Onsager’s reciprocal relations in electrolyte solutions. I. Sedimentation and electroacoustics

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In the framework of irreversible thermodynamics, we show that the sedimentation current in electrolyte solutions is mathematically equivalent to the low frequency limit of the ionic vibration current, appearing in the presence of an acoustic wave. This non-trivial result is obtained thanks to a careful choice of the reference frame used to express the mass fluxes in the context of electroacoustics. Coupled transport phenomena in electrolyte solutions can also be investigated in a mechanical framework, with a set of Newtonian equations for the dynamics of charged solutes. Both in the context of sedimentation and of electroacoustics, we show that the results obtained in the mechanical framework, in the ideal case (i.e., without interactions between ions), do satisfy the Onsager’s reciprocal relations. We also derive the general relation between corrective forces accounting for ionic interactions which must be fulfilled so that the Onsager’s reciprocal relations are verified. Finally, we show that no additional diffusion term needs to be taken into account in the flux of solutes (far from the walls), even if local concentration gradients exist, contrarily to what was done previously in the literature.

I. INTRODUCTION

Irreversible thermodynamics allows the theoretical description of coupled transport phenomena in aqueous electrolyte solution. In this article, we are particularly interested in the coupling between electric current and acoustic wave. Debye predicted this phenomenon, called electroacoustics, in 1933. Under the action of an acoustic wave, charged solutes with different densities get different velocities, creating thus an electric field in the solution. The potential difference generated between two electrodes is named the ionic vibration potential (IVP) in electrolyte solutions and the colloid vibration potential (CVP) in colloidal suspensions.

The first quantitative measurements of this phenomenon were performed by Zana in 1967 on electrolyte solutions. Then, several teams focused on the development of commercial devices devoted to the study of colloidal suspensions and to the measurement of the ζ-potential. The recent development of ultrasonic vibration potential imaging and the need for quantitative values of IVP have induced a renewed interest in the electroacoustic signal given by electrolytes. A new device was recently built at the PHENIX laboratory in Paris, which allowed new IVP measurements in electrolyte solutions. These experimental data were precisely accounted for by an analytical theory developed in a mechanical framework, with a set of Newtonian equations for the dynamics of charged solutes, starting from the pioneering work of Debye and Hermans.

Another theoretical approach of coupled transport phenomena is possible, based on irreversible thermodynamic considerations. The corresponding relations between fluxes and gradients and the famous “reciprocal relations” were introduced by Onsager in 1931. In 1952, de Groot, Mazur and Overbeek derived the Onsager reciprocal relations for sedimentation. Ohshima et al. demonstrated the validity of the Onsager relations in the case of the sedimentation potential (SP) and vibration potential for a dilute suspension of charged spherical colloidal particles. Ohshima later made an analogy between SP and CVP to establish Onsager relationships for the CVP for concentrated suspensions. A discussion about SP and CVP and the results of Ohshima et al. for (concentrated) colloids are given in Ref. 17. In 2014, Chassagne and Bedeaux extended the results of de Groot, Mazur, and Overbeek to the electroacoustic phenomena and obtained reciprocal relations between the electrophoretic mobility and the IVP/CVP.

In this context, our goal in the present paper is to study in electrolyte solutions the link between the sedimentation current, which appears under a gravity field, and the ionic vibration current (IVC, or IVI in some papers) generated by an acoustic wave. The IVP mentioned above is the electric field which is associated to the IVC. We start from the entropy production in an electrolyte solution to define the sedimentation current generated by the gravitational field and the electric current generated by a acoustic wave. As we proceed to show, provided that the reference frame used to write the fluxes of solutes is carefully defined, (i) the sedimentation current is equivalent to the low frequency limit of the ionic vibration current, and (ii) the results obtained in the mechanical framework do satisfy the Onsager’s reciprocal relations in the ideal case, without interactions between ions. Usually, in the framework of the electrolyte theory, interactions between ions are accounted for through additional corrective forces in the Newtonian equations of motions. We derive the general relation between such corrective forces which must be fulfilled.
so that the Onsager’s reciprocal relations are verified. Finally, we also show that the diffusive contribution to the motion of solutes should not be taken into account in the Newtonian set of equations of motion, even if local concentration gradients exist.

Our paper is organized as follows. In Section II, we express the entropy production in the context of sedimentation and electroacoustics, we define the sedimentation current and the electric current under a acoustic wave, and we discuss the equivalence between these quantities. Our results obtained in the framework of the mechanical approach are presented in Section III.

II. ENTROPY PRODUCTION AND ONSAGER’S RECIPROCAL RELATIONS

A. Entropy production

An isotropic system of \( k = 1, \ldots, n \) components is considered. The temperature \( T \) is assumed to be constant and uniform. No viscous forces are acting on the element of volume considered, which contains a representative amount of each of the components, typically ions in water. The ionic concentration is homogeneous. The system is, in the most general case, subjected to an electric field \( \mathbf{E} \), a gravitational field \( \mathbf{g} \), and a pressure gradient \( \nabla P \). These forces create a mass flow \( \mathbf{J}_k \) of component \( k \). Note that all the fluxes are defined per unit of surface perpendicular to the direction of the flux. This implies that, for instance, all volume fluxes have as unit \((\text{m}^3/\text{s})/(\text{m}^2) = (\text{m}/\text{s})\). The resulting total entropy creation \( \sigma \) for this system is found to be \(^{18}\)

\[
\sigma = \frac{1}{T} \sum_{k=1}^{n} (e_k \mathbf{E} + \mathbf{g} - \mathbf{V}_k \nabla P) \cdot \mathbf{J}_k, 
\]

where components \( k = 1 \) to \( m \) (ions) carry an electric charge per unit of mass \( e_k \),

\[
e_k = \frac{q_k}{m_k},
\]

where \( m_k \) is the mass of an individual particle of type \( k \) and \( q_k \) is the electric charge of particle \( k \). For ions, \( q_k = e z_k \), with \( e \) the elementary charge and \( z_k \) the valence of ion \( k \). The components \( k = m + 1 \) to \( n \) are neutral (solvent molecules, in the following considered to be water): \( e_k = 0 \). We neither consider electrode reactions nor chemical reactions.

de Groot et al.\(^{14}\) defined the partial specific volume of particle \( k \) by the symbol \( \mathbf{v}_k \). As it could be confused, in the present article, with the symbol used for the velocity’s amplitude, i.e., \( \mathbf{v}_k = |\mathbf{v}_k| \), we prefer to use the notation \( \mathbf{V}_k \) for the partial specific volume,

\[
\mathbf{V}_k = \frac{\partial \mathbf{V}_{\text{tot}}}{\partial m_{\text{tot},k}},
\]

where \( \mathbf{V}_{\text{tot}} \) is the volume of the system and \( m_{\text{tot},k} \) the total mass of component \( k \). We have therefore

\[
\mathbf{V}_{\text{tot}} = \sum_{k=1}^{n} m_{\text{tot},k} \mathbf{V}_k, 
\]

\[
1 = \sum_{k=1}^{n} \rho_k \mathbf{V}_k, 
\]

where \( \rho_k \) is the mass density of component \( k \),

\[
\rho_k = m_{\text{tot},k} \frac{\mathbf{V}_{\text{tot}}}{\mathbf{V}_k} = n_k m_k
\]

and \( n_k \) is the number of particles of type \( k \) per unit of volume. Finally, the global mass density is

\[
\rho = \sum_{k=1}^{n} \rho_k.
\]

The entropy production can be split in three parts, namely, the entropy production due to the conversion of the electrical energy into heat (Joule heating), the entropy production due to the conversion of the gravity potential energy into heat, and the entropy production due to the conversion of pressure energy into heat. This gives

\[
\sigma = \sigma_E + \sigma_g + \sigma_P,
\]

\[
\sigma_E = \frac{1}{T} \sum_{k=1}^{n} e_k E_k \cdot J_k,
\]

\[
\sigma_g = \frac{1}{T} \sum_{k=1}^{n} g \cdot J_k,
\]

\[
\sigma_P = -\frac{1}{T} \sum_{k=1}^{n} \mathbf{V}_k \nabla P \cdot J_k.
\]

It was shown in Ref. 18 that \( \sigma_E \) is independent of the frame of reference and equal to

\[
\sigma_E = \frac{\mathbf{I} \cdot \mathbf{E}}{T},
\]

where \( \mathbf{I} \) is the electric current,

\[
\mathbf{I} = \sum_{k=1}^{n} \rho_k e_k \mathbf{v}_k,
\]

and where we used the electroneutrality relation,

\[
\sum_{k=1}^{n} \rho_k e_k = 0.
\]

The mass fluxes \( \mathbf{J}_k \) and the entropy productions \( \sigma_g \) and \( \sigma_P \) are evaluated in Subsections II B–II D. It is important to note that in the general expression of the entropy production given in Eq. (7), the mass flux of species \( k, \mathbf{J}_k \), is defined in the reference frame of the center of mass of the system (also referred to hereafter as the barycentric reference frame). If that would not be the case, extra forces (due to the acceleration of this center of mass) would have to be considered. The contribution of these forces then should be included in entropy production. The entropy production being independent of the reference frame implies that \( (\sigma_g + \sigma_P) \) will have different values in different reference frames. In the case of the sedimentation, there is no acceleration of the center of mass, so that \( (\sigma_g + \sigma_P) \) can be evaluated (and has the same value) in any reference frame. On the other hand, when an acoustic wave is applied on a solution, there is an acceleration of the center of mass. We will show that in this case, it is convenient to express the volume flux in the barycentric reference frame as a function of the mass flux in the reference frame of the volume flux. Doing so, we will be able
to correlate the sedimentation current and vibration current in the limit of an acoustic wave of (very) low frequency.

B. Sedimentation current

Here, we consider a solution subjected to a gravity field, at mechanical equilibrium (there is no acceleration of the center of mass of the system). Prigogine’s theorem then states that the mass fluxes \( \mathbf{J}_k \) can be written in any frame of reference (a demonstration can be found in p. 44 of Ref. 19). de Groot et al.,\textsuperscript{14} using this theorem, defined the reference frame as the laboratory one. Their definition of the mass flow in this reference frame becomes

\[
\mathbf{J}_{lab}^k = \rho_k \mathbf{v}_{lab}^k
\]

which Mazur et al. call the “absolute flow.” In what follows, the reference frame is indicated by the superscript, here \( \text{lab} \). In this frame, the center of mass of the system is displaced at constant speed in time as the particles move downwards due to gravity, with a velocity of the center of mass denoted by \( \mathbf{v}_{\text{lab}}^k \) (subscript \( \text{lab} \) for “barycenter”) equal to

\[
\mathbf{v}_{\text{lab}}^k = \frac{1}{\rho} \sum_{k=1}^{n} \rho_k \mathbf{v}_k^k = \frac{1}{\rho} \sum_{k=1}^{n} \mathbf{J}_k^k = \frac{\mathbf{J}_{\text{lab}}}{\rho}.
\]

The entropy production \( \sigma_{g}^{lab} \) is thus

\[
\sigma_{g}^{lab} = \frac{\mathbf{g}}{T} \cdot \sum_{k=1}^{n} \rho_k \mathbf{v}_k^k = \frac{\mathbf{g}}{T} \cdot \mathbf{J}_{\text{lab}} = \rho \frac{\mathbf{g}}{T} \cdot \mathbf{v}_{\text{lab}}.
\]

The entropy production \( \sigma_{P}^{lab} \) becomes, using the zero volume flow condition (\( \mathbf{v}_{\text{vol}}^{lab} = 0 \)), that has been demonstrated in Refs. 14 and 18:

\[
\sigma_{P}^{lab} = -\frac{1}{T} \mathbf{\nabla} P \cdot \mathbf{v}_{\text{vol}}^{lab} = 0,
\]

so that the total entropy production becomes

\[
\sigma^{lab} = \frac{\mathbf{I} \cdot \mathbf{E}}{T} + \frac{\mathbf{g} \cdot \mathbf{J}_{\text{lab}}}{T}.
\]

From the law of conservation of momentum applied to a representative element of volume

\[
\rho \frac{d \mathbf{v}_{\text{lab}}}{dt} = -\mathbf{\nabla} P + \rho \mathbf{g},
\]

we find at mechanical equilibrium the hydrostatic equation

\[
\mathbf{\nabla} P = \rho \mathbf{g},
\]

so that the total entropy production can also be written as

\[
\sigma^{lab} = \frac{\mathbf{I} \cdot \mathbf{E}}{T} + \frac{\mathbf{\nabla} P \cdot \mathbf{v}_{\text{lab}}}{T}.
\]

The same expression for the entropy production would have been obtained in the barycentric reference frame. As discussed above, we have in the case of sedimentation that \( \sigma_{g}^{lab} = \sigma_{P}^{lab} \), so \( \sigma_{g}^{lab} = (\sigma_{g}^{\text{lab}} + \sigma_{P}^{\text{lab}}) \). The term associated to the mass flux becomes evidently zero in the barycentric reference frame (\( \sigma_{g}^{\text{lab}} = 0 \)), and therefore, \( \sigma_{P}^{\text{lab}} = \sigma_{g}^{\text{lab}} \).

From Eq. (18), we obtain the following linear flux-force relations:

\[
\mathbf{J}_{\text{lab}} = m_{PPE} \mathbf{g} + m_{PEE} \mathbf{E},
\]

or alternatively, from Eq. (21),

\[
\mathbf{v}_{\text{lab}} = k_{PPE} \mathbf{v}_{\text{P}} + k_{PEE} \mathbf{E},
\]

with the Onsager reciprocal relations

\[
m_{PE} = m_{EP},
\]

\[
k_{PE} = k_{EP},
\]

which are equivalent to

\[
\left( \frac{1}{g} \right)_{E=0} = \left( \frac{\mathbf{v}_{\text{vol}}^{\text{lab}}}{E} \right)_{g=0},
\]

\[
\left( \frac{1}{\mathbf{\nabla} P} \right)_{E=0} = \left( \frac{\mathbf{v}_{\text{vol}}^{\text{lab}}}{E} \right)_{\mathbf{v}_{\text{P}}=0},
\]

\[
\left( \frac{1}{E} \right)_{E=0} = \frac{1}{\rho} \left( \frac{\mathbf{J}_{\text{vol}}^{\text{lab}}}{E} \right)_{\mathbf{v}_{\text{P}}=0}.
\]

The coefficient \( m_{EE} \) is equal to \( k_{EE} \) which is the electric conductivity \( K \). The laboratory reference frame and the volume-fixed reference frame coincide, because the total volume flux is zero in the laboratory reference frame in the context of sedimentation, so we can actually use both superscripts (\( \text{vol}, \text{lab} \)), Equations (25) express the current response in the presence of either the gravity or the pressure gradient. Both are solely linked by the hydrostatic equilibrium equation.

C. Electric current generated by an acoustic wave

In the context of electroacoustics, the liquid compresses and dilates locally, so that there is an acceleration of the center of mass of the system. In the following, the space and time dependence of the sound wave will be neglected, as the characteristic times in the system are small compared to a microsecond (characteristic time for an acoustic wave of 1 MHz) and the length scales small compared to the acoustic wavelength scale (1 mm if we assume that the speed of sound in water is 1500 m/s). As discussed above and shown underneath in this section, the associated volume flux can be easily deduced in the reference frame of the laboratory. We therefore define the mass flux of particle \( k \) in the barycentric reference frame, denoted by \( \mathbf{J}_{\text{bar}}^k \), as function of variables in the reference frame of the total volume flux,

\[
\mathbf{J}_{\text{bar}}^k = \rho_k \left( \mathbf{v}_{\text{lab}}^k - \mathbf{v}_{\text{vol}}^k \right),
\]

where \( \mathbf{v}_{\text{vol}}^k \) is the velocity field of particle \( k \) in the volume-fixed reference frame and \( \mathbf{v}_{\text{lab}}^k \) is the velocity of the center of mass of the system in the volume-fixed reference frame,

\[
\mathbf{v}_{\text{vol}}^k = \frac{1}{\rho} \sum_{k=1}^{n} \rho_k \mathbf{v}_{\text{vol}}^k.
\]

The velocity field of particle \( k \) in the reference frame of the total volume flux, \( \mathbf{v}_{\text{lab}}^k \), is linked to the velocity field of particle
$k$ in the reference frame of the laboratory, $v^{lab}_{k}$, through

$$v^{vol}_{k} = v^{lab}_{k} - v^{vol}_{k},$$  \(27\)

where $v^{vol}_{k}$ is the total volume flux in the reference frame of the laboratory, due to the acoustic wave. This flux is defined by

$$v^{vol}_{k} = \sum_{k=1}^{n} v_{k} \rho_{k} v^{lab}_{k}. \quad 28$$

The velocity field $v^{vol}_{k}$ is actually defined in the reference frame associated to the total volume flux, so that in the volume-fixed reference frame, the total volume flux is (evidently) zero,

$$\sum_{k=1}^{n} V_{k} \rho_{k} v^{vol}_{k} = 0. \quad 29$$

We note that the reference frame was not clearly defined in Ref. 18: actually, in this paper, the velocity of particle $k$, $v_{k}$, was defined in the reference frame of the total volume flux and should have been denoted by $v^{vol}_{k}$, as all variables depending on the frame of reference.

The volume flux $v^{vol}_{k}$ is created by the applied pressure gradient generating the acoustic wave and ensures that the liquid compresses and dilates locally. An estimation of $v^{vol}_{k}$ in water can be obtained by considering the value for the acoustic impedance $z$ of water and the typical amplitude $P$ of the applied pressure, which gives

$$v^{vol}_{k} \approx \frac{P}{z} \approx 75,000 \frac{1}{1.5 \times 10^{6}} = 5 \text{ cm/s}. \quad 30$$

From $v^{vol}_{k}$, we can get an estimate of the total mass flow in the reference frame of the laboratory, $J^{lab}$ as $J^{lab} \approx \rho v^{vol}_{k}$. The total mass flow in the volume-fixed reference frame, $J^{vol}$, on the other hand, is quite small. For pure water $J^{vol} = 0$ but in the presence of ions, this quantity is non-zero because ions do not perfectly follow the solvent. We will show that in fact this small quantity is the one involved in the force-flux relations. It follows that even though $J^{vol}$ is much smaller than $J^{lab}$, it must not be neglected.

By using Equation (27), the mass flux of particle $k$ in the barycentric reference frame, $J^{bar}_{k}$, becomes

$$J^{bar}_{k} = \rho_{k} \left(v^{lab}_{k} - v^{bar}_{k}\right), \quad 31$$

where $v^{bar}_{k}$ is the velocity of the center of mass of the system in the reference frame of the laboratory,

$$v^{bar}_{k} =\frac{1}{\rho} \sum_{k=1}^{n} \rho_{k} v^{lab}_{k}. \quad 32$$

It is easily checked that the total mass flow in the barycentric reference frame is zero,

$$J^{bar} = \sum_{k=1}^{n} J^{bar}_{k} = 0, \quad 33$$

so that we get

$$\sigma_{g}^{bar} = \frac{1}{T} g \sum_{k=1}^{n} J^{bar}_{k} = 0. \quad 34$$

The third part of the entropy production, $\sigma^{bar}_{P}$, becomes, using Eqs. (4) and (29),

$$\sigma^{bar}_{P} = \frac{1}{T} \nabla P \cdot \sum_{k=1}^{n} V_{k} J^{bar}_{k} = \frac{1}{T} \nabla P \cdot v^{vol}_{k}. \quad 35$$

Note that even though the mass flux is expressed in the volume-fixed reference frame, the associated entropy production $\sigma^{bar}_{P}$ is still expressed, as required, in the barycentric frame of reference. The total entropy production becomes

$$\sigma = I \cdot \nabla P + \frac{1}{T} \nabla P \cdot J^{vol}. \quad 36$$

From entropy production Eq. (36), we obtain the following linear flux-force relations:

$$J^{vol} = b_{PP} \frac{\nabla P}{\rho} + b_{PE} \frac{E}{\rho}, \quad 37$$

with the Onsager relation,

$$b_{PE} = b_{EP} \quad 38$$

which implies that

$$\left(\frac{1}{\nabla P}\right)_{E=0} \cdot \frac{E}{\rho} \left(\frac{1}{\nabla P}\right)_{E=0}. \quad 39$$

The coefficient $b_{KE}$ can be identified with the electric conductivity $K$ from Eq. (37).

D. Link between the sedimentation current and the ion vibration current

Based on the results of Secs. II A–II C, it is easy to demonstrate that the Onsager relation derived in the context of electroacoustics, Eq. (39), is mathematically equivalent to the relation derived in the context of sedimentation, see last equation of Eqs. (25). These equations read

$$I_{E=0, \text{sedim}} = \frac{1}{\rho} \left(\frac{J^{vol}}{E}\right)_{\nabla P=0} \nabla P, \quad 40$$

$$I_{E=0, \text{vibration}} = \frac{1}{\rho} \left(\frac{J^{vol}}{E}\right)_{\nabla P=0} \nabla P,$$

where $\left(\frac{J^{vol}}{E}\right)_{\nabla P=0}$ depends on the frequency in the context of electroacoustics but is a static quantity in the case of sedimentation. In the literature, $I_{E=0, \text{vibration}}$ is usually expressed as function of the acceleration of the medium $\partial \omega / \partial t$ which is linked to the pressure gradient by the acoustic equation, $\rho (\partial v / \partial t) + \nabla P = 0$. The current $I_{E=0, \text{sedim}}$ is usually expressed as a function of the gravity which is linked to the pressure gradient through the hydrostatic equilibrium $\nabla P + \rho \omega P = 0$. We therefore get

$$\left(\frac{1}{g}\right)_{E=0} = \lim_{\omega \to 0} \left(\frac{1}{\nabla P / \omega}\right)_{E=0}, \quad 41$$

with $\omega$ the frequency of the acoustic wave, provided that $\nabla P$ is the same in both experiments. The sedimentation current
is therefore equivalent to the low frequency limit of the ionic vibration current.

This result might be intuitive but is non-trivial. It was obtained thanks to a careful choice of the reference frame used to express the mass flux in the context of electroacoustics (reference frame of the total volume flux).

III. VERIFICATION OF ONSAGER’S RECIPROCAL RELATIONS USING A MECHANICAL APPROACH

A. Sedimentation current

In this section, we will evaluate

\[ J_{\rho = 0}^{\text{vol}} = m_{PE} E, \]
\[ I_{E = 0} = m_{EP} g, \]

in order to prove that

\[ m_{PE} = m_{EP} \]

using the relations found in the framework of the mechanical approach, i.e., Newton equation for motion (second law of dynamics).

We assume that in the system considered, component \( n \) represents the solvent, which is water (subscript \( w \)). All other components \( k \) represent ions. From the second law of dynamics, taking into account (i) the friction due to the solvent on an ion, (ii) the force associated to the gravity, in which we have accounted for the force derived from the pressure gradient at mechanical equilibrium, and (iii) the electric force \( q_k E = e z_k E \), we get

\[ -\frac{k_B T}{D_k} (v_{k}^{\text{vol}} - v_{w}^{\text{vol}}) + m_k g - \nabla_k \nabla P + e z_k E = 0, \]

(43)

with \( k_B \) the Boltzmann’s constant and \( D_k \) the diffusion coefficient of particle \( k \). We used the partial volume \( \nabla_k \), defined by

\[ \nabla_k = \frac{\partial V_{\text{tot}}}{\partial N_k} = \frac{\partial V_{\text{tot}}}{\partial m_{\text{tot},k}} \frac{\partial m_{\text{tot},k}}{\partial N_k} = v_k m_k, \]

(44)

with \( N_k \) is the number of particles of type \( k \) present in the system.

Note that \( (v_{k}^{\text{vol}} - v_{w}^{\text{vol}}) \) could be also written \( v_{w}^{\text{vol}} \), the ionic velocity in the reference frame of the solvent. Using Eq. (20) to get an equivalent term for the pressure gradient, we obtain

\[ -\frac{k_B T}{D_k} (v_{k}^{\text{vol}} - v_{w}^{\text{vol}}) + \left( m_k - \rho \nabla_k \right) g + e z_k E = 0, \]

(45)

so that

\[ (v_{k}^{\text{vol}})_{g = 0} = (v_{w}^{\text{vol}})_{g = 0} + \frac{e z_k D_k}{k_B T} E. \]

(46)

Using

\[ v_{\text{lab}} = v_{\text{bar}} + v_{w}^{\text{vol}}, \]

(47)

we can re-write the mass flux in the reference frame of the total volume flux, using Eq. (4),

\[ J_{\rho = 0}^{\text{vol}} = \rho (v_{\text{lab}} - v_{w}^{\text{vol}}) = \sum_{k=1}^{n} \rho_k v_{\text{lab}} - \rho \sum_{k=1}^{n} \rho_k v_k v_{\text{lab}} \]

\[ = \sum_{k=1}^{n} \rho_k (1 - \rho V_k) v_{\text{lab}} \]

(48)

Using Eqs. (5) and (46), we obtain

\[ J_{g = 0}^{\text{vol}} = \sum_{k=1}^{n-1} \rho_k m_k (1 - \rho V_k) \left( \frac{e z_k D_k}{k_B T} E \right) \]

\[ = \sum_{k=1}^{n} \rho_k (1 - \rho V_k) (v_{\text{lab}} - v_{w}^{\text{lab}}). \]

(49)

The electric current can be evaluated using the electroneutrality condition,

\[ \sum_{k=1}^{n-1} \rho_k e_k = \sum_{k=1}^{n-1} e z_k n_k = 0. \]

(50)

We obtain, using Eq. (45),

\[ J_{E = 0}^{\text{vol}} = \sum_{k=1}^{n-1} e n_k z_k (v_k)_{E = 0} = \sum_{k=1}^{n} \rho_k e z_k (m_k - \rho \nabla_k) \frac{D_k}{k_B T} g. \]

(51)

Comparing Eqs. (49) and (51), we prove that the condition \( m_{PE} = m_{EP} \) is realized, and therefore, the Onsager reciprocal relation is respected.

B. Ionic vibration current

In this section, we will evaluate

\[ J_{g = 0}^{\text{vol}} = b_{PE} E, \]
\[ I_{E = 0} = b_{EP} \frac{\nabla P}{\rho}, \]

in order to prove that

\[ b_{PE} = b_{EP} \]

using the relations found in the framework of the mechanical approach.

1. Ideal case (Debye and Hermans)

We consider the case where inter-ionic interactions are neglected (ideal case), starting with the set of forces introduced by Debye in 1933 and Hermans in 1938. The second equation of Newton for an ion is in their case given by

\[ m_k \frac{\partial v_{\text{lab}}}{\partial t} = F_k^{E} + F_{\text{fric}} + F_{\text{P}} \]

(53)

where the forces are defined by

\[ F_k^{E} = e z_k E \]

the electric force,

\[ F_{\text{fric}} = -\frac{k_B T}{D_k} (v_{\text{lab}} - v_{w}^{\text{lab}}) \]

the friction force,

\[ F_{\text{P}} = -\nabla_k \nabla P \]

the pressure force.

Debye in his paper of 1933 omitted this pressure force and reported this in 1938 in a private communication with Hermans. The Onsager relation can be derived from Eq. (53)
alone; however, in order to discuss Hermans’ results, we will consider the two following relations, also given by Debye:

\[
\frac{1}{\varepsilon_0 c_1} \sum \rho_k e_k = \nabla \cdot E, \\
\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k v_k^{lab}) = 0.
\]  

(55)

The variables can be written as

\[
\rho_k = \rho_{k,eq} + \delta \rho_k \exp(i \omega t - ikx), \\
v_k^{lab} = [v_k^{vol} + \delta v_k] \exp(i \omega t - ikx), \\
E = E \exp(i \omega t - ikx) u_x,
\]

where the subscript \(eq\) stand for “equilibrium,” i.e., the state of the system in the absence of applied acoustic wave and \(u_x\) is the unit vector in the direction of the applied acoustic wave and also the direction of \(v_k\). We here make the assumption that \(\rho_{k,eq}\) does not depend on position, which is correct for ionic solutions, in a representative volume element, far from the walls/electrodes. Electro neutrality gives

\[
\sum \rho_{k,eq} e_k = 0.
\]

(57)

From the definition of the velocities in the various reference frames, given in Eq. (27), we write the following Chasles relation:

\[
v_k^{vol} = v_k^{lab} - v_k^{vol} \equiv \delta v_k.
\]

Neglecting second order terms, one obtains

\[
e_{zk} E = -\frac{k T}{D_k} (\delta v_k - \delta v_w) - \nabla_k \cdot P = i \omega m_k v_k^{vol}, \\
\sum \delta \rho_k e_k = -i \omega e_0 \varepsilon_1 k E, \\
\frac{\omega \delta \rho_k}{\omega \delta \varepsilon_1} = k \rho_{k,eq} e_k.
\]

(58)

Following the argument of Debye,\(^1\) we have assumed that \(i \omega (v_k^{vol} + \delta v_k) \approx i \omega v_k^{vol} \). This is true when

\[
\omega \ll \frac{k T}{m_k D_k} \approx \frac{300 \times 10^{-23}}{10^{-26} \times 10^{-9}} \approx 10^{14} \text{ rad/s},
\]

(59)

i.e., ions follow quite well the solvent under experimental conditions, where the frequency is of the order of MHz. Following the same arguments used to obtain Eq. (48), we can derive the following relation for \(J^{vol}\):

\[
J^{vol} = \sum_{k=1}^{n} \rho_{k,eq} (1 - \rho \nabla K) (\delta v_k - \delta v_w).
\]

(60)

From the last equation of Eqs. (55),

\[
\omega \delta \rho_k = k \rho_{k,eq} e_k^{lab}
\]

(61)

which means that \(\delta \rho_k\) is proportional to \(e_k^{lab}\) and therefore to the magnitude of the forces driven by \(\nabla P/\rho\) and \(E\). As we limit ourselves to the linear response in forces, we obtain from Eqs. (12) and (57),

\[
I = \sum_{k=1}^{n} \rho_{k,eq} e_k \delta v_k = \sum_{k=1}^{n} \rho_{k,eq} e_k (\delta v_k - \delta v_w).
\]

(62)

We obtain an expression for the pressure gradient by applying Newton’s law to a representative volume element,

\[
i \omega v^{lab}_{bar} = -\nabla P/\rho,
\]

(63)

from which we deduce

\[
v^{lab}_{par} = v^{vol}_{par} + i \nabla P/\omega \rho.
\]

(64)

As discussed previously, we can assume that \(v^{vol}_{par} \ll v^{vol}_{lab}\) (see Eq. (30)). We therefore obtain (see Ref. 13, where Hermans uses \(v^{lab}_{vol} = v_{water}\))

\[
v^{lab}_{vol} = i \nabla P/\omega \rho.
\]

(65)

We get from the first line of Eqs. (58),

\[
(\delta v_k - \delta v_w) = \frac{e_{zk} E + (m_k - \rho \nabla K) \nabla P/\rho}{k_B T / D_k}.
\]

(66)

It follows that

\[
J^{vol}_{(\varepsilon P=0)} = b_{PE} = \sum_{k=1}^{n} \rho_{k,eq} (m_k - \rho \nabla K) \frac{e_{zk}}{k_B T / D_k} = b_{PE}.
\]

(67)

\[
I = \sum_{k=1}^{n} \rho_{k,eq} e_k v^{lab}_{k} = -i \omega e_0 \varepsilon_1 E.
\]

(71)

Equating this equation with Eq. (67), we obtain

\[
\overline{K}_1 = K_1 + i \omega e_0 \varepsilon_1.
\]

(73)

Eq. (72) is the one found by Hermans, if one assumes that \(\rho \approx \rho_w\) which is true in most experimental conditions. Eq. (69)
is a particular case of Eq. (72), where the electric field is measured at low frequencies (ω → 0).

2. Integration of corrective forces

Several authors have attempted to improve the set of forces used by Hermans, taking into account interactions between ions. Oka\textsuperscript{20} added two corrections, a hydrodynamic coupling and an electrostatic relaxation, both due to the electric field. Indeed, when an ion moves forward, its ionic atmosphere lags behind and exerts a backward electric force on it: this effect is called the electrostatic relaxation, Yeager\textsuperscript{21} added a diffusion force. In 1995, Durand-Vidal\textsuperscript{22–23} accounted for the creation of a hydrodynamic coupling between ions and an electrostatic relaxation induced by the inertial force \((m_k \ddot{v}_{k}^{ob}/\partial t)\). He also included a diffusion force, but considered that the term corresponding to the pressure gradient had no proper signification for species with a negative partial molar volume and removed other forces are usually written as

\[
\mathbf{F}_{k} = \mathbf{F}_{k}^{E} + \mathbf{F}_{k}^{fric} + \mathbf{F}_{k}^{P} + \mathbf{F}_{k}^{\text{diff}} + \delta \mathbf{F}_{k}^{rel} + \delta \mathbf{F}_{k}^{hyd}, \quad (74)
\]

where the 3 first forces are given in the subsection above. The other forces are usually written as

\[
\begin{align*}
\mathbf{F}_{k}^{\text{diff}} &= -k_{B}T \nabla n_{k} \rho \quad \text{the diffusion force,} \\
\delta \mathbf{F}_{k}^{rel} &= \alpha_{k}^{rel} \mathbf{E} + \beta_{k}^{rel} \mathbf{E} = \mathbf{E} - k_{B}T \nabla P \quad \text{the relaxation force,} \\
\delta \mathbf{F}_{k}^{hyd} &= \alpha_{k}^{hyd} \mathbf{E} + \beta_{k}^{hyd} \mathbf{E} = \mathbf{E} - k_{B}T \nabla P \quad \text{the hydrodynamic force.}
\end{align*}
\]

The explicit expressions of these corrective forces and their \(\alpha_{k}\) and \(\beta_{k}\) depend on the different authors and are not detailed here. Following the steps developed in Subsection III B 1 and using the general expression of a corrective force, \(\mathbf{F}_{k} = \alpha_{k} \mathbf{E} + \beta_{k} \nabla P / \rho\), we obtain that in order to fulfill Onsager’s reciprocal relationship, the relation

\[
\sum_{k} \frac{n_{k,eq}}{k_{B}T/D_{k}} \frac{\alpha_{k}}{k_{B}T/D_{k}} = \sum_{k=1}^{n_{k,eq}} \frac{\beta_{k}}{k_{B}T/D_{k}} \frac{e_{k}}{k_{B}T/D_{k}} \quad (76)
\]

must be respected between \(\alpha_{k}\) and \(\beta_{k}\).

3. The particular case of the diffusion force

According to some authors,\textsuperscript{21–23} the diffusion force which arises from the concentration gradient created by the compression/dilatation due to the acoustic wave must be accounted for. This force comes originally from the gradient of the electrochemical potential \(\mu_{k}\) that is defined by

\[
\mu_{k} = \mu_{k}^{0} + V_{k}(P - P^{0}) + k_{B}T \ln \left( \frac{n_{k}}{n_{tot}} \right) + \zeta_{k} e \nabla \Psi, \quad (77)
\]

where \(\mu_{k}^{0}\) and \(P^{0}\) are reference values, \(\nabla \Psi = - \mathbf{E}\) and \(n_{tot} = \sum n_{k}\) is the total particle number concentration. In the previous equation, we have used the gradient of the molar fraction (equivalent to \(\nabla (n_{k}/n_{tot})\)) as is done in the general definition of the electrochemical potential.\textsuperscript{25} Note that because of the compression/dilatation due to the acoustic wave, in our case, \(\nabla (n_{k}/n_{tot}) \neq \nabla (n_{k})/n_{tot}\). This is illustrated in Fig. 1.

This is an important point because \(n_{k}/n_{tot}\) does not depend on the position (except near the walls), as the compression/dilatation due to the acoustic wave affects all the particles of the system in the same way at any position. The diffusion force is therefore analytically zero.

Moreover, in the formalism of Yeager and Durand-Vidal,\textsuperscript{21–23} \(\delta F_{k}^{\text{diff}} \neq 0\) and \(\alpha_{k} \neq 0\) so that the diffusion force modifies the electric field under a pressure gradient, but not the mass flux under the electric field. Under these conditions, the inclusion of this diffusion force is not consistent with the Onsager reciprocal relation.

Finally, another diffusive motion could arise from concentration inhomogeneities due to the particles’ accumulation and depletion in certain regions in space, at the length scale of the acoustic wave. Nevertheless, this diffusive motion is negligible: considering the characteristic length \(\lambda^{-1}\) of the acoustic wave, of the order of 1 mm, the homogenization of the concentration, due to the acoustic wave, would take a time estimated to be \(\tau \approx 1/(D\lambda^{2}) \approx 1/(2.0 \times 10^{-4}(10^{3})^{2}) = 500\) s, where \(D\) is the typical acoustic wave frequency 1 MHz, this time is million times larger than the wave’s characteristic time.

By neglecting diffusion, it follows that it is not necessary to introduce a “noise” term (as is done in Langevin-type

FIG. 1. Schematic view of two species (solvent and solute, i.e., black balls and white balls) of particle number concentrations \(n_{1}\) and \(n_{2}\) \((n_{tot} = n_{1} + n_{2})\) in two regions of space. Even if \(n_{k}/n_{tot}\) is the same in the two regions, both \(n_{k}\) and \(n_{tot}\) are different.
equations) in equations like Eqs. (43) and (53). Usually, in continuous solvent models, the noise term in the Langevin equation is included to account for mass diffusion, since diffusion results of the coupling between concentration gradient and random displacement induced by the noise term. Since we do not consider diffusion in our system, we chose the simpler Newton equation instead of the Langevin equation to describe our system, both equations yielding the same mesoscopic fluxes.

IV. CONCLUSION

In this article, we have proved that the most known theories of sedimentation and electroacoustic for ideal electrolyte solutions, developed using a set of electrokinetic equations that includes the Newtonian equation for the motion of solutes, satisfy the Onsager reciprocal relations. The Onsager relations are derived in the framework of irreversible thermodynamics, for mesoscopic (macroscopic) variables such as the average electric field and average electric current in the solution and the total mass/volume fluxes of the different components of the system. From the Onsager relations, and thanks to a smart choice of the reference frame, the link between the sedimentation current and the ionic vibration current has been established in the limit of low frequency.

We have shown that the diffusion force arising from the concentration gradient due to the compression of the solution by the acoustic wave is, at best, negligible and should therefore not be taken into account in the Newtonian set of forces. Moreover, the authors including a diffusion force in their set of forces have used expressions that are not consistent with reciprocal relations of Onsager. This could easily be demonstrated, as the expressions for their dissipative force are not compatible with the general relation we have derived and given in Eq. (76).

Several theories for the IVP of non-ideal electrolytes have been proposed over the years, based on different sets of corrective forces. In a forthcoming paper (Paper II), we review briefly these theories and discuss their validity in terms of Onsager’s reciprocal relation. We will also propose a new general expression of corrective forces for binary salts.

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