Onsager's reciprocal relations in electrolyte solutions. II. Effect of ionic interactions on electroacoustics

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In electrolyte solutions, an electric potential difference, called the Ionic Vibration Potential (IVP), related to the ionic vibration intensity, is generated by the application of an acoustic wave. Several theories based on a mechanical framework have been proposed over the years to predict the IVP for high ionic strengths, in the case where interactions between ions have to be accounted for. In this paper, it is demonstrated that most of these theories are not consistent with Onsager's reciprocal relations. A new expression for the IVP will be presented that does fulfill the Onsager's reciprocal relations. We obtained this expression by deriving general expressions of the corrective forces describing non-ideal effects in electrolyte solutions. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4927468]

I. INTRODUCTION

When an acoustic wave is applied in an electrolyte solution, water molecules and ionic solutes are set in motion. Ions get a velocity relative to water molecules, and two different ions get different velocities, because their masses and diffusion coefficients usually differ. This (small) difference in velocity creates a net electric current called the Ion Vibration Intensity (IVI). This current is associated to an electric field and a corresponding electric potential difference called the Ionic Vibration Potential (IVP). This electroacoustic phenomenon was predicted by Debye in 1933.[1] In the same paper,[1] Debye obtained a theoretical expression of the IVP for the ideal case where ions do not interact. He used in his derivation the Newton equation of motion for ions in the framework of a continuous solvent model. A few years later, Hermans[2] improved Debye's theory, so as to take into account the contribution to the applied force due to the volume of ions, which is linked to the pressure gradient.

Coupled transport phenomena in electrolyte solutions such as electroacoustics can also be investigated in the framework of irreversible thermodynamics. Forces-fluxes relations can be derived, from which Onsager reciprocal relations are obtained.[3,4] The equality between these coupling coefficients accounts for cross effects, namely, the creation of an electric current by an acoustic wave or gravity and the creation of a mass flux under an electric field. Such reciprocal relations were derived in 1952 for sedimentation potential experiments,[5] and more recently for IVP experiments.[6,7] In our previous work, which we will refer to as Paper I[7] hereafter, we have shown that the results obtained in a mechanical framework by Debye and Hermans to account for the IVP in the limit where ions do not interact (namely the ideal case) do verify the Onsager's reciprocal relations for electroacoustics. Neverthe-

less, as interactions between ions can have a strong influence on their thermodynamic and dynamic properties, especially in the concentrated range, the Debye and Hermans theory is limited to the description of dilute electrolyte solutions. Interactions between ions are usually accounted for in the electrolyte theory through additional corrective forces in the Newtonian equations of motions. In Paper I,[7] we have derived the general condition between corrective forces which must be fulfilled in order that reciprocal Onsager's relations are verified.

In the present work (Paper II), we review the existing theories for the IVP derived after the pioneer work of Debye and Hermans to check if they fulfill Onsager's reciprocal relations. The concept of corrective force was introduced by Onsager in 1932:[10] two main effects are assumed to influence the dynamics of ions in the concentrated range, namely, the hydrodynamic coupling between ions and the electrostatic relaxation effect. The hydrodynamic coupling between solute velocities is usually referred to as an electrophoretic force: As an ion moves forward, under an electric field in the case of conductivity, it draws the solvent in the same direction and thus takes also its counterions, which are locally in excess, forward. The electrostatic relaxation effect accounts for the space lag of the ionic atmosphere compared to the "central" ion, when this central ion moves forward. This space lag induces an electrostatic force which draws back the central ion. These corrective forces allowed Onsager to account for the decrease of the molar conductivity as the concentration increases. Several authors have attempted over the years to improve the set of forces used by Debye and Hermans to predict the IVP, and to account for the hydrodynamic coupling and the electrostatic relaxation effects.[11,12] More recently, the additional influence of excluded volume effects between ions was also accounted for by Durand-Vidal *et al.*[13]

Actually, the precise expression of corrective forces in the context of electroacoustics varies from one author to the other. As we proceed to show, the expressions of corrective forces proposed previously are not consistent with Onsager's reciprocal relation.

In this paper, we also propose new expressions for the corrective forces which are consistent with reciprocal Onsager's relations. Indeed, in the PHENIX laboratory, Pusset et al. have performed and interpreted new IVP measurements on several electrolyte solutions.[14] The results were analyzed using new analytical expressions for the hydrodynamic coupling and for the electrostatic relaxation effects. The general expressions of the corrective forces, which were not given in Ref. 14, are detailed in the present paper. These forces depend on the radial distribution functions between ions, $g_{ij}^0(r)$, i.e., the density probability to find an ion i at a distance r of an ion j. These radial distribution functions can be obtained analytically from the integral equations of the statistical mechanics in the mean spherical approximation (MSA), as was done in Pusset et al.,[14] or from numerical simulations at the atomic or mesoscopic scale.

In Section II, we show that previous theories of the IVP do not fulfill Onsager's reciprocal relations. In Section III, we detail the new expression of corrective forces and prove that they fulfill reciprocal relations.

II. VERIFICATION OF ONSAGER'S RECIPROCAL RELATIONS FOR EXISTING THEORIES

A. Onsager's reciprocal relation for electroacoustics

As explicated in Paper I,[7] the Onsager's reciprocal relationship for IVP reads

$$\left(\frac{\mathbf{I}}{\boldsymbol{\nabla}P}\right)_{\mathbf{E}=\mathbf{0}} = \frac{1}{\rho}\left(\frac{\mathbf{J}^{vol}}{\mathbf{E}}\right)_{\boldsymbol{\nabla}P=\mathbf{0}}, \quad (1)$$

where $\mathbf{I}$ is the electric current, $\boldsymbol{\nabla}P$ the applied pressure gradient, $\mathbf{E}$ the electric field, ρ the mass density of the solution, and $\mathbf{J}^{vol}$ the total mass flux in the reference frame of the total volume flux.

In the framework of a mechanical approach (i.e., using the second law of dynamics), the general equation of motion of an ion k is

$$m_k\frac{\partial \mathbf{v}_k^{lab}}{\partial t} = \mathbf{F}_k^E + \mathbf{F}_k^{fric} + \mathbf{F}_k^{\boldsymbol{\nabla}P} + \mathbf{F}_k^{dif} + \delta\mathbf{F}_k^{rel} + \delta\mathbf{F}_k^{hyd}, \quad (2)$$

where the left term is the product of the mass of an ion by its acceleration in the laboratory reference frame, $\mathbf{F}_k^E = ez_k\mathbf{E}$ is the electric force, and $\mathbf{F}_k^{fric} = -k_BT(\mathbf{v}_k - \mathbf{v}_w)/D_k$ is the friction force. The coefficients are as follows: e the elementary charge; m_k, z_k, and D_k the mass, valence, and the ionic diffusion coefficients of ion k; k_B the Boltzmann constant; T the temperature; and $\mathbf{v}_w$ the velocity of water. $\mathbf{F}_k^{\boldsymbol{\nabla}P} = -\overline{V}_k\boldsymbol{\nabla}P$ is the force associated with the pressure gradient $\boldsymbol{\nabla}P$ with $\overline{V}_k$ the partial volume of ion k, $\delta\mathbf{F}_k^{rel}$ is the corrective force accounting for the electrostatic relaxation effect, and $\delta\mathbf{F}_k^{hyd}$ is the corrective force accounting for the hydrodynamic coupling. $\mathbf{F}_k^{dif}$ is the diffusive force, which was shown to be zero in Paper I.[7] Of course, for ideal electrolyte solutions (i.e., with no inter-ionic

interactions), we have $\delta\mathbf{F}_k^{rel} = \mathbf{0}$ and $\delta\mathbf{F}_k^{hyd} = \mathbf{0}$. This is the case studied by Debye and Hermans,[1,2] where only the contributions $\mathbf{F}_k^E$, $\mathbf{F}_k^{fric}$, and $\mathbf{F}_k^{\boldsymbol{\nabla}P}$ are taken into account. We have shown in Paper I that, in this ideal case, the mechanical approach based on Eq. (2) fulfills the Onsager's reciprocal relationship.

The expression of the corrective forces proposed in the literature by different authors[11,12,15] can be written as functions of the electric field and of the pressure gradient in a general form,

$$\delta\mathbf{F}_k^{rel} = \alpha_k^{rel}\mathbf{E} + \beta_k^{rel}\frac{\boldsymbol{\nabla}P}{\rho} \quad \text{the electrostatic relaxation force,}$$

$$\delta\mathbf{F}_k^{hyd} = \alpha_k^{hyd}\mathbf{E} + \beta_k^{hyd}\frac{\boldsymbol{\nabla}P}{\rho} \quad \text{the hydrodynamic force,}$$

$$(3)$$

where the expressions of α_k^{rel}, α_k^{hyd}, β_k^{rel}, and β_k^{hyd} depend on the individual properties of ions, on the structural properties of the solution, and of the electrolyte concentrations. The precise expression of these quantities depends on the authors. We have shown in Paper I[7] that Onsager's reciprocal relations are fulfilled for a given corrective force $\delta\mathbf{F}_k = \alpha_k\mathbf{E} + \beta_k\boldsymbol{\nabla}P/\rho$ when

$$\sum_{k=1}^{n} n_{k,eq}\left(m_k - \rho\overline{V}_k\right)\frac{\alpha_k}{k_BT/D_k} = \sum_{k=1}^{n} n_{k,eq}\beta_k\frac{ez_k}{k_BT/D_k}, \quad (4)$$

where n is the number of different ionic species (2 for a binary electrolyte), $n_{k,eq}$ the number density of particles k (number of particles per unit of volume) at equilibrium, i.e., before applying the acoustic wave. To make the link with Paper I, we kept so far the notation $n_{k,eq}$ to name the number density at equilibrium. From now on, in order to simplify notations, we will note the number density at equilibrium simply n_k. The variation of number density, due to the existence of applied forces, is noted δn_k.

B. Corrective forces proposed in previous works

As stated in the Introduction, two main effects are assumed to influence the dynamics of ions at high ionic strength: the hydrodynamic coupling between ions and the electric relaxation effect. A schematic view of these effects is represented in Fig. 1.

The hydrodynamic coupling between solute velocities arises from the ion mobility: as an ion moves, it exerts a drag force on the neighboring solvent and ions. The hydrodynamic velocity increment, in the presence of an electric field E, can be estimated to be of the order of $ez_k\kappa E$ where the Debye length κ^{-1} is the typical lengthscale where the action of the hydrodynamic coupling plays a significant role. The corresponding hydrodynamic force can be estimated to be of the order of $ez_k\kappa Ek_BT/D_k$. The electric relaxation effect accounts for the deformation of the ionic atmosphere of the considered ("central") ion. When the central ion moves, its ionic atmosphere takes a short time to adjust. This time is of the order of the Debye time (about 50 ps for an ionic strength of 1 mol l^{-1}). The deformation of the ionic atmosphere can be estimated to be of the order of the Debye time times the velocity of the central ion. This deformation leads to an electric force which opposes the central ion's velocity, since the double layer is mainly composed of counterions.
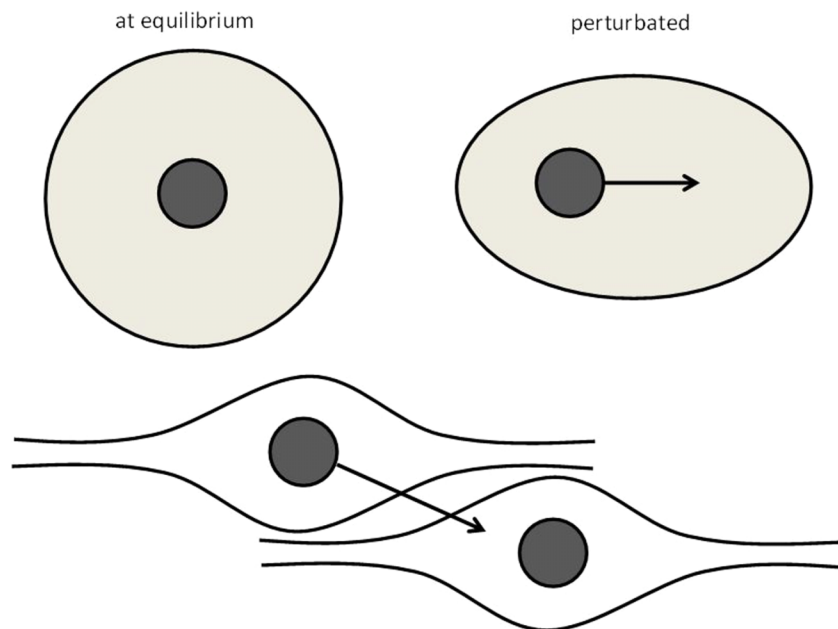
FIG. 1. Schematic view of the corrective forces. Top figure: the arrow indicates the relaxation force which originates from the deformation of the ionic atmosphere (grey) around the considered ion (dark sphere). Because of the movement of the considered ion, its ionic atmosphere takes a short time to adapt. Bottom figure: the arrow indicates the hydrodynamic force which originates from the drag force of one ion on a neighbouring one.

Following the work of Onsager on the electrical conductivity of electrolyte solutions,[10] Oka[11] tried to improve the theoretical description of the IVP proposed by Debye,[1] accounting for the hydrodynamic coupling and for the electrostatic relaxation effect. However, the expressions of corrective forces proposed by Oka were incorrect. Oka assumed that the corrective forces were only generated by the electric field. In fact, the ions move relative to the solvent as the result of the action of the electric field *and* the action of the pressure gradient. The expressions of corrective forces by Oka lead to using the general expression of the corrective force $\delta \mathbf{F}_k = \alpha_k \mathbf{E} + \beta_k \boldsymbol{\nabla} P/\rho$: $\alpha^{hyd} \neq 0$, $\alpha^{rel} \neq 0$, $\beta^{rel} = 0$, and $\beta^{hyd} = 0$. In other words, the corrective forces proposed by Oka change the motion of electrolytes in an electric field, thus modify the term $(\mathbf{J}^{vol}/\mathbf{E})_{\boldsymbol{\nabla} P=0}$ of Eq. (1) but do not modify the motion of electrolytes under a pressure gradient and thus do not change $(\mathbf{I}/\boldsymbol{\nabla} P)_{\mathbf{E}=0}$. Relation (4) cannot be fulfilled in these conditions.

In 1947, Yeager and Hovorka[12] used a theoretical approach close to the one of Oka, except that they included the pressure force and also added a diffusion force in equation of motion (2). They considered, as Oka did, that both corrective forces were created only by the electric field. Again, this set of corrective forces does not allow to fulfill Onsager's relations and is thus incorrect.

In 1995, Durand-Vidal *et al.*[15,13] improved the theories proposed by Oka and by Yeager and Hovorka in two ways.

First, Durand-Vidal *et al.* assumed that both corrective forces depend not only of the electric field but also of the pressure gradient. Doing so, any force which displaces an ion also makes it drag along its ionic atmosphere. This induces a hydrodynamic coupling between solutes. This force also creates a velocity difference between the ion and its ionic atmosphere. This, in turn, creates a polarization between the ion and its atmosphere, hence, an electric field. From this electric field, an electrostatic relaxation force can be deduced.

Second, Durand-Vidal *et al.* considered excluded volume effects between ions. In the works of Onsager, Oka and Yeager, and Hovorka, the calculation of corrective forces is based on a Debye-Hückel approximation to describe electrostatic interactions. This implies that ions are assumed to be point-like, and that the ionic atmosphere of a given ion has a non-realistic size at high concentration. The MSA[16] is a linearized approximation theory, like the Debye-Hückel approximation, but it takes into account the size of the ions in describing electrostatic interactions. Therefore, Durand-Vidal proposed to use the MSA to describe the structural properties of ions.

The theoretical description of electroacoustics proposed by Durand-Vidal *et al.* is however impaired by two facts. First, a diffusion force was taken into account in the equation of motion. As we showed in Paper I,[7] no additional diffusive term should be taken into account to describe the flux of charged solutes far from the walls in a binary electrolyte. Moreover, the expression used for the diffusion force by Durand-Vidal *et al.* is not consistent with Onsager's reciprocal relationship. Second, Durand-Vidal *et al.* do not take into account the pressure force, which leads to serious discrepancies between theory and experiments, even at moderate ionic strength (see Fig. 2). Actually, the authors considered that it was impossible, in the mechanical approach, to define the pressure for an ion which may have a negative molar volume. As explicated in Appendix A, there is no inconsistency to consider ions with negative partial molar volumes in the context of a mechanical approach. The negative molar volume can simply be linked to electrostriction, i.e., the fact that bound water around an ion can be much denser than free water. Therefore, for a constant volume of ion and bound water, the system can be heavier with than without electrostriction.

An example of the IVP predicted by previous theories for aqueous barium chloride solutions is given in Fig. 2 and compared to experimental data of Zana and Yeager.[17]

The parameters used in the computation are given in Table I.

From the figure, and from the analysis of the respective theories displayed, it is found as follows:

(1) In the whole range of ionic strength, the original theory by Debye[1] does not account for the experimental values (curve
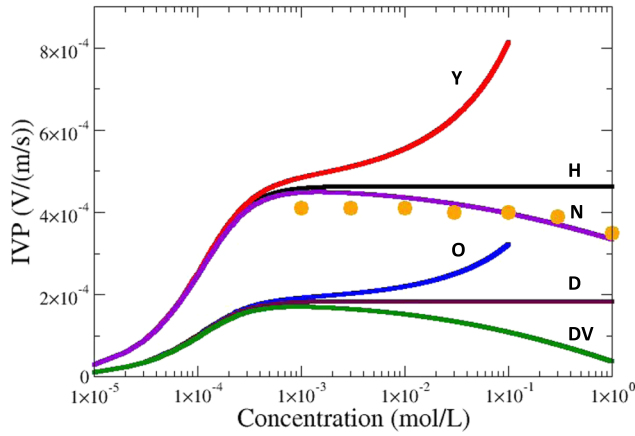
FIG. 2. IVP signal as function of ionic strength for BaCl$_2$. Symbols: experimental data of Zana and Yeager;[17] lines: theories according to (1) D: Debye; (2) H: Hermans; (3) O: Oka; (4) Y: Yeager *et al.*; (5) DV: Durand-Vidal *et al.*; (6) N: this article.

"D"). This is due to the fact that Debye omitted the pressure gradient force in his set of forces.

(2) The theory by Hermans[2] (curve "H") does account for experimental values at low and moderate ionic strengths, in the range where ionic interactions are negligible. Hermans used the set of forces introduced by Debye and included the pressure gradient force.

(3) In the whole range of ionic strength, the theory by Oka[11] (curve "O") does not account for experimental values. This is due to the fact that Oka, like Debye, omitted the pressure gradient force in his set of forces. However, he added corrective forces only due to the electric field, which leads to a systematic increase of the IVP signal at high ionic strength, for every salt. Indeed, while calculating the term α_k, Oka did not take into account the finite size of ions, which lead to irrealistic high values of the IVP at high ionic strength. For this range of ionic strength, the electrical conductivity found by Oka is approaching zero.

(4) The theory by Yeager and Hovorka[12] is in agreement with the experimental values at low and moderate ionic strengths, in the range where ionic interactions are negligible (curve "Y"). Their theory is based on the one by Hermans, with corrective forces that are similar to the ones of Oka. This theory leads thus to the same errors as Oka's theory at high ionic strengths.

(5) The theory by Durand-Vidal[15] (curve "DV") does not account for experimental values at low and moderate ionic strengths, because it is based on the theory by Debye and the pressure gradient force is omitted. At high ionic strength, however, the corrective forces introduced by the authors are in qualitative agreement with experimental values, since these corrective forces take into account the finite size of ions.

TABLE I. Parameters used in the calculations given in Fig. 2. The viscosity of water is taken to be 8.90×10^{-4} Pa s and the sound velocity is 1497 m/s. These are values at room temperature (25 °C).

	D_k (m^2/s)	M_k (g/mol)	V_k (ml/mol)	Diameter (nm)
Ba$^+$	0.847×10^{-9}	137.3	−23.5	0.58
Cl$^-$	2.032×10^{-9}	35.5	+23.4	0.36

Moreover, as a pressure-dependent term is accounted for in the corrective forces (β_k), the authors make it possible to account for either the increase or the decrease of the IVP signal at high ionic strengths.

(6) Recently, in Ref. 14, we have applied a new theory, based on the Hermans set of forces, and accounting for the hydrodynamic coupling and the electric relaxation effect, i.e., the full set of forces as given in Eq. (2) (curve "N"). We give in Sec. III the expressions of these corrective forces which allow us to account for interactions between ions even at high concentration. We will, in Subsections III A–III D, show that these expressions fulfill Onsager's reciprocal relations. A detailed proof is given in the case of binary electrolytes.

III. CORRECTIVE FORCES AS FUNCTION OF INTERACTIONS BETWEEN IONS

We start from Eq. (2), and take $\mathbf{F}_k^{dif} = 0$, since, as demonstrated in Paper I,[7] there is no diffusion force to be accounted for in the system. The corrective forces we will introduce will be such that

$$\delta\mathbf{F}_k^{rel} = \alpha_k^{rel}\mathbf{E} + \beta_k^{rel}\frac{\boldsymbol{\nabla}P}{\rho} \; ; \; \alpha_k^{rel} \neq 0 \; ; \; \beta_k^{rel} \neq 0,$$
$$\delta\mathbf{F}_k^{hyd} = \alpha_k^{hyd}\mathbf{E} + \beta_k^{hyd}\frac{\boldsymbol{\nabla}P}{\rho} \; ; \; \alpha_k^{hyd} \neq 0 \; ; \; \beta_k^{hyd} \neq 0. \tag{5}$$

These forces are based on the work of Durand-Vidal *et al.*[15,13] and are detailed underneath. We improved the formulation of Durand-Vidal *et al.* by accounting for the coupling between the hydrodynamic and electric relaxations in a slightly different way.

The evaluation of the hydrodynamic coupling and of the electrostatic relaxation effect is made from spatial averages of forces or velocities. When the acoustic wave is applied on the solution, a compression wave propagates which induces local concentration variations δn_k of the species k. In this study, the magnitude of the applied pressure is assumed to be low, so that the induced concentration inhomogeneities δn_k are small compared to the mean concentrations n_k, for every species. In the vicinity of a given species k, there exists an inhomogeneity of concentration of the other species j due to all the interactions. These relative fluctuations of concentration at equilibrium are represented by the radial pair distribution function $g_{ij}^0(r)$, which is the probability to find a particle i at the distance r from species j. At long range, when interactions have decreased enough, this function tends to 1. To represent the deviation from this limit, we use the notation $g_{ij}^0(r) = 1 + h_{ij}^0(r)$.

A. Expression of the hydrodynamic force

As discussed previously, the drag force exerted on an ion k, $\delta\mathbf{F}_k^{hyd}$, is proportional to the hydrodynamic velocity increment $\delta\mathbf{v}_k^{hyd}$ due to the displacement of neighboring ions. This force can be seen as a correction to the friction force and therefore be written as

$$\delta\mathbf{F}_k^{hyd} = \frac{k_B T}{D_k^0}\delta\mathbf{v}_k^{hyd}, \tag{6}$$

where D_k^0 is the ionic diffusion coefficient at infinite dilution. Note that in the friction force, we have defined D_k as the ionic diffusion coefficient at infinite dilution, following the notations used in earlier papers.[6,7] We here use the symbol D_k^0 to be coherent with the authors who have introduced the corrective forces.[15,13]

The hydrodynamic velocity increment $\delta \mathbf{v}_k^{hyd}$ of ion k can be calculated as the integral over space of the product of the Rotne-Prager tensor[8,9] and $\mathbf{T}(\mathbf{r})$ by the total force $\mathbf{F}_{tot[k]}$ applied on the solution due to the presence of the considered ("central") ion k,

$$\delta \mathbf{v}_k^{hyd} = \iiint \mathbf{T}(\mathbf{r}) \mathbf{F}_{tot[k]}(\mathbf{r}) d\mathbf{r}. \qquad (7)$$

The total force $\mathbf{F}_{tot[k]}$ applied on the solution due to the presence of the central ion k is the sum over all ionic species of the product of the excess of ions j, i.e., $n_j h_{kj}^0(\mathbf{r})$ in the neighborhood of ion k, by the force applied on ion j, i.e., $\mathbf{F}_j$,

$$\mathbf{F}_{tot[k]}(\mathbf{r}) = \sum_{j=0}^{n-1} n_j h_{kj}^0(\mathbf{r}) \mathbf{F_j}. \qquad (8)$$

The sum runs on every species, excluding the solvent, which is the n-th species (see Appendix B on this point). $h_{kj}^0(\mathbf{r})$ is the total correlation function between ions k and j, and $\mathbf{r}$ is the distance to the central ion k. $\mathbf{F}_j$ is the sum of forces applied on each ion j excluding the hydrodynamic force and the friction force and does not depend on the position relative to the central ion,

$$\mathbf{F}_j = \left(m_j - \rho \overline{V}_j \right) \frac{\nabla P}{\rho} + e z_j \mathbf{E}. \qquad (9)$$

The term $\left(m_j - \rho \overline{V}_j \right) \nabla P / \rho$ in Eq. (9) reflects the local modification of the density close to a given ion. This local density is given by $\rho_k(\mathbf{r}) = \sum_{j=1}^{n-1} n_j h_{kj}^0(\mathbf{r}) \left(m_j - \rho \overline{V}_j \right)$. After integration (see Eq. (11) underneath), this term will give rise to the local inertial force. Using the definition of the Rotne-Prager (or Oseen) tensor and the spherical symmetry of the total pair correlation function, we obtain

$$\delta \mathbf{v}_k^{hyd} = \sum_{j=1}^{n-1} n_j H_{kj} \mathbf{F_j} \quad \text{with} \quad H_{kj} = \frac{2}{3\eta} \int_0^\infty r h_{kj}^0 dr, \qquad (10)$$

where η is the viscosity of the solvent. The integral represents the first moment of the pair correlation function and is performed from 0 to ∞. These bounds should not be affected by the permutation of k and j. The upper bound simply implies that the integration is performed until the total pair correlation becomes negligible. This occurs for distances larger than the Debye length, over which interactions in the electrolyte are screened. In the device used in our laboratory,[14] the wave frequency is in the MHz range. The spatial variation of the pressure gradient ∇P and induced electric field $\mathbf{E}$ is therefore on the scale of millimeters. Consequently, $\mathbf{F}_j$ can be assumed to be constant at the Debye length scale and taken out of the integral in Eq. (10).

We note that using the symmetry of the total correlation functions $h_{kj}^0 = h_{jk}^0$, we get $H_{kj} = H_{jk}$. Inserting Eq. (9) in the

previous equation, one obtains

$$\delta \mathbf{F}_k^{hyd} = \left[\frac{k_B T}{D_k^0} \sum_{j=1}^{n} n_j \left(m_j - \rho \overline{V}_j \right) H_{kj} \right] \frac{\nabla P}{\rho}$$

$$+ \left[\frac{k_B T}{D_k^0} \sum_{j=1}^{n} n_j e z_j H_{kj} \right] \mathbf{E}$$

$$\equiv \beta_k^{hyd} \frac{\nabla P}{\rho} + \alpha_k^{hyd} \mathbf{E}. \qquad (11)$$

To evaluate α_k^{hyd} and β_k^{hyd}, the first moment of the pair correlation function H_{kj} is required. This first moment may be evaluated from numerical simulations or analytic expressions.[18]

B. Verification of Onsager's reciprocal relation for the hydrodynamic force

In this subsection, we demonstrate that obtained hydrodynamic force (11) satisfies Onsager reciprocal relationship (4) for any number of species, without additional hypothesis on the pair correlation function. Actually, it is easier in this case to directly prove Eq. (1), which is equivalent to Eq. (4).

The electric current, because of electroneutrality, can be shown to be independent of the reference frame (Paper I[7]). We choose to work in the reference frame of the solvent (water), which is the most appropriate when considering the Newton equation because the friction force is proportional to the velocity in this reference frame,

$$\mathbf{F}_k^{fric} = -\frac{k_B T}{D_k} (\mathbf{v}_k - \mathbf{v}_w) = -\frac{k_B T}{D_k} \mathbf{v}_k^w, \qquad (12)$$

where $\mathbf{v}_k^w$ is the velocity of ion k in the reference frame of the solvent, here water (w). The electric current is given by (see Paper I)

$$\mathbf{I} = \sum_{k=1}^{n} e z_k n_k \mathbf{v}_k^w, \qquad (13)$$

where n_k is the number of ions k per unit of volume. The velocity of ion k in the reference frame of the solvent is given by

$$\mathbf{v}_k^w = \mathbf{v}_k^H + \delta \mathbf{v}_k^{hyd}, \qquad (14)$$

where $\mathbf{v}_k^H$ is the velocity found by considering the Newton equation without any corrective force, i.e., $\delta \mathbf{F}_k^{rel} = 0$ and $\delta \mathbf{F}_k^{hyd} = 0$ in Eq. (2). The hydrodynamic increment $\delta \mathbf{v}_k^{hyd}$ can be obtained following the procedure described in Subsection III A. It follows that the electric current can be written as

$$\mathbf{I} = \sum_{k=1}^{n-1} e z_k n_k \left(\mathbf{v}_k^H + \delta \mathbf{v}_k^{hyd} \right) \qquad (15)$$

$$= \sum_{k=1}^{n-1} e z_k n_k \left(\frac{D_k}{k_B T} \left[\left(m_k - \rho \overline{V}_k \right) \frac{\nabla P}{\rho} + e z_k \mathbf{E} \right] \right. \qquad (16)$$

$$+ \left. \sum_{j=1}^{n-1} n_j H_{kj} \left[\left(m_j - \rho \overline{V}_j \right) \frac{\nabla P}{\rho} + e z_j \mathbf{E} \right] \right), \qquad (17)$$

where $\overline{V}_k$ is the partial volume of ion k. Only the electric current dependence in pressure is involved in Onsager reciprocal

relationship, so we drop the part describing the conductivity,

$$\mathbf{I}_{E=0} = \frac{\nabla P}{\rho} \left(\sum_{k=1}^{n-1} ez_k n_k \left[\frac{D_k}{k_B T} \left(m_k - \rho \overline{V}_k \right) \right. \right.$$
$$\left. \left. + \sum_{j=1}^{n-1} n_j H_{kj} \left(m_j - \rho \overline{V}_j \right) \right] \right). \tag{18}$$

Permuting summations and indices, then using the symmetry of the total correlation function $h_{kj}^0 = h_{jk}^0$,

$$\mathbf{I}_{E=0} = \frac{\nabla P}{\rho} \left(\sum_{k=1}^{n-1} en_k \left(m_k - \rho \overline{V}_k \right) \left[\frac{z_k D_k}{k_B T} + \sum_{j=1}^{n-1} z_j n_j H_{kj} \right] \right). \tag{19}$$

The flux mass in the reference frame of the total volume flux is given by (see Paper I)

$$\mathbf{J}^{vol} = \sum_{k=1}^{n} n_k m_k \mathbf{v}_k^{vol}$$
$$= \sum_{k \neq w} n_k m_k \left(\mathbf{v}_k^{vol} - \mathbf{v}_w^{vol} + \mathbf{v}_w^{vol} \right) + n_w m_w \mathbf{v}_w^{vol}$$
$$= \sum_{k \neq w} n_k m_k \left(\mathbf{v}_k^{vol} - \mathbf{v}_w^{vol} \right) + \rho \mathbf{v}_w^{vol}, \tag{20}$$

where, again, n represents the solvent (water) and all other components are ions. In Paper I, it was shown that the volume flux is by definition zero in the reference frame of the total volume flux,

$$0 = \sum_{k=1}^{n} n_k \overline{V}_k \mathbf{v}_k^{vol} = \mathbf{v}_w^{vol} + \sum_{k \neq w} n_k \overline{V}_k \left(\mathbf{v}_k^{vol} - \mathbf{v}_w^{vol} \right) \tag{21}$$

and that the sum of the volume of all the species is the volume of the solution,

$$\sum_{k=1}^{n} n_k \overline{V}_k = 1. \tag{22}$$

Combining the two previous equations in order to obtain the velocity of water in the reference frame of the total volume flux, and inserting the result in Eq. (20), as was done in Paper I, one obtains

$$\mathbf{J}^{vol} = \sum_{k \neq w} n_k (m_k - \rho \overline{V}_k) \left(\mathbf{v}_k^{vol} - \mathbf{v}_w^{vol} \right). \tag{23}$$

Following the lines used in the derivation of the electric current,

$$\mathbf{J}^{vol} = \sum_{k \neq w} n_k (m_k - \rho \overline{V}_k) \mathbf{v}_k^{w}$$
$$= \sum_{k \neq w} n_k (m_k - \rho \overline{V}_k) \left(\mathbf{v}_k^{H} + \delta \mathbf{v}_k^{hyd} \right)$$
$$= \sum_{k \neq w} n_k (m_k - \rho \overline{V}_k) \left(\frac{D_k}{k_B T} \left[(m_k - \rho \overline{V}_k) \frac{\nabla P}{\rho} + ez_k \mathbf{E} \right] \right.$$
$$\left. + \left[\sum_{j=1}^{n-1} n_j H_{kj} \left(m_j - \rho \overline{V}_j \right) \frac{\nabla P}{\rho} + ez_j \mathbf{E} \right] \right). \tag{24}$$

In order to verify the Onsager's reciprocal relation, we are only interested in the electric field dependence of mass flux in the fixed-volume reference frame,

$$\mathbf{J}_{\nabla P=0}^{vol} = \mathbf{E} \left(\sum_{k=1}^{n-1} en_k \left(m_k - \rho \overline{V}_k \right) \left[\frac{z_k D_k}{k_B T} + \sum_{j=1}^{n-1} z_j n_j H_{kj} \right] \right). \tag{25}$$

Comparison of this equation with Eq. (19) enables to demonstrate that Eq. (1) is fulfilled and therefore that the reciprocal Onsager relation for a system with any number of ions, in the presence of a corrective hydrodynamic force as defined in Subsection III A, is satisfied.

C. Expression of the electric relaxation force

As already discussed, the electric relaxation force originates from the deformation of the ionic atmosphere around the central ion when this ion moves. The deformation of the ionic atmosphere leads to an electrostatic force which opposes the central ion's velocity. In the general case, the electric relaxation force can be written as

$$\delta \mathbf{F}_k^{rel} = -\sum_j n_j \int \nabla_k V_{kj}(r, r_j) g_{kj}(\mathbf{r}, \mathbf{r}_j) d\mathbf{r}_j, \tag{26}$$

where V_{kj} is the interaction potential between k and j.[19] ∇_k is the gradient with respect to $\mathbf{r}$ which is the position of ion k, $\mathbf{r}_j$ is the position of ion j, and g_{kj} is the pair distribution function that includes both the equilibrium and the out-of-equilibrium contribution, an expression of which can be found in Ref. 20. An expression for $\delta \mathbf{F}_k^{rel}$ in the case of a solution containing three different ionic species can be found in Refs. 15 and 13. In what follows, for the sake of clarity, we restrict ourselves to case of a solution containing only two different ionic species (binary salt), referred to by indices 1 and 2.

When the electric relaxation force applied, the hydrodynamic force, evaluated in Sec. III B, is affected. Eq. (9) should be corrected to account for the electric relaxation,

$$\mathbf{F}_k^{full} = \left(m_k - \rho \overline{V}_k \right) \frac{\nabla P}{\rho} + ez_k \mathbf{E} + \delta \mathbf{F}_k^{rel}$$
$$= \mathbf{F}_k + \delta \mathbf{F}_k^{rel}. \tag{27}$$

This implies that the hydrodynamic velocity increment, defined in Eq. (10), should be corrected into

$$\delta \mathbf{v}_k^{hyd,full} = \sum_{j=1}^{2} n_j \mathbf{F}_j^{full} H_{kj}. \tag{28}$$

This hydrodynamic velocity increment of the ions in the reference frame of water can be expressed as

$$\delta \mathbf{v}_1^{hyd,full} = n_1 H_{11} \mathbf{F}_1^{full} + n_2 H_{12} \mathbf{F}_2^{full},$$
$$\delta \mathbf{v}_2^{hyd,full} = n_1 H_{21} \mathbf{F}_1^{full} + n_2 H_{21} \mathbf{F}_2^{full}, \tag{29}$$

where because of the symmetry of the total correlation function ($h_{21}^0 = h_{12}^0$),

$$H_{21} = H_{12}. \tag{30}$$

The electrostatic relaxation correction is due to the deformation of the ionic atmosphere. This deformation is caused by the difference of velocities between the ionic atmosphere and the central ion. Therefore, the electrostatic relaxation force is proportional to the difference of velocity between the ions,

$$\delta\mathbf{F}_1^{rel} = n_2 A_{12}(\mathbf{v}_1^w - \mathbf{v}_2^w),$$
$$\delta\mathbf{F}_2^{rel} = n_1 A_{21}(\mathbf{v}_2^w - \mathbf{v}_1^w). \tag{31}$$

According to the third law of Newton, the force exerted by ion 1 on ion 2 is the opposite of the force exerted by ion 2 on ion 1,

$$n_1\delta\mathbf{F}_1^{rel} + n_2\delta\mathbf{F}_2^{rel} = 0 \tag{32}$$

which implies

$$A_{21} = A_{12} = A. \tag{33}$$

This useful relation may only be derived for binary electrolytes, and this is the reason of the restriction of the current demonstration to binary electrolytes. A detailed expression of A is given in Appendix C. The velocity difference $(\mathbf{v}_1^w - \mathbf{v}_2^w)$ between both ions can be evaluated by

$$\mathbf{v}_1^w - \mathbf{v}_2^w = \mathbf{v}_1^H - \mathbf{v}_2^H + \delta\mathbf{v}_1^{hyd,full} - \delta\mathbf{v}_2^{hyd,full}$$
$$= \frac{1}{B}\left[\frac{D_1^*}{k_BT}\mathbf{F}_1 - \frac{D_2^*}{k_BT}\mathbf{F}_2\right], \tag{34}$$

where $\mathbf{F}_k$ are given by Eq. (9) and where we used the following definitions:

$$\frac{D_1^*}{k_BT} = \frac{D_1^0}{k_BT} + n_1\mathrm{H}_{11} - n_1\mathrm{H}_{12},$$
$$\frac{D_2^*}{k_BT} = \frac{D_2^0}{k_BT} + n_2\mathrm{H}_{22} - n_2\mathrm{H}_{12}, \tag{35}$$
$$B = 1 - n_2 A\frac{D_1^*}{k_BT} - n_1 A\frac{D_2^*}{k_BT}.$$

D. Verification of Onsager's reciprocal relation in the particular case of a binary electrolyte

To simplify the writing, we define now the individual flows: $j_k^w = n_k v_k^w$. With this notation, we obtain

$$\mathbf{j}_1^w = n_1\mathbf{v}_1^w = L_{11}\,\mathbf{F}_1 + L_{12}\,\mathbf{F}_2,$$
$$\mathbf{j}_2^w = n_2\mathbf{v}_2^w = L_{21}\,\mathbf{F}_1 + L_{22}\,\mathbf{F}_2 \tag{36}$$

with

$$L_{11} = n_1\left[\frac{D_1}{k_BT} + n_1\mathrm{H}_{11} + \frac{D_1^*}{k_BT}\frac{D_1^*}{k_BT}\frac{n_2 A}{B}\right], \quad L_{12} = n_1\left[n_2\mathrm{H}_{12} - \frac{D_1^*}{k_BT}\frac{D_2^*}{k_BT}\frac{n_2 A}{B}\right],$$

$$L_{21} = n_2\left[n_1\mathrm{H}_{21} - \frac{D_1^*}{k_BT}\frac{D_2^*}{k_BT}\frac{n_1 A}{B}\right], \quad L_{22} = n_2\left[\frac{D_2}{k_BT} + n_2\mathrm{H}_{22} + \frac{D_2^*}{k_BT}\frac{D_2^*}{k_BT}\frac{n_1 A}{B}\right]. \tag{37}$$

We recover the symmetry relation: $L_{12} = L_{21}$. From the general definition of the electric current and mass flow, we have

$$\mathbf{I} = \sum_{k=1}^{n} n_k e z_k \mathbf{v}_k^w = \sum_{k=1}^{n} e z_k \mathbf{j}_k^w, \tag{38}$$

$$\mathbf{J}^{vol} = \sum_{k=1}^{n-1} n_k\left(m_k - \rho\overline{V}_k\right)\mathbf{v}_k^w = \sum_{k=1}^{n-1}\left(m_k - \rho\overline{V}_k\right)\mathbf{j}_k^w. \tag{39}$$

Introducing the expressions for the fluxes given by Eqs. (36), (37) in the previous equations, then splitting each of the forces $\mathbf{F}_k$ in a contribution proportional to $\nabla P/\rho$ and another proportional to $\mathbf{E}$ (according to Eq. (9)), one obtains

$$\mathbf{I} = e\sum_{k,j}^{n-1} z_k L_{kj}\widetilde{m}_j\frac{\nabla P}{\rho} + e^2\sum_{k,j}^{n-1} z_k L_{kj} z_j\mathbf{E}, \tag{40}$$

$$\mathbf{J}^{vol} = \sum_{k,j}^{n-1}\widetilde{m}_k L_{kj}\widetilde{m}_j\frac{\nabla P}{\rho} + e\sum_{k,j}^{n-1}\widetilde{m}_k L_{kj} z_j\mathbf{E}, \tag{41}$$

where we have used the notation $\widetilde{m}_k = m_k - \rho\overline{V}_k$. Finally, we check that the Onsager reciprocal relations are satisfied, i.e.,

$$\frac{\mathbf{I}_{E=0}}{\nabla P/\rho} = \frac{\mathbf{J}_{\nabla P=0}^{vol}}{\mathbf{E}} = \frac{e}{k_BT}\sum_{k=1}^{2} n_k z_k D_k^*\widetilde{m}_k$$
$$\times\left[1 + \frac{A}{Bk_BT}\left(D_1^* n_2 + D_2^* n_1\right)\right]. \tag{42}$$

Both $(\mathbf{I}_{E=0}/(\nabla P/\rho))$ and $(\mathbf{J}_{\nabla P=0}^{vol}/\mathbf{E})$ therefore depend on the electric relaxation (the term in square brackets) in the same

way. If we adopt the theoretical procedure introduced by O'Brien,[21] because it is a natural extension of the expressions presented here, we can introduce a dynamic current defined by

$$\mathbf{I}_{dyn} = \varepsilon_0\varepsilon_r\frac{\partial\mathbf{E}}{\partial t} + \mathbf{I}. \tag{43}$$

Then using the relation $\nabla\cdot\mathbf{I}_{dyn} = 0$, the electroacoustic potential can be deduced. This approach is equivalent to that of Hermans in the ideal case. When the applied frequency is low and the concentrations are sufficiently high, then $\varepsilon_0\varepsilon_r(\partial\mathbf{E}/\partial t) \ll \mathbf{I}$. Under these conditions, as it was shown in a previous article,[14] the electroacoustic potential can be inferred, considering that the current defined by Eq. (40) is zero. Under these conditions, from Eq. (40), we find

$$\frac{\mathbf{I}_{\nabla P=0}}{\mathbf{E}} \equiv K = \frac{e^2}{k_BT}\sum_{k=1}^{2} n_k z_k^2 D_k^*$$
$$\times\left[1 + \frac{A}{Bk_BT}\left(D_1^* n_2 + D_2^* n_1\right)\right]. \tag{44}$$

The ratio of expressions (42) and (44) allows to evaluate the electroacoustic field under the condition of zero current,

$$\left(\frac{\mathbf{E}}{\nabla P/\rho}\right)_{\mathbf{I}=0} = \frac{(\mathbf{I}/(\nabla P/\rho))_{\mathbf{E}=0}}{(\mathbf{I}/\mathbf{E})_{\nabla P=0}} = \frac{\sum_{k=1}^{2} n_k z_k D_k^*\widetilde{m}_k}{e\sum_{k=1}^{2} n_k z_k^2 D_k^*}. \tag{45}$$

As the term in square brackets in Eqs. (42) and (44) appears in both the numerator and the denominator of the last equation, it cancels out. Consequently, the electric relaxation does

not modify $(\mathbf{E}/(\boldsymbol{\nabla}P/\rho))_{I=0}$, as already explained in Ref. 14. Indeed, under a condition of zero electric current, for a binary electrolyte, both ions have the same velocity, so there is no net electrostatic relaxation. The electrostatic relaxation should therefore be included in the calculation of the IVI, but is not necessary for the IVP in the case of binary electrolytes. Eq. (44) allows also to calculate the conductivity K of the solution which depends on the relaxation of forces. The accuracy of the conductivity measurement is much larger than those of electro-potentials. When the theoretical application of Eqs. (42) and (44) allows to account simultaneously of the experimental conductivities and electroacoustic potentials, the reliability of the used theoretical model appears strengthened.

IV. CONCLUSION

In Paper I[7] of this series of articles, we demonstrated that the theories derived by Debye and Hermans for the electroacoustics satisfy the Onsager reciprocal relation. Here, we have shown that all theories published later, even though they contributed to a better modelling of the data by the inclusion of inter-ionic forces, did not satisfy the Onsager relationship. The theories by Oka,[11] Yeager,[12] and coworkers, for example, accounted for the decrease of the molar conductivity with concentration, but not for the decrease of the IVI by unit of pressure with concentration. Durand-Vidal *et al.*[15,13] later took into account the pressure-dependence of the corrective forces, but raised objections about using the pressure force for ions, since this could lead to negative partial specific volumes. We addressed these objections in Appendix A, and demonstrated that there is no contradiction in defining negative partial volumes in the context of Newton's equation of motion. More importantly, not using the pressure force would lead to erroneous results, even in the moderate ionic strength range, as can be seen in Fig. 2.

In Subsections III A–III D, we gave a new expression for the IVP that was already used in Ref. 14 to account for new experimental data. The expression of the electric current which includes the new hydrodynamic correction, Eq. (15), is quite general, and respects the Onsager reciprocal relation. In particular, from this IVI expression, the IVP expression can be deduced and subsequently used to interpret the data for binary salts.[14] In this case, it was demonstrated that there is no contribution of the electrostatic relaxation corrective force to the IVP.[14] There is, nonetheless, a contribution of the electric relaxation to the IVI. The inclusion of both the hydrodynamic coupling and electric relaxation was also addressed in this article. We have shown that in the case of a binary electrolyte, the general expressions of the IVI/IVP including all relevant forces, in particular the new the hydrodynamic coupling and the electric relaxation corrective forces presented in this article, verify the Onsager reciprocal relation. This new formulation also predicts the measured data in a satisfactory way.

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APPENDIX A: PARTIAL VOLUMES FROM MECHANICAL CONSIDERATIONS

In this appendix, we like to comment on the fact that (1) it is important to include the pressure gradient force when considering the second law of dynamics in the general case and (2) the partial volume $\overline{V}_k$ within the pressure gradient force can be negative in the case of an ion. The Newton equation of motion was found to be in the general case, see Eq. (2),

$$m_k \frac{\partial \mathbf{v}_k^{lab}}{\partial t} = -\overline{V}_k \boldsymbol{\nabla} P + \mathbf{F}_k^*, \tag{A1}$$

where $\mathbf{F}_k^*$ are all the forces, but the pressure gradient force $\mathbf{F}_k^{\boldsymbol{\nabla}P} = -\overline{V}_k \boldsymbol{\nabla} P$, applied to object k. This equation is valid for any object, not only ions. For simplicity, we will consider that the only forces applied to the object k are the pressure gradient force and the solvent friction. Newton's equation, in this case, becomes

$$m_k \frac{\partial \mathbf{v}_k^{lab}}{\partial t} = -\frac{k_B T}{D_k} \left(\mathbf{v}_k^{lab} - \mathbf{v}_w^{lab} \right) - \overline{V}_k \boldsymbol{\nabla} P. \tag{A2}$$

In the case of large spherical objects of radius a (for instance, colloidal particles), the friction coefficient can be related to a by $k_B T/D_k = 6\pi\eta a$. In good approximation, $\partial \mathbf{v}_k^{lab}/\partial t$ is equal to the acceleration of water if $\overline{\rho}_w \simeq \rho$ (which is the case when the suspension is diluted or when particles and solvent have similar densities)

$$\frac{\partial \mathbf{v}_k^{lab}}{\partial t} \simeq -\frac{\boldsymbol{\nabla} P}{\overline{\rho}_w}, \tag{A3}$$

we obtain

$$\left(m_k - \overline{\rho}_w \overline{V}_k \right) \frac{\partial \mathbf{v}_k^{lab}}{\partial t} = -\frac{k_B T}{D_k} \left(\mathbf{v}_k^{lab} - \mathbf{v}_w^{lab} \right). \tag{A4}$$

When the object k has exactly the same density as the solvent (i.e., $m_k - \overline{\rho}_w \overline{V}_k = 0$), its velocity is equal to the one of the solvent ($\mathbf{v}_k^{lab} = \mathbf{v}_w^{lab}$). If we had neglected the pressure gradient force (which corresponds to take $\overline{V}_k = 0$), there would be a velocity difference between the object and the solvent, which is impossible when the mechanical equilibrium is reached. We have therefore demonstrated the importance of including the pressure gradient force in the set of equations.

In the case of large objects (macroions or colloid), the partial volume $\overline{V}_k$ can be seen as the volume of the macroion, i.e., $V_a = 4\pi a^3/3$, where a is the radius of the macroion, as with a good approximation

$$\overline{V}_k \equiv \frac{\partial V_{tot}}{\partial N_k} = \frac{\partial \left(V + N_k V_a \right)}{\partial N_k} = V_a, \tag{A5}$$

where V is the difference between the total volume of the suspension V_{tot} and the volume of all the colloidal particles. The volume V does not depend on N_k. The pressure gradient force $-\overline{V}_k \boldsymbol{\nabla} P$ is, as expected, directed towards the smallest

pressure. The contradiction pointed out by Durand *et al.*[15,13] is that, in the case of ions, one can have $\overline{V}_k < 0$ and this would, by analogy with large objects, imply that the pressure gradient force $-\overline{V}_k \boldsymbol{\nabla} P$ is directed towards the largest pressure. In fact, by doing this analogy, the mistake is to assimilate $\overline{V}_k$ to the volume of the hydrated ion, $V_{ion\ hyd}^k = V_{ion}^k + V_{hyd}^k$, where V_{ion}^k is the volume of the bare ion k, and V_{hyd}^k the volume of its hydration shell. The pressure gradient force is formally defined as

$$\mathbf{F}^{\nabla P} = -\iint_S P d\mathbf{S} = -\iiint_V \boldsymbol{\nabla} P dV = -V_{enclosed}\boldsymbol{\nabla} P, \quad \text{(A6)}$$

where $\mathbf{S}$ is oriented toward the exterior of the considered surface that encompasses the corresponding volume $V_{enclosed}$. If $V_{enclosed} = V_{ion\ hyd}^k$, there is no contradiction, but there is one when we make the equivalence $V_{enclosed} = \overline{V}_k$ since $\overline{V}_k$ can be negative.

If we write Newton's equation for the hydrated ion, then we obtain the result (with, for any ion, $\overline{V}_k = V_{ion\ hyd}^k > 0$),

$$\left(m_{ion\ hyd}^k - \overline{\rho}_w V_{ion\ hyd}^k\right) \frac{\partial \mathbf{v}_k^{lab}}{\partial t} = \mathbf{F}_k^*. \quad \text{(A7)}$$

Unfortunately, $V_{ion\ hyd}^k$ is not accessible by experiments. For ions, only the partial volume is accessible, which, in some cases, can be negative. Negative partial volumes arise when electrostriction plays a role: by adding dN_k ions to the solution, some volume within the ionic hydration shell gets a density that is larger than the density of bulk water; hence, the total volume of the solution becomes smaller: $dV_{tot} < 0$ and therefore $\overline{V}_k < 0$. We are however going to demonstrate, that, in the dilute case, i.e., where $\rho \simeq \overline{\rho}_w$ and for situations where $\overline{V}_k$ does not depend on the concentration of ions in solution that

$$\left(m_{ion\ hyd}^k - \overline{\rho}_w V_{ion\ hyd}^k\right) = \left(m_k - \overline{\rho}_w \overline{V}_k\right) \quad \text{(A8)}$$

for any $\overline{V}_k$ (>0 or <0). To do so, we are going to evaluate $M_{tot} - \overline{\rho}_w V_{tot}$, where

$$
\begin{aligned}
V_{tot} &= \sum N_k \overline{V}_k = N_{free} V_{water} + \sum_{k \neq w} N_k V_{ion\ hyd}^k \\
&= N_{init} V_{water} + \sum_{k \neq w} N_k \overline{V}_k, \\
M_{tot} &= \sum N_k m_k = M_{free} + \sum_{k \neq w} N_k M_{ion\ hyd}^k \\
&= M_{init} + \sum_{k \neq w} N_k m_k.
\end{aligned}
\quad \text{(A9)}
$$

We define N_{free} as the number of water molecules within the solution that are not in the hydration shell of the ions ("free water") and N_{init} as the number of water molecules in the absence of any ions ("initial water"). For the "free water" and the "initial water," the volume of each water molecule is V_{water}. We also have $M_{free} = N_{free} m_w$ and $M_{init} = N_{init} m_w$, where $m_w = \overline{\rho}_w V_{water}$. From Eq. (A9), we obtain

$$
\begin{aligned}
M_{tot} - \overline{\rho}_w V_{tot} &= \sum_{k \neq w} N_k \left(M_{ion\ hyd}^k - \overline{\rho}_w V_{ion\ hyd}^k\right) \\
&= \sum_{k \neq w} N_k \left(m_k - \overline{\rho}_w \overline{V}_k\right). \quad \text{(A10)}
\end{aligned}
$$

From which follows, for any k and any $\overline{V}_k$ (>0 or <0), the equivalence

$$\left(m_{ion\ hyd}^k - \overline{\rho}_w V_{ion\ hyd}^k\right) = \left(m_k - \overline{\rho}_w \overline{V}_k\right). \quad \text{(A11)}$$

From the last equation, we note that when $\overline{V}_k < 0$, the right-hand side term is larger than m_k (the mass of the bare ion). This implies that $m_{ion\ hyd}^k = m_k + m_{hyd.\ shell}^k > m_k + \overline{\rho}_w V_{ion\ hyd}^k$ and therefore $m_{hyd.\ shell}^k > \overline{\rho}_w V_{ion\ hyd}^k$, i.e., the water within the hydration shell is much denser than $\overline{\rho}_w$, as happens in the case of electrostriction.

In conclusion, the fact that some ions can have a negative partial volume does not prevent one to define the pressure and an associated mechanical force in the context of electroacoustics.

APPENDIX B: TOTAL FORCE APPLIED ON THE SOLUTION

By using Eq. (7), the hydrodynamic velocity increment $\delta \mathbf{v}_k^{hyd}$ can be calculated from the forces $\mathbf{F}_{tot[k]}(\mathbf{r})$. When calculating the hydrodynamic velocity increment under the action of an electric field, only the distribution of charged species around a given ion is taken into account. The influence of the solvent, which is neutral, is negligible. When the force includes contributions due to inertia and pressure gradient, the solvent feels the influence of these forces. Therefore, in the definition of $\mathbf{F}_{tot[k]}(\mathbf{r})$, it may seem more natural to consider also the contribution of the solvent on the one hand and to replace the total correlation function $h_{kj}^0(r)$ with the distribution function $g_{kj}^0(r)$,

$$\mathbf{F}_{tot[k]}(\mathbf{r}) = \sum_{j=0}^n n_j g_{kj}^0(r) \mathbf{F}_j \quad \text{(B1)}$$

with $g_{kj}^0(r) = 1 + h_{kj}^0(r)$ and $\mathbf{F}_j$ given by Eq. (9). At large distances, this force tends to $\sum_{j=0}^n n_j \mathbf{F}_j$. This sum does not depend on the total correlation functions $h_{kj}^0(r)$, which appears to result in a hydrodynamic contribution even without of interactions. Fortunately, this sum is zero, which cancels such a long distance contribution. Owing to this fact, the solvent contribution can be expressed as a function of the sum of the forces on the solutes. Then assuming that the solvent is a uniform continuum, the force $\mathbf{F}_{tot[k]}(\mathbf{r})$ can be written as the sum only over the solutes as in Eq. (8) which leads to Eq. (10) for the total hydrodynamic velocity increment which depends only on total correlation functions.

APPENDIX C: NUMERICAL PREFACTOR IN THE ELECTRIC RELAXATION TERM

The equation for the electric relaxation of binary electrolyte is given by Eq. (21) in Ref. 13 or Eq. (63) in Ref. 22. We reformulated it here with adapted notations, to be able to identify the parameter A. We define σ as the distance of minimal approach between anion and cation, and the distance κ_q^{-1} which is of the order of the Debye length

$$\kappa_q^2 = \frac{1}{\epsilon_0 \epsilon_r k_B T} \frac{n_1 e_1^2 D_1 + n_2 e_2^2 D_2}{D_1 + D_2}, \quad \text{(C1)}$$

where $\epsilon_0\epsilon_r$ is the electric absolute permittivity of the water. The parameter A reads

$$A = -\frac{e_1 e_2}{3\epsilon_0\epsilon_r(D_1 + D_2)}\left(i_0(\kappa_q\sigma) + \frac{\epsilon_0\epsilon_r k_B T}{4\pi e_1 e_2}\kappa_q\sigma^2 i_1(\kappa_q\sigma)\right)$$

$$\times \int_\sigma^\infty r h_{12}^0(r)\exp(-\kappa_q r)\mathrm{d}r \qquad (C2)$$

with

$$i_0(\kappa_q\sigma) = \frac{\sinh(\kappa_q\sigma)}{\kappa_q\sigma},$$

$$i_1(\kappa_q\sigma) = \frac{\cosh(\kappa_q\sigma)}{\kappa_q\sigma} - \frac{\sinh(\kappa_q\sigma)}{(\kappa_q\sigma)^2}.$$

A is negative: when ion 2 moves at a larger velocity than ion 1, i.e., $(\mathbf{v}_1^w - \mathbf{v}_2^w) < 0$, ion 1 is dragged in the same direction by the electrostatic relaxation correction $\delta\mathbf{F}_1^{rel} > 0$. From the relation $\delta\mathbf{F}_1^{rel} = n_2 A_{12}(\mathbf{v}_1^w - \mathbf{v}_2^w)$, we deduce that *A* must be negative.

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