpha\gamma}},$$

(4)

is a linear combination of partial mobility coefficients. Note that its physical dimension differs from that of the kinetic mobility coefficients $\mu^{L}_{\alpha\gamma}$.

The steady-state average electric current density in the solution is related to the applied electric field by Ohm’s law,

$$\langle j^{el} \rangle_{st} = \sum_{\alpha=1}^{m} n_{\alpha} z_{\alpha} e \langle V_{\alpha} \rangle_{st} = \sigma E,$$

(5)

where the so-called specific conductivity of the electrolyte solution,

$$\sigma = \sum_{\alpha,\gamma=1}^{m} \left( n_{\alpha} n_{\gamma} \right)^{1/2} \frac{z_{\gamma} e^{2}}{\mu^{L}_{\alpha\gamma}},$$

(6)

is likewise given by a linear combination of partial long-time mobilities.

The partial ionic molar conductivity of an ion component $\alpha$, i.e., the specific conductivity contribution of this species divided by its molar concentration $c_{\alpha} = n_{\alpha}/N_{A}$, is given by

$$\lambda^{el}_{\alpha} = z_{\alpha} \mu^{el}_{\alpha} F,$$

(7)

where $F = N_{A} e$ is Faraday’s constant, and $N_{A}$ is Avogadro’s number. The electrophoretic mobilities are essentially ionic molar conductivities.

The ability of a solution to conduct an electric current is commonly quantified in terms of the molar conductivity, $\Lambda$, instead of the specific conductivity. The molar conductivity of an $m$-component electrolyte solution is defined as the specific conductivity divided by the molar concentration, $\sigma^{*}$, of electrolyte solute units which, for a strong electrolyte solution, are completely dissociated into the $m$ ion components with partial molar concentrations $c_{\alpha}$. With $\Lambda = \sigma/c^{*}$, it follows:

$$\Lambda = \sum_{\alpha=1}^{m} v_{\alpha} \lambda^{el}_{\alpha} = F \sum_{\alpha=1}^{m} v_{\alpha} z_{\alpha} \mu^{el}_{\alpha},$$

(8)

where the positive integers $\{v_{\alpha} = c_{\alpha}/c^{*}\}$ are the stoichiometric coefficients of the various ion components. A vast range of data for the molar conductivity of various electrolyte solutions has been compiled in the literature.

The electrophoretic mobility of an isolated $\alpha$-type ion at infinite dilution is

$$\mu^{el,0}_{\alpha} = \frac{z_{\alpha} e}{k_{B} T} D^{0}_{\alpha},$$

(9)

and the associated mean electrophoretic velocity is given by

$$V^{(0)}_{\alpha} = \mu^{el,0}_{\alpha} E.$$  

(10)

For strong electrolyte solutions, the total molar electrolyte ion concentration, $c$, is equal to the total number density,

$$n_{T} = \sum_{\alpha=1}^{m} n_{\alpha},$$

(11)

of dissociated ions expressed in mol/l, i.e., $c = n_{T}/N_{A} = c^{*} \sum_{\alpha} v_{\alpha}$. The long-time self-diffusion coefficient, $D^{L}_{\alpha}$, of a Brownian particle $i \in \alpha$ is determined in linear response by

$$\langle V^{el}_{i} \rangle_{st} = \beta D^{L}_{\alpha} F^{2}_{i}.$$  

(12)

Different from electrophoresis, in self-diffusion one considers the situation where only a single particle $i \in \alpha$ is subjected to a constant weak force $F^{2}_{i}$. Consequently, the self-diffusion coefficients can be expressed as

$$D^{L}_{\alpha} = k_{B} T (\mu^{L}_{\alpha\alpha})^{\text{elf}},$$

(13)

where

$$\mu^{L}_{\alpha\alpha} = \delta_{\alpha\alpha} (\mu^{L}_{\alpha\alpha})^{\text{elf}} + (\mu^{L}_{\alpha\alpha})^{\text{cross}}.$$  

(14)

The long-time mobility self part, $(\mu^{L}_{\alpha\alpha})^{\text{elf}}$, is due to self-correlations (in the velocity) of the singled-out particle $i$. Cross correlations with other ions are contained in the second mobility part. The self-part mobility contribution is obtained from mentally singling out a few $\alpha$-type particles to form a fictitious additional component $\alpha' = m + 1$, taking then the limit $n_{\alpha'} \to 0$ of $\mu^{L}_{\alpha\alpha'}$ while keeping all the other $m$ partial concentrations fixed.

Accordinly, the electrophoretic mobility of $\alpha$-type ions can be re-expressed as

$$\mu^{el}_{\alpha} = \frac{z_{\alpha} e}{k_{B} T} D^{L}_{\alpha} + \sum_{\gamma=1}^{m} \left( \frac{n_{\gamma}}{n_{\alpha}} \right)^{1/2} \frac{z_{\gamma} e}{\mu^{L}_{\alpha\gamma}} (\mu^{L}_{\alpha\gamma})^{\text{cross}},$$

(15)

or equivalently as

$$\mu^{el}_{\alpha} = \mu^{el,0}_{\alpha} D^{L}_{\alpha} + (\mu^{el}_{\alpha})^{\text{cross}},$$

(16)

where the definition in Eq. (9) of the single-ion electrophoretic mobility has been used.
If dynamic cross correlations of ions are completely neglected, the following approximate Nernst-Einstein (NE) relations are obtained:

$$\mu^e_{ij} \approx \frac{z_ia_i e^2}{k_B T} D_L^{ij}$$  \hspace{1cm} (17)

and

$$\sigma \approx \sum_{\gamma=1}^m n_{\omega} z_\gamma^2 e^2 \frac{D_L^{\gamma}}{k_B T},$$  \hspace{1cm} (18)

which express the collective properties $\mu^e_{ij}$ and $\sigma$ in terms of long-time self-diffusion coefficients. The MCT-HIs approach developed in this paper allows for scrutinizing the applicability of these simplifying NE relations. A general discussion on the validity of NE relations, and so-called generalized Stokes-Einstein relations between conduction-diffusion and rheological properties, will be given in a separate communication.

We point out that diffusion transport coefficients not considered in the present paper, such as the interdiffusion coefficients and chemical ion diffusion coefficients characterizing diffusional relaxation of weak concentration gradients, and the partial mean sedimentation velocities of slowly settling particles, can also be expressed in terms of the $\mu^e_{ij}$. The application of the present MCT scheme to the chemical diffusion of electrolytes will be the topic of a separate article.

III. LINEAR TRANSPORT IN SMOLUCHOWSKI DYNAMICS

We derive here a GK relation for the long-time mobility matrix, using linear response theory in the framework of the Smoluchowski dynamics. The GK relation will be subsequently linked to the time derivative of the matrix of partial dynamic structure factors of the unperturbed system. To evaluate this matrix, the many-component MCT scheme will be used.

To this end, consider an $m$-component dispersion of overall $N = \sum_{\gamma=1}^m N_\gamma$ spherical Brownian particles in an incompressible Newtonian fluid. The particle Reynolds number, and the convection Péclet number quantifying the relative strength of external to Brownian forces are both assumed to be small. Inertial effects are then negligible, with the fluid motion governed by the Stokes equation, and linear response theory can be applied. The particles are assumed to be confined to a finite volume $V$ by some sort of (electrically neutral) wall-like potential. The thermodynamic limit, $N \to \infty$ and $V \to \infty$, with all $n_\gamma$ kept constant, is taken finally so that the influence of the confining potential becomes negligible.

In the absence of the external forces, the system is assumed to be in thermodynamic equilibrium, and the configurational probability density function is given by

$$P_{eq}(R^N) = \exp(-\beta U(R^N))/Z. \hspace{1cm} (19)$$

Here, $Z = \int dR^N \exp(-\beta U(R^N))$, $R^N = (R_1, \ldots, R_N)$ is the set of position vectors of the particle centers, $dR^N = (dR_1, \ldots, dR_N)$ is the $3N$-dimensional volume element, and $U(R^N)$ is the total $N$-particle potential energy due to the solvent-averaged direct particle interactions and the wall-like potential. In the PM used in this work, the pair interactions are Coulomb plus excluded volume interactions. Equilibrium averages with respect to $P_{eq}(R^N)$ are denoted by $(\ldots)_{eq}$.

We assume that starting at time $t = 0$, the particles are exposed to a stationary and spatially periodic external potential

$$\Phi_q(R^N) = -\frac{1}{i q} \sum_{l=1}^N F_l \exp[i q \cdot R_l],$$  \hspace{1cm} (20)

implying that each particle $l \in \{1, \ldots, N\}$ is subjected to a spatially periodic, time-independent force,

$$F_l(R_l) = -\nabla_l \Phi_q(R^N) = q \hat{q} F_l \exp[i q \cdot R_l]$$  \hspace{1cm} (21)

acting at its center and being aligned with the vector $q = q \hat{q}$ of magnitude $q$. The $q$-dependent exponential phase factor has been introduced here to serve two purposes: First, to obtain unambiguous expressions for the ionic conduction-diffusion transport coefficients in presence of long-range HIs, and second, to make contact with the Mori-Zwanzig memory function formalism for dynamic structure factors (partially) accessible in scattering experiments. The steady-state electroosmosis of ions under a constant electric field $E = E \hat{q}$ is recovered from taking successively the limits $q \to 0$ and $t \to \infty$. These limits are performed once the thermodynamic limit has been taken.

The probability density function $P(R^N, t)$, describing the configurational evolution at times $t > 0$ in presence of the external field, is the solution of the GSE

$$\frac{\partial}{\partial t} P(R^N, t) = -\sum_{l=1}^N V_l \cdot (V_l P(R^N, t)), \hspace{1cm} (22)$$

with initial condition $P(R^N, t = 0) = P_{eq}(R^N)$. Here,

$$V_l(R^N, t) = \sum_{p=1}^N D_{lp}(R^N) \cdot [\beta \nabla_p U(R^N) - \nabla_p \ln P(R^N, t)] - \beta \nabla_p \Phi_q(R^N)$$  \hspace{1cm} (23)

is the configuration-dependent microscopic velocity of a particle $l$. We have introduced here the translational hydrodynamic diffusivity tensors, $D_{lp}(R^N)$, of spheres in an infinite Newtonian fluid. The tensors linearly relate the hydrodynamic force on particle $p$ at position $R_p$ to the resulting velocity change of particle $l$ at position $R_l$. They can be obtained, in principle, from solving the Stokes equation with hydrodynamic boundary conditions specified on the particle surfaces.

To linear order in the external forces, the probability density function for $t \geq 0$ is given formally by

$$P(R^N, t) = P_{eq}(R^N) \left[ 1 + \beta \int_0^t du \epsilon_q^{l}(R^N(t-u)) \delta \Phi_q(R^N) \right]$$  \hspace{1cm} (24)

where $\delta P(R^N, t = 0) = 0$ for the initial value of the perturbation part. We have introduced here the time-independent
backward Smoluchowski differential operator,\textsuperscript{50,51}
\[
\hat{O}_B^{(un)}(\mathbf{R}^N) = \sum_{i,j=1}^{N} [\nabla_i - \beta \nabla_i U(\mathbf{R}^N)] \cdot \mathbf{D}_{ij}(\mathbf{R}^N) \cdot \nabla_j,
\] (25)
of the spatially isotropic unperturbed system. The operator \(\exp(\hat{O}_B^{(un)}(\mathbf{R}^N)t)\) acts as the unperturbed time evolution operator for an arbitrary configuration space variable \(A(\mathbf{R}^N)\) during the time span \(t\).

We introduce next the microscopic longitudinal single-particle current, \(j_{q,l}\), of the unperturbed system by
\[
j_{q,l}(\mathbf{R}^N) = \frac{1}{i\mathbf{q}} \hat{O}_B^{(un)} \exp[i\mathbf{q} \cdot \mathbf{R}_l] = \left[\hat{\mathbf{q}} \cdot \mathbf{V}^{D,(un)}_l(\mathbf{R}^N) + i\mathbf{q} \cdot \mathbf{D}_{il}(\mathbf{R}^N) \cdot \hat{\mathbf{q}}\right] \times \exp[i\mathbf{q} \cdot \mathbf{R}_l],
\] (26)
where
\[
\mathbf{V}^{D,(un)}_l(\mathbf{R}^N) = \hat{O}_B^{(un)} \mathbf{R}_l = \sum_{p=1}^{N} [\beta \mathbf{D}_{lp}(\mathbf{R}^N) \cdot \nabla_p U(\mathbf{R}^N) + \nabla_p \cdot \mathbf{D}_{lp}(\mathbf{R}^N)]
\] (27)
is the microscopic drift velocity of particle \(l\) in the absence of the external force field. The second contribution to \(\mathbf{V}^{D,(un)}_l\), invoking the divergence of the diffusivity tensor, is of purely hydrodynamic origin and plays a role at higher concentrations. Note here that \(j_{q,l} = \hat{\mathbf{q}} \cdot \mathbf{V}^{D,(un)}_l + \mathcal{O}(q)\), so that
\[
\hat{O}_B^{(un)} \Phi_q = -\sum_{p=1}^{N} j_{q,p} F_p = -\sum_{p=1}^{N} \hat{\mathbf{q}} \cdot \mathbf{V}^{D,(un)}_p F_p + \mathcal{O}(q).
\] (28)

From inserting the linear response probability density function into Eq. (23), and expanding the resulting equation to first order in the external force field, we obtain
\[
\mathbf{V}_l(\mathbf{R}^N, t) = \beta \sum_{p=1}^{N} \mathbf{D}_{lp}(\mathbf{R}^N) \cdot F_p(\mathbf{R}_p) - \sum_{p=1}^{N} \mathbf{D}_{lp}(\mathbf{R}^N) \cdot \nabla_p \left(\delta P(\mathbf{R}^N, t)/P_{eq}(\mathbf{R}^N)\right).
\] (29)
The unperturbed part of \(\mathbf{V}_l\) is zero, as expected.

To make contact with Eq. (1), we evaluate the non-equilibrium average,
\[
\langle \hat{\mathbf{q}} \cdot \mathbf{V}_l \exp[-i\mathbf{q} \cdot \mathbf{R}_l]\rangle_{eq}(t) = \int d\mathbf{R}^N P(\mathbf{R}^N, t) \hat{\mathbf{q}} \cdot \mathbf{V}_l(\mathbf{R}^N, t) \exp[-i\mathbf{q} \cdot \mathbf{R}_l]
\] (30)
of the \(q\)th Fourier component of the microscopic velocity in the linearly perturbed system. Substitution of Eq. (29) into Eq. (30), followed by partial integration of the time-dependent term using \(\delta P = 0 = P_{eq}\) for \(\mathbf{R}_p\) posited outside \(V\), leads together with Eq. (26) to
\[
\begin{align*}
\langle \hat{\mathbf{q}} \cdot \mathbf{V}_l \exp[-i\mathbf{q} \cdot \mathbf{R}_l]\rangle_{eq}(t) &= \beta \sum_{p=1}^{N} \langle \hat{\mathbf{q}} \cdot \mathbf{D}_{lp}(\mathbf{R}^N) \cdot \hat{\mathbf{q}} \exp[i\mathbf{q} \cdot (\mathbf{R}_p - \mathbf{R}_l)]\rangle_{eq} F_p \\
&+ \int d\mathbf{R}^N \delta P(\mathbf{R}^N, t) j_{-\mathbf{q},l}(\mathbf{R}^N).
\end{align*}
\] (31)

By inserting \(\delta P\) according to Eq. (26) and (28) into the last equation, the average longitudinal velocity of a particle \(l\) given by
\[
\langle \hat{\mathbf{q}} \cdot \mathbf{V}_l \exp[-i\mathbf{q} \cdot \mathbf{R}_l]\rangle_{eq}(t) = \beta \sum_{p=1}^{N} \left\{\langle \hat{\mathbf{q}} \cdot \mathbf{D}_{lp} \cdot \hat{\mathbf{q}} \exp[i\mathbf{q} \cdot (\mathbf{R}_p - \mathbf{R}_l)]\rangle_{eq} \\
- \int_0^t du \langle j_{-\mathbf{q},l}(e^{\hat{O}_B^{(un)}(t-u)\mathbf{R}_p})\rangle_{eq} F_p\right\}
\] (32)
is expressed in terms of equilibrium averages. The first velocity contribution on the right-hand side of Eq. (32) is the instantaneous linear response to the external forces. The second, so-called relaxation term, describes the retarded velocity response to the external forces. It invokes the equilibrium longitudinal current time correlation function, and the backward Smoluchowski differential operator, \(\hat{O}_B^{(un)}(\mathbf{R}^N)\), of the unperturbed system. The form of the backward operator in the explicit notation for a mixture is given below.

For convenience, in Eqs. (19)–(32) we have used the most general notation where all \(N\) ions are allowed to be different from each other. We return now to the explicit notation for mixtures by considering an \(m\)-component mixture where equal external forces are acting on particles of the same component. In addition, we specialize Eq. (32) to the long-time limit where the system has reached a steady-state described by \(P_{eq}(\mathbf{R}^N) = P(\mathbf{R}^N, t \rightarrow \infty)\), and we take the thermodynamic limit followed by the constant force field limit \(q \rightarrow 0\). Owing to the long-range nature of the HIs, proper performance of the small-\(q\) limit is crucial to guarantee convergence of the equilibrium averages on the right-hand side of Eq. (32). This amounts to account properly for the solvent back-flow contribution in electrophoresis or sedimentation. The ensuing result gained from taking the consecutive limits is of the form given in Eq. (1), but now a microscopic expression for the long-time mobility matrix, \(\mu^L\), is obtained. The derivation of this expression is described in the following.

The partial mobilities consist of a short-time part (labeled by the superscript \(S\)), and a relaxation or memory part \(\Delta \mu_{\alpha \beta}\). Explicitly,
\[
\mu^L_{\alpha \beta} = \mu^S_{\alpha \beta} + \Delta \mu_{\alpha \beta},
\] (33)
with the short-time mobility part given by
\[
k_B T \mu^S_{\alpha \beta} = \lim_{q \rightarrow 0} H_{\alpha \beta}(q).
\] (34)
Here,\textsuperscript{51}
\[
H_{\alpha \beta}(q) = \delta_{\alpha \beta} D^S_\alpha + H^d_{\alpha \beta}(q)
\] (35)
are the partial hydrodynamic functions, where
\[ D_{α}^S = \lim_{∞} (q \cdot D_{11}^S (R^N) \cdot \dot{q})_{eq} \]
(36)
is the short-time self-diffusion coefficient of an α-component particle, and
\[ H_{αβ}^q (q) = (n_α n_β)^{1/2} \lim_{∞} V (q \cdot D_{ij}^β (R^N) \cdot \dot{q} e^q (R^N - R^i))_{eq} \]
(37)
are the wavenumber-dependent distinct parts of \( H_{αβ}(q) \). According to Eq. (32), the physical meaning of the \( H_{αβ}(q) \) is that of short-time partial sedimentation coefficient generalized to a sinusoidally varying force field of wavenumber \( q \) (we refer also to Ladd and others\(^{38,49}\)). The partial diffusivity tensor, \( D_{ij}^β (R^N) \), relates the hydrodynamic force on a spherical particle \( j ∈ β \) at position \( R^j \) to the velocity change of a particle \( i ∈ α \) at position \( R^i \). The limit symbol \( \lim_{∞} \) in Eqs. (36) and (37) abbreviates the thermodynamic limit, \( V → ∞ \), where all partial number concentrations, \( n_α \), are kept constant.

As genuine equilibrium averages of hydrodynamic diffusivity tensors, the \( μ_{αβ}^S \) and the associated short-time electrohydrodynamic mobility of α-type ions (see Eq. (4)),
\[ μ_{αβ}^{el,S} = \lim_{q → 0} \sum_{γ=1}^{m} (n_γ n_α)^{1/2} \zeta_γ e k_B T H_{αγ}(q), \]
(38)
are rather straightforwardly calculated using the PM equilibrium pair distribution functions as input, for moderately concentrated systems where two-body HIs contributions prevail.

The short-time electrohydrodynamic mobility \( μ_{αβ}^{el,S} \) is the sum,
\[ μ_{αβ}^{el,S} = μ_{αβ}^{el,0} + Δμ_{αβ}^{el,S}, \]
(39)
of the single-ion mobility part, \( μ_{αβ}^{el,0} \), given in Eq. (9), and the electrohydrodynamic mobility correction, \( Δμ_{αβ}^{el,S} \), arising from the HIs. The latter accounts for the slowing effect on the electric field-induced ion migration owing to the instantaneous hydrodynamic coupling of the ion motions. This coupling is particularly pronounced between cations and anions which migrate, on average, in opposite directions. According to Eq. (33),
\[ μ_{αβ}^{el} = μ_{αβ}^{el,0} + Δμ_{αβ}^{el,0} + Δμ_{αβ}^{el}, \]
(40)
and a similar decomposition into ideal (i.e., interaction-free), short-time and relaxation parts applies for the other linear conduction-diffusion transport coefficients. The relaxation part of the electrohydrodynamic mobility of α-type ions is
\[ Δμ_{αβ}^{el} = \sum_{γ=1}^{m} \left( \frac{n_γ}{n_α} \right)^{1/2} \zeta_γ e Δμ_{αγ}. \]
(42)
In accordance with Eq. (14), the non-ideal mobility parts are the respective sum of self- and cross-correlation contributions,
\[ Δμ_{αβ}^S = δ_{αβ} (Δμ_{αα}^S)^{self} + (Δμ_{αβ}^S)^{cross}, \]
(43)
\[ Δμ_{αβ} = δ_{αβ} (Δμ_{αα})^{self} + (Δμ_{αβ})^{cross}. \]
(44)
Similar decompositions hold sway also for other conduction-diffusion transport coefficients, since these are all expressible as linear combinations of the \( μ_{αβ}^{el} \). In the simplifying RP approximation of the HIs introduced further down, the short-time self-correlation contribution to the mobility coefficients vanishes. The only short-time contribution arises then from the electrophoretic effect. This is a cross-correlation contribution quantified by the zero-q limit of \( H^q(q) \). Explicit expressions for the self- and cross-correlation contributions to \( Δμ_{αβ}^L \) and \( Δμ_{αβ}^L \) are derived further down.

The calculation of the relaxation mobility contributions, \( Δμ_{αβ}^L \), to the electric conductivity and long-time electrohydrodynamic mobilities is considerably more difficult, for these relate to the relaxation of perturbed ion atmospheres under the action of electro-steric and hydrodynamic forces. Using Eq. (32), the relaxation mobilities can be expressed in form of a GK relation involving the time integral of a longitudinal current time correlation function, i.e.,
\[ k_B T (n_α n_β)^{1/2} Δμ_{αβ}^L = −\lim_{q → 0} 1 k_B T \int_0^∞ dt e^{-q^2 t/2} \langle j^β_q (e^{q^2 t} j^α_q) \rangle_{eq}. \]
(45)
Here, \( j^α_q \) is the qth Fourier component of the microscopic longitudinal current density of α-type particles,
\[ j^α_q = \frac{1}{i q} \mathcal{O}^{(αn)}_B \sum_{l=1}^{N_α} \exp \{ i q \cdot R^l \} = \dot{q} \cdot \sum_{l=1}^{N_α} \mathbf{V}_l^α \cdot \mathbf{D}^α_l (R^N) \cdot \nabla_j. \]
(46)
where \( \mathbf{V}_l^α \cdot \mathbf{D}^α_l (R^N) \) is the unperturbed microscopic drift velocity of an α-type particle, and \( ε \) is a positive infinitesimal (not to be confused with the solvent dielectric constant), introduced to guarantee convergence of the time integral.\(^{52}\) The backward Smoluchowski operator of the unperturbed ion mixture follows from Eq. (25) as\(^{50}\)
\[ \mathcal{O}^{(αn)}_B (R^N) = \sum_{α,β=1}^{N_α, N_β} \left[ \nabla_j - β \nabla_j U(R^N) \right] \cdot \mathbf{D}^α_l (R^N) \cdot \nabla_j. \]
(47)
Introducing the microscopic longitudinal current density of α-type ions,
\[ j^α_q^{el} = κ_α e j^α_q, \]
(48)
and the total longitudinal electric current density,
\[ j^el_q = \sum_{γ=1}^{m} \zeta_γ e j^γ_q, \]
(49)
a GK relation for the relaxation part of the specific conductivity is obtained which reads explicitly
\[ k_B T Δσ = −\lim_{q → 0} 1 k_B T \int_0^∞ dt e^{-q^2 t/2} \langle j^el_q (e^{q^2 t} j^el_q) \rangle_{eq}. \]
(50)
Likewise,
\[ k_B T n_α z_α e^2 Δμ_{αβ}^{el} = −\lim_{q → 0} 1 k_B T \int_0^∞ dt e^{-q^2 t/2} \langle j^el_q (e^{q^2 t} j^el_q) \rangle_{eq}. \]
(51)
is the GK relation for the relaxation part of the electrophoretic mobility. The unspecified limit symbol appearing in the above expressions is an abbreviation for the three consecutive limits in Eq. (45).

Owing the longitudinal projection matrix, \( \hat{q} \), which appears explicitly in \( H_{\alpha\gamma}(q) \), and implicitly in the GK relations through the longitudinal current \( j_{\alpha}^{\mu} = \hat{q} \cdot \tilde{j}_{\alpha}^{\mu} \), any Fourier-transformed divergence-free flux vector can be subtracted from \( \tilde{j}_{\alpha}^{\mu} \) and its short-time counterpart, without changing the values of the two transport coefficients. In particular, the \( q \)th Fourier component of the incompressible local mean volume flow velocity\(^{53,54} \) can be subtracted, implying that Eqs. (38) and (51) are the short-time and relaxation parts, respectively, of the electrophoretic mobility of \( \alpha \)-type ions as measured in the zero mean volume velocity reference frame.

### IV. MODE COUPLING THEORY OF PARTIAL MOBILITIES

#### A. Relation between partial mobilities and dynamic scattering functions

GK relations are very useful in computer simulation calculations.\(^{55-61} \) However, to obtain analytically tractable expressions for \( \Delta \mu^L_{\alpha\gamma} \), it is advantageous to relate the mobility matrix to the symmetric \( m \times m \) matrix, \( F(q, t) \), of partial dynamic structure factors,

\[
F_{\alpha\beta}(q, t) = \lim_{\infty} \langle e^{i \hat{q} \cdot \mathbf{R}_x} \rangle_{eq},
\]

of the unperturbed system, where

\[
c_{\alpha}^q = \frac{1}{\sqrt{N_{\alpha}}} \sum_{\gamma=1}^{N_{\alpha}} \exp \left[ i \mathbf{q} \cdot \mathbf{R}_\gamma \right] - \sqrt{N_{\alpha}} \delta_{q,0}
\]

is, up to the factor of \( 1/\sqrt{N_{\alpha}} \), the \( q \)th Fourier component of microscopic density fluctuations of \( \alpha \)-type particles. Specific linear combinations of partial dynamic structure factors are accessible in dynamic scattering experiments, where \( \mathbf{q} \) plays the role of the scattering wave vector. For clarity, we use the notation \( S_{\alpha\beta}(q, t = 0) \) for the initial values, which are referred to as the equilibrium partial static structure factors. The factor \( 1/\sqrt{N_{\alpha}} \) is included in the definition of \( c_{\alpha}^q \) to render \( F(q, t) \) intensive, and to obtain composition-independent large-\( q \) asymptotic initial values \( S_{\alpha\beta}(q \to \infty) = \delta_{\alpha\beta} \).

To relate \( \mu^L_{\alpha\beta} \) to \( F_{\alpha\beta}(q, t) \), we start from

\[
\frac{\partial^2}{\partial t^2} \frac{1}{q^2} F_{\alpha\beta}(q, t) = \lim_{\infty} \langle (\tilde{\hat{O}}_{\beta}^{(j\mu)} c_{\alpha}) \rangle_{eq} = -q^2 \Delta \mu_{\alpha\beta}
\]

where the second equality follows from \( \tilde{\hat{O}}_{\beta}^{(j\mu)} c_{\alpha} = i q j_{\alpha}^{\mu} / \sqrt{N_{\alpha}} \). On realizing that the partial hydrodynamic functions are given by

\[
\lim_{\infty} \langle e^{i \hat{q} \cdot \mathbf{R}_x} \rangle_{eq} = -q^2 H_{\alpha\beta}(q),
\]

time integration of Eq. (54) results in

\[
\frac{\partial}{\partial t} F_{\alpha\beta}(q, t) = -q^2 H_{\alpha\beta}(q)
\]

\[
+q^2 (n_{\alpha} n_{\beta})^{-1/2} \lim_{\infty} \frac{1}{q} \int_0^q du \langle j_x^{\alpha} (\delta^{\mu \nu} u j_x^{\beta}) \rangle_{eq},
\]

which relates the rate of change of \( F(q, t) \) to the longitudinal current autocorrelation function matrix. Comparison with the GK relations in Eqs. (32) and (45) shows that

\[
k_{\beta} T \mu_{\alpha\beta}^{L} = -\lim_{q \to 0} q^2 \frac{\partial}{\partial q} F_{\alpha\beta}(q, t).
\]

The relation in Eq. (57) between the searched-for mobility matrix and the time derivative of the equilibrium dynamic structure factor matrix is very useful, since the right-hand side of Eq. (57) can be obtained using well-developed solution schemes, such as MCT.

The conductivity and ion electrophoretic mobilities can be expressed in terms of global dynamic structure factors,

\[
F_{\alpha\alpha}(q, t) = \sum_{a=1}^m (x_{a\alpha} x_{a\beta})^{1/2} z_{a\alpha} z_{a\beta} F_{\alpha\beta}(q, t) = \frac{e^2}{k_B T} \text{Tr}[\mathbf{P} \cdot \mathbf{F}(q, t)],
\]

\[
F_{\alpha\alpha}(q, t) = \sum_{a=1}^m (x_{a\alpha} x_{a\beta})^{1/2} z_{a\alpha} z_{a\beta} F_{\alpha\beta}(q, t) = \text{Tr}[\mathbf{P} \cdot \mathbf{F}(q, t)],
\]

\[
F_{\alpha\beta}(q, t) = \sum_{a=1}^m (x_{a\alpha} x_{a\beta})^{1/2} z_{a\alpha} z_{a\beta} F_{\alpha\beta}(q, t),
\]

describing correlations in the microscopic fluctuations of the total charge-density (\( Z \)) and the total number density (\( N \)) around their mean values zero and \( n_T \), respectively. Here, \( \text{Tr} \) denotes the trace operation. Using Eq. (57) in conjunction with Eqs. (4) and (6), one obtains

\[
k_B T \sigma = -n_T e^2 \lim_{q \to 0} q^2 \frac{\partial}{\partial q} F_{\alpha\alpha}(q, t),
\]

\[
k_B T \sum_{a=1}^m x_{a\alpha} \mu_{a\alpha}^{L} = -\lim_{q \to 0} q^2 \frac{\partial}{\partial q} F_{\alpha\alpha}(q, t),
\]

where \( x_{a\alpha} = n_{a\alpha} n_T \) is the molar fraction of \( \alpha \)-type ions. The matrix \( \mathbf{P} \) with elements

\[
P_{a\beta} = \frac{(x_{a\alpha} x_{a\beta})^{1/2} z_{a\alpha} z_{a\beta}}{\overline{z}^2}
\]

is the projector (i.e., \( \mathbf{P} \cdot \mathbf{P} = \mathbf{P} \)) on the charge-density fluctuations subspace spanned by the \( m \)-dimensional vector \( \mathbf{u} \) of elements \( \{x_{a\gamma} z_{a\gamma}^{\gamma}\} \). Here,

\[
\overline{z}^2 = \sum_{y=1}^m x_{y\gamma} z_{y\gamma}^{\gamma}
\]

is the \( \mu \)th moment of the ion valency distribution (with \( \mu = 1, 2, \ldots \)), which for purely monovalent ions is equal to one for \( \mu \) even and zero for \( \mu \) odd. The Debye screening length, \( 1/\kappa \), characterizing the range of electrostatic ion
correlations, is related to the second moment by
\[ \kappa^2 = 4\pi L_B n_T c^2. \] (63)
The matrix, \( P_n \), of components \((x_n x_p)^{1/2}\) is the projector on the subspace of total number density fluctuations.

**B. General MCT scheme**

While a more simple one-component version of MCT can be directly applied to \( F_{zzz}(q, t) \) to obtain the conductivity, it is advantageous and more general to stick to the multi-component description, by treating the partial dynamic structure factors individually on basis of the exact matrix memory equation,\(^33\)
\[
\frac{\partial}{\partial t} F(q, t) = -q^2 \mathbf{H} \cdot \mathbf{S}^{-1}(q) \cdot F(q, t)
\]
\[ - \int_0^t du M^{c, irr}(q, t-u) \cdot \mathbf{H}^{-1}(q) \cdot \frac{\partial}{\partial u} F(q, u), \] (64)
for \( F(q, t) \) in Smoluchowski dynamics. Here, \( M^{c, irr}(q, t) \) is the symmetric \( m \times m \) matrix of irreducible collective memory functions, \( M^{c, irr}_{\alpha\beta}(q, t) \), which has been introduced for hydrodynamically interacting particles by one of the present authors. For its microscopic expression in terms of a force correlation expression involving a reduced time evolution operator, we refer to Nägele et al.\(^33\)

By taking the Laplace transform of Eq. (64) in conjunction with Eq. (57), we obtain the result\(^33\)
\[
k_B T \mu^L = \left[ 1 + m^{c, irr} \cdot \mathbf{H}^{-1} \right]^{-1} \cdot \mathbf{H}, \] (65)
which expresses \( \mu^L \) in terms of the zero-wavenumber limit of the time-integrated memory function matrix,
\[
m^{c, irr} = \lim_{q \to 0} \int_0^\infty dt M^{c, irr}(q, t), \] (66)
and in terms of
\[
\mathbf{H} = \lim_{q \to 0} \mathbf{H}(q). \] (67)

Using the Woodbury matrix inversion formula,\(^62\) we can deduce from Eq. (65), the relaxation part of the mobility matrix, with the result
\[
k_B T \Delta \mu_{\alpha\beta} = -\left( m^{c, irr} \cdot \left[ 1 + \mathbf{H}^{-1} \cdot m^{c, irr} \right]^{-1} \right)_{\alpha\beta}. \] (68)
One easily verifies the symmetry of the matrix on the right-hand side of Eq. (68), in accordance with the required symmetry of \( \Delta \mu \). MCT approximations for Brownian particle mixtures should be introduced on the level of the irreducible memory function matrix,\(^33,63-65\) in order to preserve the positive definiteness of long-time self-diffusion and collective diffusion coefficients, and to obtain for colloidal suspensions at large concentrations a consistent glass-like dynamic arrest scenario.

A MCT scheme for diffusion properties of Brownian mixtures was formulated before,\(^31,33\) where HIs have been accounted for on a pairwise level using the far-field RP hydrodynamic diffusivity tensors. In this so-called MCT-HIs approach, the time-integrated and zero-\( q \) limiting irreducible partial memory functions are approximated by
\[
m^{c, irr}_{\alpha\beta} = \frac{D_0^\alpha D_0^\beta}{2(2\pi)^2(n_{\alpha\beta}^\prime)} \int_0^\infty dt \sum_{\gamma, \delta, \gamma', \delta'} \int d^3 k V_{\alpha\gamma\delta}(0, k) V_{\beta\gamma'\delta'}(0, k) \times F_{\gamma'\delta'}(k, t) \] (69)

Here, \( V_{\alpha\gamma\delta}(0, k) \) abbreviates the zero-\( q \) limit of the vertex function,
\[
V_{\alpha\gamma\delta}(q, k) = V^p_{\alpha\gamma\delta}(q, k) + V^h_{\alpha\gamma\delta}(q, k) \] (70)
consisting of a pair potential (p) and a hydrodynamic (h) part.\(^33\)

Explicit expressions for the vertex function, and a detailed discussion of the assumptions and approximations underlying Eq. (69) have been given in Refs. 31 and 33. For readers familiar with MCT, we note that the HIs have been included using the same factorization of the four-point dynamic density correlator as employed in the MCT of atomic mixtures.\(^66-69\) The MCT-HIs scheme underlying Eq. (69) includes therefore the standard MCT result for non-hydrodynamically interacting Brownian particles as a limiting case. We further note that the convolution approximation of static triplet distribution functions employed in the multicomponent MCT is consistent with the equilibrium local electro-neutrality condition.\(^8,9\)

If HIs are neglected in the vertex contribution, i.e., if \( V^h_{\alpha\gamma\delta}(q, k) = 0 \) is assumed, Eq. (69) reduces to
\[
m^{c, irr}_{\alpha\beta} = \frac{D_0^\alpha D_0^\beta}{6\pi^2(n_{\alpha\beta}^\prime)^{1/2}} \int_0^\infty dt \int_0^\infty d^3 k \kappa^4(F_{\alpha\beta}(k, t)(C(k) \cdot \mathbf{F}(k, t) \cdot \mathbf{C}(k))_{\alpha\beta} - (C(k) \cdot \mathbf{F}(k, t))_{\alpha\beta}(C(k))_{\alpha\beta}). \] (71)

Here, \( C(q) \) is the \( m \times m \) matrix of concentration-scaled partial direct correlation functions in Fourier space, \( (n_{\alpha\beta}^\prime)^{1/2}C_{\alpha\beta}(q) \), related to the static structure factor matrix of the unperturbed system by the Ornstein-Zernike matrix equation\(^8,51\)
\[
S(q) = \left[ 1 - C(q) \right]^{-1}. \] (72)

The present MCT-HIs scheme for \( \Delta \mu_{\alpha\beta}^L \) has the static pair distribution functions as the only input. In the PM, the direct correlation function matrix is of the form\(^8\)
\[
C(q) = C^{(c)}(q) - \frac{\kappa^2}{q^2} P, \] (73)
where the non-ideal matrix part, \( C^{(c)}(q) \), is regular at \( q = 0 \). It describes the shorter-range part of the direct correlations arising, in particular, from ion excluded volume interactions, and it can be calculated on different levels of approximation. Particularly convenient for MCT calculations is Blum’s analytic MSA solution\(^70,71\) for the unrestricted PM, and the analytic direct correlation function matrix of equal sized ions given by Attard.\(^8\) Blum’s and Attard’s solutions satisfy the local electroneutrality and charge-oscillation moment conditions,\(^9\) and
in the point-ion limit they both reduce to the DH form of the direct correlation function matrix where $C^{ij}(q)$ is taken to be zero.

The HIs in the MCT-HIs scheme are here accounted for on the RP level of approximation where hydrodynamic flow reflections are neglected, and stick hydrodynamic boundary conditions on the PM ion surfaces are assumed.\(^{72}\) The diffusivity tensors in RP approximation are given by $D_{i,i}^{αβ} = D_{α}^{0}$ and $D_{i,j}^{αβ} = k_BT \Gamma_{αβ}^{R,P}(r)$ for ion pairs $i \neq j$, where

$$
\Gamma_{αβ}^{R,P}(r) = \frac{1}{8\pi\eta_0} \left[ \frac{1}{r} (1 + \hat{r} \hat{r}) + \frac{a_α^2 + a_β^2}{3r^3} (1 - 3\hat{r} \hat{r}) \right]
$$

and $r = R_α^i - R_β^j$. Thus, $D_{α}^{0}$ is approximated on the RP level by its zero concentration value $D_{α}^{0}$. The distinct part of $H(q)$ is given in RP approximation by the integral

$$
H^{d}_{αβ}(q) = (n_α n_β)^{1/2} \int_{0}^{\infty} drr R_{αβ}(q, r) h_{αβ}(r)
$$

$$
- \frac{2k_BT}{3\eta_0} \left( a_α^2 + a_β^2 + 3a_α a_β \right) j_1(q(a_α + a_β))
$$

$$
\cdot \left[ \frac{a_α}{a_α + a_β} \right],
$$

(74)

involving the RP kernel function

$$
K_{αβ}(q, r)
$$

$$
= \frac{k_BT}{3\eta_0} \left[ 3 \left( j_0(qr) - \frac{j_1(qr)}{qr} \right) + q^2 \left( a_α^2 + a_β^2 \right) \frac{j_2(qr)}{(qr)^2} \right].
$$

(75)

Here, $h_{αβ}(r)$ is the real-space partial total correlation function for an $(α, β)$ pair of ions separated by the distance $r$, $J_α$ is the spherical Bessel function of order $α$, and $a_α$ is the hydrodynamic radius of $α$-component ions. The expression for $H^{d}_{αβ}(q)$ in Eq. (75) is already regularized at $q = 0$, and it describes an $O(q^{-2})$ asymptotic decay for large $q$. While constituting an approximation, the RP approximation has the desirable features of accounting for the salient monopolar and dipolar HIs contributions, and of preserving the positive definiteness of the exact hydrodynamic function matrix $H^{dd}(q)$. The derivation of the RP approximation on basis of a minimal dissipation theorem\(^{39,73,74}\) implies the positive definiteness also of $H^{R,P}(q) - H^{dd}(q)$. The RP approximation can be thus used to obtain upper bounds on the exact short-time diffusion and sedimentation coefficients (see, e.g., Gilleland et al.\(^{39}\)).

The MCT-HIs scheme for $Δμ_{αβ}^{EL}$ allows in principle for a unified analysis of conduction-diffusion properties of electrolyte mixtures and charge-stabilized colloidal suspensions, with the salient influence of the HIs accounted for. In recent work,\(^{30}\) we have derived a related MCT-HIs scheme for the viscosity and shear stress relaxation function of electrolyte mixtures. The electroviscosity results from the MCT-HIs scheme\(^{30}\) have been obtained using a simplified treatment of the associated coupled MCT-HIs equations. A simplified MCT treatment of conduction-diffusion properties is discussed in the following.

### C. Simplified treatment

The numerical evaluation of the MCT-HIs expressions for the mobility coefficients, $Δμ_{αβ}^{EL}$, of an $m$-component electrolyte requires as an intermediate step the self-consistent numerical MCT calculation of all $(m+1)/2$ dynamic structure factors $F_{αβ}(q, t)$. This is a cumbersome task, in particular when HIs are included. However, as discussed before,\(^{30}\) for moderately concentrated electrolytes, $F(q, t)$ can be expected to be only modestly perturbed from its short-time form $F_0(q, t)$. It is then reasonable to solve the coupled equations approximately in a single iterative step, by using the short-time form

$$
F_0(q, t) = e^{-q^2\Delta t} H(q) \cdot S(q),
$$

(77)

of $F(q, t)$ as the dynamic input to Eqs. (69) and (71), and on neglecting in addition the hydrodynamic vertex contribution so that Eq. (71) for $m_{α,\text{irr}}$ can be used. This simplified MCT-HIs scheme allows for great analytic progress, as it was shown in related calculations of the electrolyte viscosity,\(^{30}\) and it can be profitably used for analyzing general trends.

The short-time form of $F(q, t)$ is the sum of $m$ exponentially decaying normal modes,

$$
F(q, t) = \left( \sum_{i=1}^{m} \Lambda_i(q) e^{-\lambda_i(q)t} \right) \cdot S(q),
$$

(78)

where the $λ_i(q)$ are the positive eigenvalues (relaxation rates) of the positive definite short-time relaxation matrix $q^2 H(q) \cdot S(q)$. There are a few cases where the normal mode expansion can be carried out analytically, including the PM mixtures consisting of ions of equal single-particle diffusion coefficient, binary electrolytes of differently mobile ions, and mixtures of two binary electrolytes.

According to the Abel-Galois-Ruffini theorem, it is in general not possible to determine the eigenmodes analytically for more than four ion components. In general, a numerical calculation is required to obtain the $λ_i(q)$, and the associated mode amplitude matrices $A_i(q)$. For ions with nearly equal $D_{α}^{0}$, a perturbation expansion method with respect to the relative difference in the diffusion coefficients can be used, as employed in the work by Onsager.\(^{3}\) For an analytically diagonalizable relaxation matrix, the normal modes can be constructed from the application of the Cayley-Hamilton theorem, as implemented in the method of Cheng and Yau\(^{15}\) used in the present work.

In the $m$-component PM, there exists a non-diffusive, so-called Debye mode, whose eigenvalue

$$
λ_{EL}(q) = κ^2 \text{Tr}[P \cdot H] + O(q^2),
$$

(79)

is non-zero at $q = 0$, different from all the other $m - 1$ eigenvalues which are of $O(q^2)$. Here, $P$ is the projector on charge-density fluctuations defined in Eq. (61) and $κ$ is the Debye-Hückel parameter defined in Eq. (63). Local electroneutrality commands that $A_{EL}(q) \cdot S(q) = O(q^2)$. The Debye mode originates from the long-range nature of the Coulomb forces. The associated Debye time, $τ_{EL} = 1/κ_{EL}(0)$, is the characteristic relaxation time required for a spatial charge density fluctuation of wavelength $\sim 1/κ$ to relax towards equilibrium, under the slowing influence of the HIs.
bodied in $\mathbf{H}$. For a one-molar aqueous 1:1 electrolyte solution, $\tau_{el} \sim 14$ ns.

Numerical results for conduction-diffusion transport coefficients of more concentrated solutions, obtained from the present simplified MCT-HIs using Attard’s static input for finite-sized ions, are discussed in Paper II.\textsuperscript{84} In the following, we restrict ourselves to mixtures of pointlike ions where fully analytical results can be obtained. We show that, as a basic requirement, the DFOF limiting law expressions for the molar conductivity, electrophoretic mobilities, and self-diffusion coefficients are recovered from our MCT-HIs scheme in the limit of very low concentrations.

We close this section by noting that for more concentrated electrolyte systems (concentrations typically larger than 1–2 M) the memory contributions in Eq. (64), i.e., the longer-time ion cloud relaxation contributions, are significant and lead to an overall slower decay of $F(q, t)$ at longer times. The slower decay can be approximately accounted for, while preserving the form of an $m$-mode exponential decay, on using instead of $F^M(q, t)$ the symmetric matrix,

$$ F^M(q, t) = \exp[-q^2 t (\mathbf{H}(q) + k_B T (\Delta \mu)^{self} \cdot \mathbf{S}^{-1}(q)) \cdot \mathbf{S}(q)], $$

(80)

as an approximation for the dynamic structure factor matrix $\mathbf{F}(q, t)$ entering into Eq. (71). The searched-for long-time mobility tensor $\mu^L(q)$, with its self-correlation relaxation part $k_B T (\Delta \mu)^{self}$ consisting of the diagonal matrices of $\mathbf{D}^L_{\alpha \beta} = \delta_{\alpha \beta} D^L_{\alpha}$ and $\mathbf{(D}^{s\,}_{\alpha \beta} = \delta_{\alpha \beta} D^s_{\alpha}$, can be calculated self-consistently via iteration using $\mathbf{D}^M = \mathbf{D}^S$ as the starting input. For large values of $q$ where $\mathbf{S}(q) \rightarrow \mathbf{I}$ and $\mathbf{H}(q) \rightarrow \mathbf{D}^S$, $\mathbf{F}^M(q, t)$ reduces to a diagonal matrix which has the self-intermediate partial scattering functions in the long-time Markovian limit, given by $-q^2 D^L_{\alpha}(t)$, as its non-zero entries. In using Eq. (80) as an approximation for the exact $\mathbf{F}(q, t)$, one assumes that cross-correlation relaxation contributions, in addition to those contained in $\mathbf{H}(q)$, can be disregarded relative to the stronger self-correlations. Refined calculations based on a self-consistent approach such as the one discussed here will be analyzed elsewhere. For the special case of (colloidal) self-diffusion, a self-consistent simplified MCT-HIs approach similar to the one discussed here has been employed before.\textsuperscript{31,76}

V. ANALYTIC RESULTS FOR POINTLIKE IONS

At very low electrolyte concentrations (i.e., $n_T \lesssim 0.01$ M), we can neglect $\mathbf{C}^{(3)}(q)$ in Eq. (73) and treat the ions as pointlike particles. This results in the DH approximation for the direct correlation function matrix, $\mathbf{C}^{DH}(q) = -\kappa^2 \mathbf{P}/q^2$, with the corresponding DH static structure factor matrix given by

$$ S^{DH}(q) = \mathbf{Q} + \frac{q^2}{q^2 + \kappa^2} \mathbf{P}. $$

(81)

Here, $\mathbf{Q} = 1 - \mathbf{P}$ is the $m \times m$ projector matrix on the $m - 1$ dimensional subspace orthogonal to the subspace of charge-density fluctuations, with the matrix elements of $\mathbf{P}$ defined in Eq. (61).

The HIs between point particles are accounted for exactly on the Oseen level, where the distinct part of the hydrodynamic function matrix is obtained from taking the zero-ion radius limit, $a_q \to 0$, in Eq. (75). The subsequent insertion of the DH radial distribution functions leads to the pointlike ion result,

$$ H_{q,\alpha}^d(q) = -D_k F^{O}(q/\kappa) P_{\alpha\beta}, $$

(82)

which contains the Oseen function

$$ F^{O}(x) = \frac{3}{4\kappa^6} [x + (x^2 - 1) \arctan(x)]. $$

(83)

This function decays monotonically with increasing $x$ from the initial value $F^{O}(0) = 1$ to the limiting value zero for large $x$. The function $H_{q,\alpha}^d(q)$ for pointlike ions has an $1/q^2$ asymptotic decay which is slower than that of its non-zero ion diameter counterpart. The latter decays asymptotically like $1/q^6$.

In Eq. (82),

$$ D_k = \frac{k_B T}{6\pi \eta} \kappa $$

(84)

is a diffusion coefficient associated with the Debye screening length $1/\kappa$. The complete hydrodynamic function matrix of pointlike ions with DH pair correlations is given in projector representation by

$$ H_{q,\alpha}^d(q) = D_k^0 Q_{\alpha\beta} + (D_k^0 - D_k F^{O}(q/\kappa)) P_{\alpha\beta}. $$

(85)

where for pointlike ions the $D_k^0$ are treated as independent input parameters. For a dilute electrolyte, $D_k \ll D_k^0$ holds for all ion components.

A. Short-time transport properties

Using Eq. (85) for $\mathbf{H}(q)$, the short-time part of the mobility matrix follows as

$$ k_B T \mu^{S}_{\alpha\beta} = \delta_{\alpha\beta} D_k^0 - D_k P_{\alpha\beta}. $$

(86)

Together with Eq. (38), this leads to the well-known DFOF limiting law result,\textsuperscript{4}

$$ \mu^{el.\, S}_{\alpha} = \mu^{el.\, 0}_{\alpha} - \frac{z_a e}{6\pi \eta_0 \kappa}, $$

(87)

for the short-time part of the steady-state electrophoretic mobility of $\alpha$-type ions. The electrophoretic mobility of an isolated $\alpha$-type ion, $\mu^{el.\, 0}_{\alpha}$, is reduced by the electrophoretic effect which, according to $\kappa \propto \sqrt{\pi e_T}$, leads to a negative-valued contribution with a square-root in concentration dependence. According to Eqs. (39) and (87), this dependence is explicitly

$$ \Delta \mu^{el.\, S}_{\alpha} = (\Delta \mu^{el.\, S}_{\alpha})^{cross} = -\frac{z_a e^2}{k_B T D_k}. $$

(88)

The short-time part of the molar conductivity of $\alpha$-type ions follows readily from the short-time version of Eq. (7) as

$$ \lambda^{el.\, S}_{\alpha} = \lambda^{el.\, 0}_{\alpha} - \frac{z_a e^2 F}{6\pi \eta_0 \kappa}. $$

(89)
Likewise, the short-time specific conductivity and molar conductivity are obtained, using Eqs. (6) and (8), as
\[
\sigma^S = \sigma^0 - n_T \frac{\bar{e}^2}{k_B T} D_\kappa
\] (90)
and
\[
\Lambda^S = \Lambda^0 - \left( \sum_{a=1}^m \nu_a \bar{z}^2_a \right) \frac{e_F}{6 \pi \eta_0} \kappa,
\] (91)
respectively. Here,
\[
\sigma^0 = n_T \frac{\bar{e}^2}{k_B T} \sum_a \nu_a D_a^0
\] (92)
and
\[
\Lambda^0 = \sum_{a=1}^m \nu_a \alpha_a^{el,0}
\] (93)
are the zero concentration limiting values of \(\sigma\) and \(\Lambda\).

All the considered short-time transport properties show the characteristic square-root in concentration dependence, characteristic of the limiting law transport properties of strong electrolytes. We recall that the electrophoretic effect caused by the HIs is operating on the short-time level. HIs contribute also to the relaxation effect, but only at larger than linear order in \(\kappa\). Thus, in the limiting law regime of very small ion concentrations, the relaxation effect part of the conduction-diffusion properties is determined solely by the electrostatic interactions.

B. Limiting law results for long-time properties

In the following, we show that for very low concentrations where \(D_e \ll D_a^0\) is valid, the DFOF limiting law results for conduction-diffusion properties are recovered from our MCT-HIs scheme. In previous work,\(^{30}\) we have shown that the limiting law expressions for the electrolyte viscosity and shear modulus are recovered from a corresponding MCT-HIs scheme describing linear viscoelasticity of Brownian particles.

Before embarking into the discussion of specific systems, we note that in a strongly dilute mixture \(F(q, t)\) is represented, to good accuracy, by its short-time form given in Eq. (77), specialized to pointlike ions with \(S(q) = S_{DFOF}(q)\) and \(H(q)\) given by Eq. (85). Furthermore, Eq. (71) can be used for \(m^{el, irr}\) since, to linear order in \(\kappa \propto \sqrt{\eta_T}\), the time-integrated memory function matrix is independent of the HIs. This follows from \(V^{el, irr}_{a, b, \gamma} = O(\kappa^0)\) and \(V^{el, irr}_{a, \gamma} = O(\kappa)\), with the latter relation being valid\(^{33}\) owing to \(H^{el}(q) \propto \kappa\), and to the fact that \(m^{el, irr}\) is of \(O(\kappa)\) already without HIs. Thus, in agreement with the DFOF theory, the MCT-HIs predict that the first-order in \(\kappa\) relaxation parts of the transport coefficients are independent of the HIs.

1. Ions with equal individual diffusion coefficients

For pointlike ions where for all ion components \(D_a^0 = D_0\), the normal mode expansion for \(F^S(q, t)\) is obtained analytically as
\[
F^S(q, t) = e^{-q^2 D_0^2 t} Q + \frac{q^2}{q^2 + \kappa^2} e^{-\kappa \delta_{q,0} D_0^2 t} P,
\] (94)
with the Debye mode relaxation rate given by
\[
\kappa_D(q) = (q^2 + \kappa^2)(D_0^2 - D_a^0 F^O_{ab}(q/\kappa)).
\] (95)
The Debye rate includes the slowing influence of the HIs on the relaxation of charge concentration fluctuations by means of the term proportional to \(D_a^0 F^O_{ab}\).

Substitution of \(S_{DFOF}(q) = -\kappa^2 P/q^2\), and Eq. (94) for the \(F^S(q, t)\) without HIs into Eq. (71), leads after a straightforward calculation to the result,
\[
\frac{1}{D_0} m^{el, irr}_{a, b} = f^p_k L_B z_a z_b (\delta_{a, b} - P_{a, b}),
\] (96)
for the time-integrated memory function matrix. Here, \(f^p = (2 - \sqrt{2})/6\) is a numerical coefficient characteristic of the electrostatic interactions, and \(P_{a, b}\) is defined in Eq. (61). One notices from Eq. (96) that \(m^{el, irr} \propto \kappa\) without HIs, and that HIs contribute to the MCT memory (relaxation) part first to \(O(\kappa^2)\). Recall here that the (short-time ) electrophoretic contribution to the electrophoretic velocity of pointlike ions is also linear in \(\kappa\).

According to Eq. (68), the relaxation part of the long-time mobility coefficients is obtained to first order in \(\kappa\) from
\[
k_B T \Delta \mu_{a, b} = m^{el, irr}_{a, b} + O(\kappa^2).
\] (97)
Using Eq. (44), DFOF results for the self- and cross correlation contributions to the relaxation part of the mobility matrix are readily identified on basis of Eq. (96) as
\[
k_B T \frac{D_0}{D^0}(\Delta \mu_{a, b})^{self} = -z_a^2 \frac{f^p}{k} L_B + O(\kappa^2)
\] (98)
and
\[
k_B T \frac{D_0}{D^0}(\Delta \mu_{a, b})^{cross} = z_a z_b \frac{f^p}{k} L_B P_{a, b} + O(\kappa^2),
\] (99)
respectively.

The corresponding DFOF-type self- and cross terms of the relaxation contribution to the ion-component-specific electrophoretic mobilities follow with Eq. (42) as
\[
(\Delta \mu_{a}^{el, irr})^{self} / \mu_{a, 0}^{el} = -z_a^2 \frac{f^p}{k} L_B + O(\kappa^2).
\] (100)
and
\[
(\Delta \mu_{a}^{el, irr})^{cross} / \mu_{a, 0}^{el} = z_a z_b \frac{f^p}{k} L_B + O(\kappa^2).
\] (101)
The relaxation contribution to the electrophoretic mobility is of quadratic order in the valencies, whereas the short-time electrophoretic contribution has a linear charge dependence. From Eqs. (16) and (100), we obtain
\[
\frac{D_a^L}{D_a^0} = 1 - z_a^2 \frac{f^p}{k} L_B + O(\kappa^2)
\] (102)
for the limiting law long-time self-diffusion coefficient of \(\alpha\)-type ions. Moreover, from collecting the parts in Eq. (41)
given in Eqs. (88) and (101),
\[
(\mu^c_{a})^{\text{cross}} = \frac{z_a e}{k_B T} D_c + \frac{z_3}{z^2} z_a f_p k L_B \mu_d^{c,0} + O(\kappa^2) \tag{103}
\]
is obtained for the low-concentration cross-correlation contribution to the electrophoretic mobility. Here, \(z_3\) is the third moment of the ion valency distribution (cf. Eq. (62)). For purely monovalent ions, \(z_3 = 0\) and the cross-correlation relaxation mobility contribution vanishes.

The MCT-HIs results presented here agree with the DFOF limiting law results for the electrophoretic mobility,\(^4\) and the long-time self-diffusion coefficient,\(^8\) respectively. Equations (16) and (103) quantify, in the limiting law regime, the relative importance of the cross correlations contribution to the electrophoretic mobility which is left out in the Nernst-Einstein relation in Eq. (17).

We note that if HIs are neglected regarding the relaxation effect contributions, and \(D^\alpha_c = D^0_c\) is used in conjunction with the DH approximation, an analytic expression for \(\Delta \mu_{a\beta}\) is obtained for all (physically allowed) values of \(\kappa\). The derivation of this expression is included in the Appendix.

2. Binary electrolyte solution

Consider next a binary \(zc,za\) electrolyte solution of pointlike cations and anions, with valencies \([zc, za]\) and single-ion diffusion coefficients \((D^c_0, D^a_0)\), where \(D^\alpha_0\) can be different from \(D^0_\alpha\). As in Subsection V B 1, HIs are ignored in the relaxation effect, implying \(H(q) = 0\) with a 2 \(\times\) 2 diagonal matrix \((D^\alpha_0, D^\beta_0) = D^\alpha_0 \delta_{\alpha \beta}\) which for \(D^\alpha_0 \neq D^0_\alpha\) does not commute with \(S^{-1}(q)\). This makes the normal mode expansion somewhat more difficult to perform. After some calculations, we obtain the symmetric dyadic form
\[
m^c_{a\beta}^{\text{cross}} = (-1)^{\sigma+c} (|za|/z^2)^{1/2} D^\alpha_0 D^\beta_0 \frac{x_{\alpha|x_{\beta}}}{x_{\alpha|x_{\beta}}} f_{\beta \alpha \beta} k L_B, \tag{104}
\]
for the MCT memory function without HIs, where \(\alpha \in \{c, a\}\), \(D^0_+ + D^0_c\), and \(x_{\alpha|x_{\beta}} = x_{\alpha|x_{\beta}}\). Furthermore, \(f_{\beta \alpha \beta}\) and
\[
f_{\beta \alpha \beta} = \frac{1}{3(1 + \sqrt{D^+/D_+})} \tag{105}
\]
and
\[
D = \frac{z_c D^0_c - z_a D^0_a}{z_c - z_a} = \frac{D^0_c D^0_a}{D^0_{NH}}, \tag{106}
\]
where \(D^0_{NH}\) is the Nernst-Hartley mutual diffusion coefficient,\(^4,7\)
\[
D^0_{NH} = D^0_c D^0_a P_{cc} + P_{aa}, \tag{107}
\]
of an ultradilute binary electrolyte, referred to in the literature also as the chemical or ambipolar diffusion coefficient. It quantifies the coupled diffusion, enforced by local electroneutrality, of cation-anion complexes along thermally induced density gradients. Equation (107) shows explicitly that \(D^0_{NH} > 0\). For cations and anions with equal diffusion coefficient, it follows that \(D^0_{NH} = D^0_+\) and \(f_{\beta \alpha \beta} = 2 f_0\).

To make contact with Eq. (96), valid for ions of equal individual diffusion coefficients, note that \(m^{c,\beta}_{a\beta}\) in Eq. (104) can be alternatively expressed for a binary electrolyte by the sum of self- and cross-correlation parts,
\[
m^{c,\beta}_{a\beta} = \frac{D^0_0 D^0_0}{D^0_+} L_B \kappa^2 \frac{z_c z_a (\delta_{a\beta} - P_{a\beta})}{3 \kappa + k_d} \tag{108}
\]
where the square root of
\[
k_d = 4 \pi L_B n_T \sum_{\epsilon=1}^m D^0_0 x_{\alpha|x_{\beta}}^2 \tag{109}
\]
reduces to \(k_d = \kappa/\sqrt{2}\) for anions and cations of same individual diffusion coefficients. As before, \(P_{a\beta}\) is defined in Eq. (61).

The relaxational mobility matrix, \(\Delta \mu\), is obtained using Eq. (68) from noting that \(1 + \mathbf{H}^{-1}\cdot \mathbf{m}^{\text{cross}}\) is of the dyadic form \(1 + \mathbf{w}_\alpha \cdot \mathbf{v}_\alpha\), with \(v_\alpha = (-1)^{\sigma+c}(|za|)^{1/2} x_{\alpha|x_{\beta}} f_{\beta \alpha \beta} k L_B/D_\alpha\), and \(w_\beta = D^0_\beta v_\beta\), so that \(m^{c,\beta}_{a\beta} = u_{a\beta} w_\beta\). Application of the Sherman-Morrison matrix inversion formula leads to the result
\[
k_B T \Delta \mu_{a\beta} = -\frac{u_{a\beta} w_\beta}{1 + \mathbf{w}^T \cdot \mathbf{v}}, \tag{110}
\]
The relaxation part of the electrophoretic mobility of \(\alpha\)-type ions follows from this expression as (see Eq. (4))
\[
\Delta \mu_{a\alpha}^{\text{el}} = -\mu_{a\alpha}^{\text{el},0} \frac{\mathbf{w}^T \cdot \mathbf{v}}{1 + \mathbf{w}^T \cdot \mathbf{v}}, \tag{111}
\]
where we have used that \(\mathbf{w}^T \cdot \mathbf{v} = -\frac{z_c z_a}{3} \frac{D^0_0 D^0_0}{D^0_+ D^0_{NH}} \kappa L_B\).\(^{112}\)

To leading order in \(\kappa\), the MCT expression for \(\Delta \mu_{a\alpha}^{\text{el}}\) in Eq. (111) agrees with the limiting law result by Onsager\(^7\) who has obtained
\[
\frac{\Delta E}{E} = \frac{z_c z_a}{3} \frac{D^0_0 D^0_0}{D^0_+ D^0_{NH}} \kappa L_B < 0, \tag{113}
\]
for the relaxation electric field part, \(\Delta E\), experienced by an ion in a binary electrolyte, and originating from its distorted microion cloud. Here, \(E\) is the strength of the external electric field. The anions and cations experience the same relaxation field which is collinear with the external field.

The total partial mobilities are given, using
\[
k_B T \mu_{a\alpha}^{L} = k_B T (\mu_{a\alpha}^{S} + \Delta \mu_{a\alpha})
\]
\(= \delta_{a\beta} D_\beta - D_\alpha P_{a\beta} - \frac{z_c z_a}{k_B T} \frac{u_{a\beta} w_\beta}{1 + \mathbf{w}^T \cdot \mathbf{v}}, \tag{114}\)
as the sum of the zero-concentration, electrophoretic and relaxation effect parts. The electrophoretic mobility of \(\alpha\)-type pointlike ions follows from Eqs. (87), (111), and (84), as
\[
\mu_{a\alpha}^{\text{el}} = \mu_{a\alpha}^{\text{el},0} + \Delta \mu_{a\alpha}^{\text{el}}
\]
\(= \mu_{a\alpha}^{\text{el},0} - \frac{z_c z_a}{k_B T} D_\alpha - \mu_{a\alpha}^{\text{el},0} \frac{\mathbf{w}^T \cdot \mathbf{v}}{1 + \mathbf{w}^T \cdot \mathbf{v}}, \tag{115}\)
According to Eq. (111),
\[
\frac{\Delta \mu_{el}^c}{\mu_{el}^c,0} = \frac{\Delta \mu_{el}^d}{\mu_{el}^d,0},
\]
which tells us that the ratio of the relaxation electrophoretic mobility part and the zero-concentration electrophoretic mobility is the same for cations and anions. The cationic and anionic electrophoretic mobilities of pointlike ions predicted by MCT fulfill this symmetry property also for larger values of \(k\), and not only to linear order as in the limiting law results. A corresponding symmetry relation does not hold for the ratio of the long-time and short-time self-diffusion coefficients of pointlike ions given by
\[
\frac{D_{el}^L}{D_{el}^0} = 1 - k_2 \frac{D_{el}^0}{D_{el}^0 (1 + w^2v)} \approx 1 - \frac{k_2}{3D_{el}^0} \left( \frac{k}{k + k_d} \right) k_{LB} + O(\chi^2).
\]
This ratio depends quadratically on \(z_0\). We do not quote here the MCT expression for the specific conductivity, since it is readily obtained using Eq. (6).

3. Mixture of two binary electrolytes

We analyze here an aqueous electrolyte mixture (with \(L_B = 7.1\ \text{Å} \) and \(T = 25\ \text{°C}\)) of two binary electrolytes with different mobile ions. The mixture consists of a symmetric 1:1 electrolyte of ions with total concentration \(2n_s\) and equal free diffusion coefficient \(D_0^0\), and an asymmetric \(z_p:1\) electrolyte of polyions with valency \(z_p > 1\), number concentration \(n_p\), and diffusion coefficient \(D_p^0 < D_0^0\), together with monovalent counterions of diffusion coefficient \(D_0^0\) equal to that of the symmetric electrolyte. The ions of the 1:1 electrolyte are referred to in the following as the salt ions. As we discuss now, this system reveals an unexpected, non-monotonic dependence of the polyion electrophoretic mobility, \(\mu_{el}^p\), on the polyion concentration \(n_p\). A related non-monotonic concentration dependence of the excess shear viscosity in this mixture, as a function of \(n_s\) instead of \(n_p\), was discussed in our previous work.\(^{30}\)

Since the non-monotonicity of \(\mu_{el}^p\) is observed at low concentrations, we can restrict our analysis to the point-ion limit without having to account for HIs in the relaxation part. Each of the two electrolytes is globally electroneutral, so that
\[
k^2 = 4\pi L_B \left[ \left( 1 + \frac{1}{z_p} \right) n_p z_p^2 + 2n_s \right]
\]
is valid for the square of the Debye screening parameter, and
\[
\omega = 4\pi L_B \left[ \left( \frac{D_p^0 + D_0^0}{z_p} \right) n_p z_p^2 + 2D_0^0 n_s \right]
\]
for the Debye frequency \(\omega = \lambda_{D0}(q = 0)\). In writing these last two relations we have made use of Eq. (63) and of the fact that \(-n_c z_c = n_s z_p\), where \(n_c\) is the counter-ion number density associated with the polyion species and \(z_c = -1\). Thus, \(k\) and \(\omega\) can be varied independently by changing either the 1:1 electrolyte concentration \(n_s\), or the polyion concentration \(n_p\).

We have derived analytic MCT expressions for the partial electrophoretic mobilities in this four-component system which, when expanded to first order in \(k\), reduce to the DFOF limiting law results.\(^{4}\) We refrain from showing the lengthy mobility expressions and discuss instead their numerical predictions.

The unexpected behavior of the polyion electrophoretic mobility as a function of \(n_p\) is exemplified in Fig. 1, where \(\mu_{el}^p\) is shown for three different salt concentrations. On first sight, \(\mu_{el}^p\) is expected to decrease monotonically with increasing \(n_p\), and this is indeed what happens in the absence of the symmetric electrolyte (solid curve in Fig. 1). The polyion mobility result for \(n_s = 0\) and small values of \(n_p\) conforms with the limiting law behavior \(\mu_{el}^p = \mu_{el,0}^p - A/\sqrt{\pi n_p}\) for a binary electrolyte, where \(A\) is concentration independent. For non-zero salt concentration, however, a non-monotonic polyion concentration dependence of \(\mu_{el}^p\) is observed, with a mobility maximum occurring at a very small value of \(n_p\) (dashed and dotted curves in Fig. 1). With increasing \(n_s\), the maximum becomes less pronounced, and its position is shifted to larger polyion concentrations.

To understand the non-monotonic behavior of \(\mu_{el}^p\), we first realize that it originates from the relaxation effect, since the short-time electrophoretic mobility contribution, \(\Delta \mu_{el}^p = \mu_{el}^{p,0} - \mu_{el}^{p,0} = -z_p D_x/(k_B T)\), decreases with increasing \(n_p\). The depolarizing and relaxation effect contributions to the electrophoretic mobilities (and conductivities) are in general comparable in magnitude. This is illustrated in Fig. 2 showing the ratio, \(\Delta \mu_{el}^p/\Delta \mu_{el}^p, S\), of relaxation and electrophoretic mobility parts as a function of \(n_p\), for salt concentrations as in Fig. 1. The relaxation mobility contribution dominates for small polyion concentrations.

The non-monotonic behavior of \(\mu_{el}^p\) caused by the relaxation effect is explained by the interplay of two characteristic lengths and their associated time scales. The two lengths are, respectively, the Debye length \(1/k\), characterizing the size of the ionic atmosphere formed around each polyion, and the mean geometric distance, \(d_p = n_p^{-1/3}\), between two...
polynomials. The associated time scales are, respectively, the Debye relaxation time $\tau_D = 1/\omega_D$, characterizing the relaxation of the ion atmosphere, and the structural relaxation time, $\tau_p = d_p^2/D_p^0$, characterizing the relaxation of next-neighbor polion concentration fluctuations. We first note that the two ratios, $\kappa^{-1}/\tau_p$ and $\tau_D/\tau_p$, are also non-monotonic in $n_p$. The concentration values of their respective maxima are related to that of $\mu_p^{el}/\mu_p^{el,0}$ by an essentially constant factor, which is independent of $n_s$. At very low values of $n_p$ below the concentration value at the mobility peak where salt ions contribute predominantly to $\kappa$ in Eq. (18), the decrease of $1/\kappa$ with increasing $n_p$ is less strong than that of $d_p$, so that the ion atmospheres of two neighboring polions approach each other. Since, in addition, $\tau_D$ decreases faster than $\tau_p$, the relaxation effect becomes weaker and, in consequence, $\mu_p^{el}$ is increased.

In fact, for $n_p \ll n_s$ and fixed salt concentration, $\mu_p^{el}$ increases initially linearly in $n_p$. For polinon concentrations exceeding the concentration at the mobility maximum, $\kappa$ is predominantly determined by the polions. The resulting decline of $\mu_p^{el}$ with increasing $n_p$ becomes increasingly similar to that of a pure binary $z_p:1$ electrolyte.

The unusual concentration dependence of $\mu_p^{el}$ discussed here nicely illustrates a general statement by Onsager that unexpected phenomena can appear in asymmetric electrolytes consisting of several components.

C. Leading-order HIs contributions to the relaxation effect

The HIs contributions to the relaxation parts of the conduction-diffusion properties have been disregarded so far. The leading-order HIs contributions to the relaxation parts of the electrophoretic mobilities, as predicted by the simplified MCT-HIs approximation with DH input, are quadratic in $\kappa$, i.e., linear in $n_T$. To obtain these contributions analytically, we assume that all ions have the same single-particle diffusion coefficient $D_p^0$. From substituting $C_H^{DH}(q) = -k^2 P/q^2$, and Eqs. (94) and (95) with the HIs contribution to $\lambda_{EE}(q)$ included, into Eq. (71), we obtain

$$\frac{1}{D_p^0} m_{a\beta}^{c,irr} = z_\alpha z_\beta f^{ch}(\kappa) \kappa L_B (\delta_{a\beta} - P_{a\beta})$$

(120)

for the time-integrated memory function matrix, where the function

$$f^{ch}(\kappa) = \frac{2}{3\pi} \int_0^\infty dx \frac{x^2}{(1 + x^2)^2} F_m(x, \kappa)$$

(121)

includes the contribution by the HIs. Here,

$$F_m(x, \kappa) = \frac{1 + 2x^2}{1 + x^2} - \frac{D_x}{D_0} F_{Os}(x),$$

(122)

and $F_{Os}(x)$ is defined in Eq. (83). If HIs are ignored, $f^{ch}(\kappa) \approx f^p$ in agreement with Eq. (96) for $m_{a\beta}^{c,irr}$. Remember that $P_{a\beta}$ is defined in Eq. (61).

The integral in Eq. (121) cannot be evaluated analytically. However, since $(D_x/D^0) \ll 1$ for small electrolyte concentrations, we can expand the integrand to first order in $D_x/D^0$. The resulting integral is

$$f^{ch}(\kappa) \approx f^p + f^h \frac{D_x}{D^0},$$

(123)

where $f^h$ is a small number given by

$$f^h =\frac{1}{16} (4\sqrt{2} + \ln(4) - 3 - 4\text{arcoth}(\sqrt{2})) \approx 0.032,$$

(124)

which characterizes the strength of the leading-order HIs contribution.

The memory function matrix in Eq. (120) can thus be written as the sum

$$m_{a\beta}^{c,irr} = (m_{a\beta}^{c,irr})^p + (m_{a\beta}^{c,irr})^h,$$

(125)

where $(m_{a\beta}^{c,irr})^p$ is the memory function matrix without HIs given in Eq. (96), and

$$(m_{a\beta}^{c,irr})^h = z_\alpha z_\beta D_x f^h \kappa L_B (\delta_{a\beta} - P_{a\beta}) + O(\kappa^3)$$

(126)

is the MCT-HIs hydrodynamic contribution up to quadratic order in $\kappa$. While the leading HIs part of $O(\kappa^2)$ is relevant from a general viewpoint as a non-trivial hydrodynamic contribution, its magnitude is very small: For an aqueous electrolyte solution of monovalent ions at $n_T \approx 0.01$ M, the relative contribution of $(m_{a\beta}^{c,irr})^h$ to $(m_{a\beta}^{c,irr})^p$ is about 7%. Regarding the electrolyte viscosity, a similarly small leading-order hydrodynamic contribution was obtained.

Since the matrix in Eq. (120) is of the same structure as the one in Eq. (96), $\Delta\mu_{a\beta}$ and $\mu_p^{el}$ follow readily by the substitution $f^h \rightarrow f^{ch}$. We are thus in the position to discuss the leading-order HIs contributions to the relaxation parts of the mobilities. From the results in the Appendix, and on recalling Eqs. (98) and (99), we obtain

$$\frac{k_BT}{D_0^0} (\Delta\mu_{a\beta})^{relf} = -z_\alpha^2 f^p \kappa L_B + (z_\beta^2 f^p \kappa L_B)^2$$

$$- \left\{ \frac{D_x}{D_0^0} z_\alpha^2 f^p \kappa L_B \right\} + O(\kappa^3)$$

(127)
for the self part, and
\[ \frac{k_B T}{D_0^a}(\Delta \mu_{\alpha \beta})_{cross}^{self} \]
\[ = z_\alpha z_\beta P_{\alpha \beta} f^p \kappa L_B + \left( \zeta_\alpha^2 - \left( \zeta_\alpha^2 + \frac{z_\alpha^2}{z_\beta^2} \right) \right) (f^p \kappa L_B)^2 \]
\[ + \left[ z_\alpha z_\beta P_{\alpha \beta} \frac{D_\alpha}{D_0^a} f^h \kappa L_B \right] + O(\kappa^3) \]  
(128)
for the cross correlation part.

Furthermore, on recalling Eqs. (16), (13), and (102), the long-time self-diffusion coefficient of \( \alpha \)-type ions with the leading-order hydrodynamic contribution included is obtained as
\[ \frac{D_{\alpha \ell}}{D_0^a} = 1 - z_\alpha^2 f^p \kappa L_B + \left( z_\alpha^2 f^p \kappa L_B \right)^2 - \frac{D_\alpha}{D_0^a} z_\alpha^2 f^h \kappa L_B + O(\kappa^3). \]  
(129)

The cross-correlation contribution to the electrophoretic mobility is given, using Eqs. (128), (33), and (4), by
\[ \left( \mu_{\alpha \ell}^{cross} \right)^{self} = \frac{z_\alpha e}{k_B T} D_\kappa + \frac{z_\alpha}{z_\alpha} \frac{z_\alpha}{z_\alpha} f^p \kappa L_B \mu_{\alpha \ell}^{self,0} \]
\[ + \frac{z_\alpha}{z_\alpha} \frac{z_\alpha}{z_\alpha} \left( \frac{z_\alpha}{z_\alpha} \frac{z_\alpha}{z_\alpha} + \frac{z_\alpha}{z_\alpha} \right) \right) (f^p \kappa L_B)^2 \mu_{\alpha \ell}^{self,0} \]
\[ + \left[ \frac{z_\alpha}{z_\alpha} \frac{z_\alpha}{z_\alpha} \frac{D_\kappa}{D_0^a} f^h \kappa L_B \right] \mu_{\alpha \ell}^{self,0} + O(\kappa^3). \]  
(130)

The terms proportional to \( D_{\alpha \ell} f^h \) in Eqs. (129) and (130) are the leading-order HIs contributions to the transport properties. For purely monovalent ions where \( \zeta^3 = 0 = \zeta \), the electrophoretic part is, to \( O(\kappa^3) \), the only non-zero cross-correlation contribution to \( \mu_{\alpha \ell}^{cross} \).

The HIs contribution to the long-time self-diffusion coefficient \( D_{\alpha \ell}^S \) in Eq. (129) is of negative sign. The sign of the total quadratic-order in \( \kappa \) contribution to \( D_{\alpha \ell}^S \) according to
\[ \text{Sign} \left( (z_\alpha f^p)^2 - f^h \frac{k_B T}{6 \pi \eta_0 L_B D_0^a} \right) \]  
(131)
is positive or negative depending on the solvent and the employed value for \( D_0^a \). Using the values for the single-ion diffusion coefficients of Na\(^+\) and Cl\(^-\) in water at room temperature,\(^79\) the sign in Eq. (131) is positive, and a small enhancement of \( D_{\alpha \ell}^S \) by the quadratic-order terms is predicted. For Li\(^+\) and Ca\(^2+\) ions, however, the value for \( D_{\alpha \ell}^S \) is lowered.

As a consistency check of the MCT-HIs result for \( D_{\alpha \ell}^S \) in Eq. (129), we determine \( D_{\alpha \ell}^S \) alternatively from the MCT expression for the self-intermediate scattering function, \( G_\alpha(k, t) \), of \( \alpha \)-type ions.\(^12,31\) In this self-dynamics approach, \( D_{\alpha \ell}^S \) is obtained from the exact relation,\(^31\)
\[ D_{\alpha \ell}^S = D_\alpha^0 \left( 1 + \frac{\Delta \zeta_{\alpha \ell}}{\zeta_\alpha^S} \right)^{-1}, \]  
(132)
where \( \Delta \zeta_{\alpha \ell} \) is the self-correlation friction contribution due to electrostatic and hydrodynamic interactions, and \( D_{\alpha \ell}^S \) and \( \zeta_\alpha^S \) are the short-time self-diffusion and self-friction coefficients, respectively. Within the RP approximation of HIs employed in this work, \( D_{\alpha \ell}^S = D_\alpha^0 \) and \( \zeta_\alpha^S = k_B T / D_\alpha^0 \), and the friction coefficient is approximated in MCT by\(^12,31\)
\[ \Delta \zeta_\alpha = \frac{D_\alpha^0}{(2\pi)^3 \eta_0} \int_0^\infty dt \int d^3 k G_\alpha(k, t) \]
\[ \times \sum_{\beta, \gamma \neq \alpha} V_{\alpha \beta p} (\kappa) F_{\beta \gamma}(k, t) V_{\alpha \gamma p}^{self}(k), \]  
(133)
with the MCT self-vertex functions given by
\[ V_{\alpha \beta p}^{self}(k) = -(\hat{\kappa} \cdot \hat{k}) \sum_{\delta \neq \alpha} (n_{\alpha n}\bar{n})^{1/2} [h_{\alpha \delta}(k) - \frac{1}{D_\alpha^0} h_{\alpha \delta}^d(k)] \]  
(134)
where the \( h_{\alpha \delta}(k) \) are the partial total correlation functions in Fourier space (see Eq. (72)), and \( h_{\alpha \delta}^d(k) = H_{\alpha \delta}(k)/(n_{\alpha n}\bar{n})^{1/2} \) are the concentration-scaled distinct partial hydrodynamic functions. Using in the evaluation of Eq. (133) the same approximations as for the collective dynamics case, i.e., ignoring HIs in the self-vertex functions and employing the short-time forms \( \Phi(k, t) \) and \( G_\alpha^S = \exp(-k^2 D_\alpha^0 t) \) as input, we obtain
\[ \frac{\Delta \zeta_\alpha}{\zeta_\alpha^0} = z_\alpha^2 f^eh(k) \kappa L_B, \]  
(135)
where in addition identical coefficients \( D_\alpha^0 = D_0^a = k_B T / \zeta_\alpha^0 \) for all ion components have been assumed. Next, we use the relation,
\[ \frac{\Delta \zeta_\alpha}{\zeta_\alpha^0} = \left( m_{\alpha \alpha \alpha}^{c, irr} \right)^{self} f^{\ell \ell} \]  
(136)
which in fact is exact except for the RP treatment of the HIs. Finally, the comparison with Eq. (120) shows that the self-correlation part of the time-integrated memory function is recovered indeed from Eq. (135), and in consequence also Eq. (129) for \( D_{\alpha \ell}^S \).

VI. SUMMARY AND OUTLOOK

In summary, we have derived a versatile MCT scheme for the calculation of linear conduction-diffusion transport properties in strong electrolyte mixtures, which includes the molar conductivity, and the long-time electrophoretic mobilities and self-diffusion coefficients of the ion components. The ions are treated on the primitive model level with the solvent described as a dielectric continuum. The influence of the HIs is accounted for on a RP level both in the instantaneous (electrophoretic) and memory (relaxation) contributions to the transport properties. The only external inputs are the static pair correlation functions of the unperturbed system. These can be obtained on different levels of approximation, e.g., using the analytic MSA\(^70,71\) and Attard\(^8\) solutions for monovalent ions. For size or charge-asymmetric electrolytes with ion pairing and non-linear screening tendencies, Monte Carlo simulation, non-linear Ornstein-Zernike integral equation, and dressed-ion theory results are available.\(^80-83\) Note that while the present MCT scheme has been developed for steady-state transport properties, with some additional effort it can be extended to frequency-dependent transport coefficients.
In the derivation of the MCT scheme, we took advantage of a linear response relation between the unperturbed dynamic structure factors and the long-time partial mobilities. The mobilities are expressed in terms of time-integrated, long-wavelength limiting collective memory functions to which a MCT approximation is applied subsequently. The partial mobilities are of central importance since conduction-diffusion transport coefficients are linearly related to these quantities. This is also the case for diffusion properties not considered in this paper, such as the chemical and interdiffusion coefficients. In combination with a related MCT method for the viscosity, a unifying scheme for linear transport in electrolytes is at our disposal which can be used, e.g., to test generalized Stokes-Einstein and Nernst-Einstein relations between diffusion, conduction, and viscosity properties. These tests will be the topic of a separate paper.

In this work, the general framework of the MCT method has been provided as a firm basis for later applications (see Paper II84). Using the DH equilibrium pair distribution functions as input, fully analytic MCT expressions have been derived for the partial mobilities and conduction-diffusion properties of pointlike ions with HIs included. As an application, we investigated the non-monotonic concentration dependence of the polyion electrophoretic mobility in a four-component mixture. We could show that this unusual behavior of the electrophoretic mobility is due to the different concentration dependence of the strength of the relaxation effect in the polyion- and salt-ion dominated regimes, respectively. The maximum of the polyion mobility occurs at a polyion concentration small enough that the point-ion approximation can be applied.

The DFOF low-concentration limiting law results with their characteristic $\sqrt{n_T}$ concentration dependence of the conduction-diffusion properties are straightforwardly recovered from the analytic MCT results in the limit of very low concentrations. Hydrodynamic contributions to the relaxation part of the transport coefficients are predicted by the MCT-HIs scheme to appear first to quadratic order in the Debye electrostatic screening parameter $\kappa$. In the point-ion limit where HIs are described exactly on the Oseen level, an essentially analytic expression for the memory function matrix has been obtained in Eq. (120), from which the $O(\kappa^2)$ contributions to the transport coefficients have been deduced. These contributions reduce the electrophoretic mobilities by a few percent only. Note that an additional $O(\kappa^2)$ contribution to the mobilities, arising from the hydrodynamic vertex functions, has been disregarded in Sec. V C. The MCT hydrodynamic vertex functions for conduction-diffusion are non-zero in the point-ion limit, while the vertex function for the viscosity vanishes, for the reason that point particles do not create hydrodynamic contact stress.30

At larger electrolyte concentrations, the ion excluded volumes are of importance in addition to the HIs. For moderately large concentrations, we have described a simplified MCT solution scheme in Sec. IV C which is based on the short-time dynamic structure factor matrix as the dynamic input to the time-integrated memory function matrix. Quite importantly, we have applied the MCT scheme plus aforementioned simplifications to the multi-component matrix memory equation, instead of starting from a single-variable memory equation for $F_{2f}(q, t)$ and calculating the specific conductivity according to Eq. (59). In this way, cross-component correlations are incorporated at least on an approximate level.

The simplified MCT-HIs method accounts for the non-zero ion sizes by means of the non-ideal direct correlation function matrix $C^{ii}(q)$, and the ion-size dependent hydrodynamic function matrix $H(q)$. The latter is treated using, e.g., the Rotne-Prager far-field approximation for the HIs. The simplified MCT-HIs method has been successfully applied already to the calculation of the viscosity of a binary electrolyte solution.30 For large electrolyte concentrations, this method is not applicable any more, and refined solution schemes are required such as the self-consistent scheme discussed at the end of Sec. IV C.

In Paper II84 of same title, the simplified MCT-HIs scheme is used in deriving semi-analytic expressions for conduction-diffusion properties of size symmetric electrolytes. It is shown that these expressions apply for concentrations extending even up to 2 M. The conduction-diffusion expressions are numerically evaluated and compared to experimental data, and to results by another MCT-based theoretical method. To estimate the significance of ion-specific features such as hydration shells, the implications for the transport coefficients of using mixed slip-stick hydrodynamic surface boundary conditions, and the effect of solvent permeability are analyzed. The numerical analysis of electrolyte transport properties in Paper II84 encloses, in addition, the electrolyte solution viscosity and the sedimentation coefficient.

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APPENDIX: RELAXATION MOBILITIES OF POINTLIKE IONS IN DH APPROXIMATION

An analytic expression for the mobility matrix coefficients of ions with equal diffusion coefficients follows from inserting the MCT memory function matrix without HI given in Eq. (96) into Eq. (68), and from realizing using $H^{-1} = I/D^0$ that the matrix $C = I + H^{-1}$. $\mathbf{m}^{irr}$ is of the special form $C = A + \mathbf{v}^T$, with $v_a = (f^{\mu}kLB/z^2)^{1/2} \sqrt{\kappa_0} z_\alpha$ and $(A^{-1})_{ab} = B_{ab} = \delta_{ab}/(1 + f^{\mu}kLB z_\alpha z_\beta)$. Using the Sherman-Morrison matrix inversion formula for $C$, we obtain

$$\frac{k_B T}{D^0} \Delta \mu_{ab} = -B_{ab} z_\alpha z_\beta f^{\mu} kLB + \frac{B_{aa} v_\alpha v_\beta B_{bg}}{1 - \mathbf{v}^T \cdot \mathbf{B} \cdot \mathbf{v}},$$

(A1)

for the MCT relaxation mobility matrix of pointlike ions without HIs. The associated relaxation part of the electrophoretic ion mobilities is

$$\Delta \mu_{\alpha}^{\text{el}} / \mu_{\alpha}^{\text{el},0} = -B_{aa} z_\alpha z_\beta f^{\mu} kLB + \frac{B_{aa} z_\alpha \sum_{\beta} B_{bg} P_{bg} z_\beta}{1 - \mathbf{v}^T \cdot \mathbf{B} \cdot \mathbf{v}} f^{\mu} kLB,$$

(A2)
which reduces to the DFOF limiting law expressions in Eqs. (100) and (101) when expanded to first order in $\kappa L_g$. The quantity $v^f \cdot B \cdot \nu$ on the right-hand side of Eq. (A2) increases with increasing concentration from zero to the value one reached for $\kappa \rightarrow 1/(z^f_0 f^f L_g)$, which for a solution of monovalent ions corresponds to the very large concentration $\nu_T \rightarrow 40.42 M$. However, the result in Eq. (A2) is not useful for larger concentrations well above the limiting law regime since then the combined effects of HIs and non-zero ion sizes must be accounted for.