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Some rigorous relations for partial conductivities in ionic liquids

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Starting with the rigorous expressions, derived previously for the generalized transport coefficients of a multi-component fluid, we obtained several exact relations for partial conductivities of ionic charge-asymmetric mixtures. For a simpler case of a charge-symmetric binary mixture such kind of relations was discovered experimentally by Sundheim more than 50 years ago and is known as the “universal golden rule”. Some more complicate models, describing in particular the cases of ternary and multi-component mixtures, are considered. The general relation for partial ionic conductivities is derived for a multi-component ionic fluid. It is shown that such relations can be considered in fact as an example of a more general class of rigorous expressions valid for (k,ω)-dependent quantities.

Key words: *Ionic liquids, transport coefficients, mutual diffusion coefficient, ionic conductivity, molten salt*

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Introduction

About 50 years ago a phenomenological “universal golden rule” for the ratio of partial conductivities of ions in molten salts was proposed by Sundheim [1] from the analysis of experimental data. This rule is expressed in a very simple form

$$\frac{\sigma_+}{\sigma_-} = \frac{m_-}{m_+}\,. \tag{1}$$

Recently, there were made several theoretical attempts [2] to derive this relation using the equations of motion, the Langevin equation as well as molecular dynamics studies for the model of binary charge symmetrical molten salts. A few years later using similar approaches such relation was also obtained for pseudo-binary molten salt KCl–NaCl [3].

Our goal is to consider this problem in a more general framework. We start with the rigorous relations derived by us previously for generalized transport coefficients of a multi-component fluid [4, 5]. We obtain the “universal golden rule” for (k,ω)-dependent partial conductivities of an ionic charge-asymmetric binary mixture as well as the relations for the partial ionic conductivities in some cases of ternary and four-component ionic liquids.

1. Theoretical framework

Let us start with some introductory remarks and consider the general framework that can be used for the description of both kinds of multi-component mixtures, in particular mixtures of neutral particles as well as mixtures containing charged particles. In general case we deal with a ν-component fluid in the volume V, containing N_α particles in the αth species ($\alpha = 1, 2, \ldots, \nu$). To derive hydrodynamic equations one has to define the microscopic basic set of the slowest (hydrodynamic) variables [5], which for a multi-component mixture may be introduced as follows

$\hat{P}^{\rm hyd}_{\mathbf{k}} = \{\hat{\mathcal{N}}_{\mathbf{k}}, \hat{\mathbf{J}}_{\mathbf{k}}, \hat{E}_{\mathbf{k}}\}$, where $\hat{\mathcal{N}}_{\mathbf{k}} = \{\hat{N}_{\mathbf{k},\alpha}\}$ is a column-vector with the components

$$\hat{N}_{\mathbf{k},\alpha} = \sum_{i=1}^{N_\alpha} \exp\{\mathrm{i}\mathbf{k}\mathbf{R}_i^\alpha\}, \tag{2}$$

being the number density of particles in the α-th species; $\hat{\mathbf{J}}_{\mathbf{k}}$ is the density of the *total* current,

$$\hat{\mathbf{J}}_{\mathbf{k}} = \sum_\alpha \hat{\mathbf{J}}_{\mathbf{k},\alpha}\,, \qquad \hat{\mathbf{J}}_{\mathbf{k},\alpha} = \sum_{i=1}^{N_\alpha} \mathbf{p}_i^\alpha \exp\{\mathrm{i}\mathbf{k}\mathbf{R}_i^\alpha\}, \tag{3}$$

with $\hat{\mathbf{J}}_{\mathbf{k},\alpha}$ being the current densities of particles in the α-th species, and

$$\hat{E}_{\mathbf{k}} = \sum_\alpha \hat{E}_{\mathbf{k},\alpha} = \sum_\alpha \sum_{i=1}^{N_\alpha} e_i^\alpha \exp\{\mathrm{i}\mathbf{k}\mathbf{R}_i^\alpha\} \tag{4}$$

is the *total* energy density, where the one-particle energy e_j^α can be expressed via the sum of kinetic energy and potential energy of pair interactions:

$$e_j^\alpha = \frac{[\mathbf{p}_j^\alpha]^2}{2m_\alpha} + \sum_{l\neq j,\beta} V_{jl}^{\beta\alpha}.$$

The set of dynamic variables $\hat{P}^{\rm hyd}_{\mathbf{k}} = \{\hat{\mathcal{N}}_{\mathbf{k}}, \hat{\mathbf{J}}_{\mathbf{k}}, \hat{E}_{\mathbf{k}}\}$ includes the densities of all the additive integrals of motion for a mixture. In the case of longitudinal dynamics, as it follows from the symmetrical properties, the scalar densities $\hat{n}_{\mathbf{k},\alpha}$ and $\hat{E}_{\mathbf{k}}$ interact only with the longitudinal component of $\hat{\mathbf{J}}_{\mathbf{k}}$, namely $\hat{J}^{\rm L}_{\mathbf{k}}$, that is the projection of $\hat{\mathbf{J}}_{\mathbf{k}}$ onto the direction of wave-vector $\mathbf{k}$. Hence, the total number of longitudinal hydrodynamic variables for ν-component mixture is equal to $\nu+2$, namely $\hat{P}^{\rm L}_{\mathbf{k}} = \{\hat{P}^\iota_{\mathbf{k}}\}$ with $\iota = 1, 2, \ldots, \nu+2$.

In practical applications it may be more convenient [4, 5] to use the set of orthogonalized dynamic variables possessing the following properties $(\hat{P}^\iota_{\mathbf{k}}, \hat{P}^\kappa_{-\mathbf{k}}) = \delta_{\iota\kappa}\ (\hat{P}^\iota_{\mathbf{k}}, \hat{P}^\kappa_{-\mathbf{k}})$. Such an orthogonalized set of longitudinal hydrodynamical variables can be defined as follows

$$\hat{P}^{\rm L}_{\mathbf{k}} = \{\hat{\mathcal{N}}_{\mathbf{k}}, \hat{J}^{\rm L}_{\mathbf{k}}, \hat{H}_{\mathbf{k}}\} \tag{5}$$

where

$$\hat{H}_{\mathbf{k}} = \hat{E}_{\mathbf{k}} - (\hat{E}_{\mathbf{k}}, \hat{\mathcal{N}}^+_{\mathbf{k}})(\hat{\mathcal{N}}_{\mathbf{k}}, \hat{\mathcal{N}}^+_{\mathbf{k}})^{-1}\hat{\mathcal{N}}_{\mathbf{k}} = (1 - \mathcal{P}_{\mathcal{N}})\hat{E}_{\mathbf{k}}$$

is the so-called enthalpy density, the Mori-like projection operator denotes as

$$\mathcal{P}_{\mathcal{N}} \ldots = (\ldots, \mathcal{N}^+_{\mathbf{k}})(\hat{\mathcal{N}}_{\mathbf{k}}, \hat{\mathcal{N}}^+_{\mathbf{k}})^{-1}\hat{\mathcal{N}} = \sum_{\alpha\gamma} (\ldots, \hat{N}_{-\mathbf{k},\alpha})\ (\hat{\mathcal{N}}_{\mathbf{k}}, \hat{\mathcal{N}}^+_{\mathbf{k}})^{-1}_{\alpha\gamma}\ \hat{N}_{\mathbf{k},\gamma}\,, \tag{6}$$

and the notation $(\ldots, \ldots)$ is used for the definition of an equilibrium correlation function

$$(A, B) = \langle (A - \langle A\rangle)(B - \langle B\rangle)\rangle$$

with $\langle\ldots\rangle$ denoting the equilibrium averaging.

The generalized hydrodynamic fluxes $I^d_{\mathbf{k},\iota}$ can be defined in the standard way:

$$\mathrm{i}kI^d_{\mathbf{k},\iota} = (1 - \mathcal{P}_{\rm H})\mathrm{i}L_N \hat{P}^\iota_{\mathbf{k}}\,, \tag{7}$$

where $\mathcal{P}_{\rm H}$ is the Mori-like projection operator, constructed on the set of all hydrodynamic variables (5), and $\mathrm{i}L_N$ is the Liouville operator. Thus, for the number density flux one can easily obtain

$$\mathrm{i}kI^d_{\mathbf{k},\alpha} = \frac{\mathrm{i}k}{m_\alpha}\left(\hat{J}^{\rm L}_{\mathbf{k},\alpha} - \frac{m_\alpha c_\alpha}{\bar{m}}\hat{J}^{\rm L}_{\mathbf{k}}\right), \tag{8}$$

where m_α is the particle mass in the α-th species, $c_\alpha = N_\alpha/N = n_\alpha/n$ denotes concentrations, and $\bar{m} = \sum_\alpha c_\alpha m_\alpha$ is the mean mass per particle.

The generalized (k,z)-dependent transport coefficients are defined via the generalized fluxes $I^d_{\mathbf{k},\iota}$ as follows [4, 5]

$$L_{\iota\kappa}(k,z) = \frac{\beta}{V}\int\limits_0^\infty \mathrm{d}t \exp\{-zt\}\left(I^d_{\mathbf{k},\iota}, \exp\{-(1-\mathcal{P}_\mathrm{H})\mathrm{i}L_N t\} I^d_{-k,\kappa}\right). \tag{9}$$

Note that the expression (9) has the structure of the well-known Green-Kubo formulas [6], but the evolution operator is more complicated and additionally involves the projection operator $\mathcal{P}_\mathrm{H}$. However, in the hydrodynamic limit $(k,z) \to 0$ one gets the expression

$$L_{\iota\kappa} = \lim_{k,z\to 0} L_{\iota\kappa}(k,z) = \frac{\beta}{V}\int\limits_0^\infty \mathrm{d}t\left(I^d_\iota, \exp\{-\mathrm{i}L_N t\} I^d_\kappa\right), \tag{10}$$

that is commonplace in numerous textbooks (e.g. [7]) and has been routinely employed in computer simulations.

In the context of this paper we are mainly interested in the behavior of the generalized mutual diffusion coefficients $D_{\alpha\gamma}(k,z)$ that are simply related to the corresponding transport coefficients $L^{\alpha\gamma}(k,z)$. Namely, one has

$$L^{\alpha\gamma}(k,z) = nc_\alpha c_\gamma D_{\alpha\gamma}(k,z)/k_\mathrm{B}T, \tag{11}$$

where $n = N/V$. The explicit frequency dependence in (9) can be found by taking into account that $z = \mathrm{i}\omega + \varepsilon$ and $\varepsilon \to +0$.

In general for a ν-component mixture the matrix of mutual diffusion coefficients $\mathbf{D}(k,\omega) = \|D_{\alpha\gamma}(k,\omega)\|$ has $\nu \times \nu$ elements. Due to the symmetry properties $D_{\alpha\gamma}(k,\omega) = D_{\gamma\alpha}(k,\omega)$ this number is reduced to the $\nu(\nu+1)/2$ independent elements. However, there are still additional ν explicit relations that follow from the total momentum conversation law. Namely, taking into account that

$$\sum_{\alpha=1}^{\nu} m_\alpha I^d_{\mathbf{k},\alpha} = \sum_{\alpha=1}^{\nu}\left(\hat{J}^\mathrm{L}_{\mathbf{k},\alpha} - \frac{m_\alpha c_\alpha}{\bar{m}}\hat{J}^\mathrm{L}_{\mathbf{k}}\right) \equiv 0 \tag{12}$$

and using the definition (9), the set of new useful relations for generalized transport coefficients, that involve the processes caused by number densities fluctuations, can be easily derived. In particular, one gets

$$\sum_{\alpha=1}^{\nu} m_\alpha c_\alpha D_{\alpha\gamma}(k,\omega) = \sum_{\gamma=1}^{\nu} D_{\alpha\gamma}(k,\omega) c_\gamma m_\gamma \equiv 0. \tag{13}$$

Hence, taking into account the relations (13) one can conclude that the total number of independent matrix elements in the matrix $\mathbf{D}(k,\omega) = \|D_{\alpha\gamma}(k,\omega)\|$ is equal to $\nu(\nu-1)/2$. In a particular case of binary mixture ($\nu = 2$) we have $\nu(\nu-1)/2 = 1$ and

$$\frac{D_{11}(k,\omega)}{D_{12}(k,\omega)} = -\frac{m_2}{m_1}\frac{c_2}{c_1}, \qquad \frac{D_{11}(k,\omega)}{D_{22}(k,\omega)} = \frac{m_2^2}{m_1^2}\frac{c_2^2}{c_1^2}. \tag{14}$$

These relations directly follow from the identity (13). Being valid for an arbitrary binary mixture, they are of rather general character.

2. Binary mixture of charged particles

Let us now consider the case of a binary mixture composed of oppositely charged particles with charges q_+ and q_-, masses m_+ and m_-, and densities n_+, n_-. The total electroneutrality condition is satisfied, so that $q_+n_+ + q_-n_- = 0$.

The electrical conductivity can be calculated by means of the Green-Kubo formula [8, 9]

$$\sigma = \frac{\beta}{V}\int\limits_0^\infty \mathrm{d}t \langle \mathbf{I}^q(t)\mathbf{I}^q(0)\rangle, \tag{15}$$

where $\mathbf{I}^q(t) = \sum\limits_\alpha \mathbf{I}^q_\alpha(t)$ with

$$\mathbf{I}^q_\alpha(t) = q_\alpha n_\alpha \sum_{i=1}^{N_\alpha} \mathbf{v}_i^\alpha$$

being the partial ionic electrical current ($\alpha = +,-$). Ionic conductivity is also connected with the mutual diffusion coefficients [9]:

$$\sigma = \frac{n}{k_\mathrm{B}T}\sum_{\alpha,\beta} q_\alpha q_\beta c_\alpha c_\beta D_{\alpha\beta}\,, \tag{16}$$

where mutual diffusion coefficients are defined as follows

$$D_{\alpha\beta} = \frac{N}{N_\alpha N_\beta}\sum_{i,j=1}^{N_\alpha,N_\beta}\int\limits_0^\infty \mathrm{d}t\left\langle \mathbf{v}_i^\alpha(t)\mathbf{v}_j^\beta(0)\right\rangle$$

with $\alpha,\beta = +,-$. In the center of mass reference frame the expression (16) can be easily derived from (15) with the help of equations (8), (9) and (11). For generalized (k,ω)-dependent ionic conductivity one can use the definition

$$\sigma(k,\omega) = \frac{n}{k_\mathrm{B}T}\sum_{\alpha,\beta} q_\alpha q_\beta c_\alpha c_\beta D_{\alpha\beta}(k,\omega). \tag{17}$$

It is seen from (17) that the total ionic conductivity can be presented as the sum of partial ionic conductivity $\sigma = \sigma_+ + \sigma_-$, where $\sigma_\alpha \sim q_\alpha c_\alpha \sum_\beta q_\beta c_\beta D_{\alpha\beta}$, so that for the ratio of partial ionic conductivity one gets

$$\frac{\sigma_+}{\sigma_-} = \frac{q_+^2 c_+^2 D_{++} + q_+c_+q_-c_-D_{+-}}{q_-^2 c_-^2 D_{--} + q_+c_+q_-c_-D_{+-}}\,. \tag{18}$$

This expression can be significantly simplified if we use the relations that follow from (14), namely: $D_{++}/D_{--} = (m_-^2/m_+^2)(c_-^2/c_+^2)$, $D_{++}/D_{+-} = -(m_-/m_+)(c_-/c_+)$, $D_{--}/D_{-+} = -(m_+/m_-)(c_+/c_-)$, $D_{+-} = D_{-+}$. Taking into account the electroneutrality condition $q_+c_+ + q_-c_- = 0$, one gets

$$\frac{\sigma_+(k,\omega)}{\sigma_-(k,\omega)} = -\frac{q_+}{q_-}\frac{m_-}{m_+}\,. \tag{19}$$

In the case of charge-symmetric systems with $q_- = -q_+$ (in particular, for molten salts NaCl, KCl, NaF, KF, RbBr) we obtain

$$\frac{\sigma_+(k,\omega)}{\sigma_-(k,\omega)} = \frac{m_-}{m_+}\,. \tag{20}$$

In fact, the expression (20) represents the generalized version of the so-called "universal golden rule" (1) valid for binary charge-symmetric ionic liquids with arbitrary values (k,ω). In a more general form (19) such a relation is derived for a charge-asymmetric binary mixture by means of the rigorous expressions (13) obtained for the generalized mutual diffusion coefficients of a multi-component fluid.

3. Ternary mixtures

3.1. Charged particles in solvent

Let us consider a more complicated model of a ternary mixture that is composed of oppositely charged particles in neutral solvent with the particle charges q_+ and q_-, the particle masses m_+, m_-, and m_0, and concentrations c_+, c_-, c_0 ($c_+ + c_- + c_0 = 1$). The total electro-neutrality condition can be written in the form: $q_+c_+ + q_-c_- = 0$.

From the relations (13) one obtains the equations

$$\begin{aligned} m_+c_+D_{++}(k,\omega) + m_-c_-D_{-+}(k,\omega) + m_0c_0D_{0+}(k,\omega) &\equiv 0, \\ m_+c_+D_{+-}(k,\omega) + m_-c_-D_{--}(k,\omega) + m_0c_0D_{0-}(k,\omega) &\equiv 0, \\ m_+c_+D_{+0}(k,\omega) + m_-c_-D_{-0}(k,\omega) + m_0c_0D_{00}(k,\omega) &\equiv 0, \end{aligned} \tag{21}$$

where $D_{\alpha\beta} = D_{\beta\alpha}$. The electroneutrality condition enables us to express the concentrations of charged particles via c_0, namely: $c_+ = (1-c_0)q_-/(q_- - q_+)$, $c_- = (1-c_0)q_+/(q_+ - q_-)$. It is obvious that

$$\begin{aligned} q_+^2c_+^2 &= q_-^2c_-^2 = (1-c_0)^2\frac{q_+^2q_-^2}{(q_+ - q_-)^2} \equiv Q^2, \\ q_+c_+q_-c_- &= -(1-c_0)^2\frac{q_+^2q_-^2}{(q_+ - q_-)^2} \equiv -Q^2. \end{aligned}$$

Therefore, one gets $\sigma_+ = Q^2(D_{++} - D_{+-})$ and $\sigma_- = Q^2(D_{--} - D_{+-})$, so that the expression (18) for the ratio of partial ionic conductivities can be rewritten in the form

$$\frac{\sigma_+(k,\omega)}{\sigma_-(k,\omega)} = \frac{D_{++}(k,\omega) - D_{+-}(k,\omega)}{D_{--}(k,\omega) - D_{+-}(k,\omega)}\,. \tag{22}$$

Combining the first two equations in (21), one can obtain:

$$m_+c_+(D_{++} - D_{+-}) - m_-c_-(D_{--} - D_{+-}) + m_0c_0(D_{0+} - D_{0-}) \equiv 0 \tag{23}$$

or

$$m_+c_+\sigma_+ - m_-c_-\sigma_- + m_0c_0\Delta = 0, \tag{24}$$

where the quantity $\Delta \equiv Q^2(D_{0+} - D_{0-})$ is expressed in terms of the mutual diffusion coefficients for ions in solvent. The relation (24) could be considered as the generalization of “universal golden rule” for solutions of electrolytes. Note that in the limit $c_0 \to 0$ the expression (22) can be easily recovered from (22).

3.2. Pseudo-binary molten salts

A special class of ternary ionic liquids is formed by the so-called pseudo-binary molten salts, for instance $\mathrm{KCl-NaCl}$. In this case we deal with a ternary mixture of ions. In particular, for $\mathrm{KCl-NaCl}$ in the system with the elementary charge $e = 1$ the ionic charges are $q_{\mathrm{Na}} = q_{\mathrm{K}} = 1$ and $q_{\mathrm{Cl}} = -1$ with the electro-neutrality condition $c_{\mathrm{Na}} + c_{\mathrm{K}} = c_{\mathrm{Cl}}$, where $c_{\mathrm{Na}} + c_{\mathrm{K}} + c_{\mathrm{Cl}} = 1$.

For the mutual diffusion coefficients from (13) one has:

$$\begin{aligned} m_1c_1D_{11}(k,\omega) + m_2c_2D_{21}(k,\omega) + m_3c_3D_{31}(k,\omega) &\equiv 0, \\ m_1c_1D_{12}(k,\omega) + m_2c_2D_{22}(k,\omega) + m_3c_3D_{32}(k,\omega) &\equiv 0, \\ m_1c_1D_{13}(k,\omega) + m_2c_2D_{23}(k,\omega) + m_3c_3D_{33}(k,\omega) &\equiv 0, \end{aligned} \tag{25}$$

where $\{\mathrm{K},\mathrm{Na},\mathrm{Cl}\} \leftrightarrow \{1,2,3\}$.

Using the definition for partial ionic conductivities $\sigma_\alpha(k,\omega)$,

$$\sigma_\alpha(k,\omega) = q_\alpha c_\alpha \sum_\beta q_\beta c_\beta D_{\alpha\beta}(k,\omega), \tag{26}$$

we obtain the expressions:

$$\begin{aligned}\sigma_{\rm K}(k,\omega) &\equiv \sigma_1(k,\omega) = c_1\;[c_1D_{11}(k,\omega)+c_2D_{12}(k,\omega)-c_3D_{13}(k,\omega)],\\ \sigma_{\rm Na}(k,\omega) &\equiv \sigma_2(k,\omega) = c_2\;[c_1D_{21}(k,\omega)+c_2D_{22}(k,\omega)-c_3D_{23}(k,\omega)],\\ \sigma_{\rm Cl}(k,\omega) &\equiv \sigma_3(k,\omega) = -c_3\;[c_1D_{31}(k,\omega)+c_2D_{32}(k,\omega)-c_3D_{33}(k,\omega)].\end{aligned} \tag{27}$$

If we multiply each equation in (27) by m_1, m_2 and (-m_3), respectively, add them and use the identities (25), it is easy to obtain the following relation

$$m_1\sigma_1(k,\omega)+m_2\sigma_2(k,\omega)=m_3\sigma_3(k,\omega), \tag{28}$$

or

$$m_{\rm K}\sigma_{\rm K}(k,\omega)+m_{\rm Na}\sigma_{\rm Na}(k,\omega)=m_{\rm Cl}\sigma_{\rm Cl}(k,\omega). \tag{29}$$

In the hydrodynamic limit when $(k,\omega)\to 0$ this result was obtained in [3] by means of the Langevin equation and confirmed directly by molecular dynamics simulations. We note that relation (29)is valid for arbitrary (k,ω).

Using (28) one can write

$$m_{\rm A}\sigma_{\rm A}(k,\omega)+m_{\rm B}\sigma_{\rm B}(k,\omega)=m_{\rm I}\sigma_{\rm I}(k,\omega), \tag{30}$$

for a pseudo-binary electrolyte $\rm AI-BI$ with ion charges $q_{\rm A}=q_{\rm B}=-q_{\rm I}$.

4. Multi-component mixture of charged particles

Let us now consider the model of a multi-component fluid composed of N_α ions with charges q_α in the αth species ($\alpha=1,2,\ldots,\nu$). Mutual diffusion coefficients $D_{\alpha\beta}(k,\omega)$ of the system should satisfy the relations (13). For partial ionic conductivities one has the definition (26), so that if we multiply $\sigma_\alpha(k,\omega)$ by m_α/q_α one can write

$$\sum_\alpha\frac{m_\alpha}{q_\alpha}\;\sigma_\alpha(k,\omega)=\sum_\alpha m_\alpha c_\alpha\left[\sum_\beta q_\beta c_\beta D_{\alpha\beta}(k,\omega)\right]=\sum_\beta q_\beta c_\beta\left[\sum_\alpha m_\alpha c_\alpha D_{\alpha\beta}(k,\omega)\right]. \tag{31}$$

Taking into account (13) we finally obtain

$$\sum_\alpha\frac{m_\alpha}{q_\alpha}\;\sigma_\alpha(k,\omega)\equiv 0. \tag{32}$$

This is a rather general result that includes, as a particular case, the relation (30), derived above. For example, using (32) it is easy to obtain the relation for partial ionic conductivities for pseudo-binary four-component mixture $\rm A_nI_l-B_kY_j$ with different charges of ions.

A more complicated case corresponds to the model of a $(\nu+\bar\nu)$-component fluid that is composed of N_α ions with charges q_α ($\alpha=1,2,\ldots,\nu$) and $N_{\bar\alpha}$ neutral particles belonging to the $\bar\alpha$th species ($\bar\alpha=1,2,\ldots,\bar\nu$). In this case the equation (31) should be rewritten in the form

$$\sum_{\alpha=1}^{\nu}\frac{m_\alpha}{q_\alpha}\;\sigma_\alpha(k,\omega)=\sum_{\beta=1}^{\nu}q_\beta c_\beta\left[\sum_{\alpha=1}^{\nu}m_\alpha c_\alpha D_{\alpha\beta}(k,\omega)\right]=-\sum_{\beta=1}^{\nu}q_\beta c_\beta\left[\sum_{\bar\alpha=1}^{\bar\nu}m_{\bar\alpha}c_{\bar\alpha}D_{\bar\alpha\beta}(k,\omega)\right], \tag{33}$$

where the relations (13) have been used. Note that the index $\bar\alpha$ denotes the neutral particles. Therefore, on the right hand side of (33) the effects of mutual diffusion of all the ions in solvent are included. It is obvious that in particular case of a ternary mixture of charged particles in neutral solvent, the expression (24) can be easily recovered from (33).

The expression (33) can be further simplified if we introduce two new densities, namely the mass density of solvent $\hat{M}_{\mathbf{k}}$ (formed by neutral particles only) and the charge density $\hat{Q}_{\mathbf{k}}$:

$$\hat{M}_{\mathbf{k}} = \sum_{\bar{\alpha}=1}^{\bar{\nu}} m_{\bar{\alpha}} c_{\bar{\alpha}} \hat{N}_{\mathbf{k},\bar{\alpha}}\,, \qquad \hat{Q}_{\mathbf{k}} = \sum_{\alpha=1}^{\nu} q_{\alpha} c_{\alpha} \hat{N}_{\mathbf{k},\alpha}\,. \tag{34}$$

Now we can rewrite (34) in the form

$$\sum_{\alpha=1}^{\nu} \frac{m_{\alpha}}{q_{\alpha}}\, \sigma_{\alpha}(k,\omega) = -D_{\mathrm{MQ}}(k,\omega), \tag{35}$$

where the generalized transport coefficient

$$D_{\mathrm{MQ}}(k,\omega) = \sum_{\bar{\alpha}=1}^{\bar{\nu}} \sum_{\beta=1}^{\nu}\, m_{\bar{\alpha}} c_{\bar{\alpha}}\; D_{\bar{\alpha}\beta}(k,\omega)\; q_{\beta} c_{\beta}$$

describes the diffusive ion-solvent cross-correlations. The relation (35) yields, in fact, the most general form of identity valid for partial ionic conductivities of classical systems of charged particles at arbitrary (k,ω).

5. Conclusions

It is shown that the general relations, that link partial ionic conductivities in a binary mixture of charged particles, three- and four-component pseudo-binary molten salts as well as in multi-component classical fluids of charged particles, can be derived by means of rigorous expressions, obtained previously for the mutual diffusion coefficients of multi-component liquids. Some of these relations generalize the results known in the literature (see, for instance, [2]), but most of them are new. Moreover, all of these relations are valid for (k,ω)-dependent quantities and this, in particular, explains the results of molecular dynamic simulations of the frequency-dependent partial conductivities carried out [10] for molten NaCl and NaI.

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Деякі строгі співвідношення для парціальних провідностей в іонних рідинах

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Стартуючи з точних співвідношень, що були виведені нами нещодавно для узагальнених коефіцієнтів переносу в багатокомпонентних плинах, ми отримали кілька строгих співвідношень для парціальних провідностей в іонних зарядово-асиметричних сумішах. Для найпростішого випадку зарядово-симетричної бінарної системи таке співвідношення було виявлене експериментально Сундхеймом більш ніж 50 років тому і відоме як “універсальне золоте правило”. Розглянуто також деякі більш складні моделі, що описують, зокрема, випадки потрійних та багатокомпонентних сумішей. Виведено загальне співвідношення для парціальних іонних провідностей багатокомпонентного іонного плину. Показано, що такого типу співвідношення є фактично лише одним з прикладів більш широкого класу виразів, що дійсні для (k,ω)-залежних величин.

Ключові слова: *іонні рідини, коефіцієнти переносу, коефіцієнти взаємної дифузії, іонна провідність, розплави солей*