Quasihydrodynamic theory of ionic conductance in spatially homogeneous solutions of strong electrolytes

Quasihydrodynamic theory of ionic conductance in spatially homogeneous solutions of strong electrolytes†

A R Altenberger

Institute of Physical Chemistry of the Polish Academy of Sciences, 01-224 Warsaw, Poland

Abstract. A generalised formulation of the quasihydrodynamic theory of ionic conductance in an electrolyte solution is presented. Correlation function expressions are derived for the contributions of the frequency-dependent relaxation effect to the conductivity and dielectric permittivity of the electrolyte solution. The evolution equation for the time-dependent irreducible ionic pair correlation function is derived in the mean field approximation by the application of the generating functional method.

1. Introduction

Fundamental physical ideas of the quasihydrodynamic theory of transport processes in spatially homogeneous electrolyte solutions were set forth by Debye and Hückel (1923), Onsager (1926, 1927), Debye and Falkenhagen (1928) and Onsager and Fuoss (1932). These authors proposed a Brownian particle model of an electrolyte solution in which charged, solvated ionic particles are moving in the continuous medium formed by the molecules of the solvent. Their approach was of a mean field type. The internal electric field acting on the ions was calculated from the Poisson equation, and in a more advanced version of the theory (Resibois and Hasselle-Schuermans 1966) a similar mean field approach was also used to describe the effects of interionic hydrodynamic interactions. The theory worked well at very low electrolyte concentrations, but its extension to regions of higher concentration proved to be difficult. This could be caused partially by the primitiveness of the model, and most recent formulations of the theory (Fuoss and Onsager 1962, 1963, 1964, Pitts 1953, Pitts *et al* 1969, 1970, Murphy and Cohen 1970) dealt mainly with the problem of proper inclusion of the excluded volume effects which result from the presence of the short-range repulsion between the ions. More recently also an alternative, 'global' approach to the problem was introduced by Strelzova (1957, 1959, 1962), Falkenhagen and Ebeling (1966) and Ebeling *et al* (1978) in which a multiparticle equation was applied for the description of the ionic diffusion. This later approach allows us in principle to derive the equations of evolution for the reduced position distribution functions of the ionic particles, and thus to analyse conditions under which the older mean field theory was valid. Also, inclusion of other than Coulombic forces became possible. The aim of the present paper is to suggest a new form of the 'global' approach to the problem of ionic conductivity in spatially homogeneous solutions. Applying linear response theory, we are able to derive a most

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general, correlation function type expression for the frequency-dependent ionic conductivity and dielectric permittivity of the electrolyte solution, which can be obtained within the framework of the quasihydrodynamic theory. In the next section the derivation of the correlation function formula for the contribution of the relaxation effect to the ionic conductivity is given. Section 3 is devoted to the problem of derivation of the evolution equations for the irreducible ionic correlation functions, and §4 to the analysis of the mean field approximation. In the last section a general discussion of results is given.

2. Linear response theory and the Smoluchowski equation

Let us consider a dilute multicomponent electrolyte solution consisting of s ionic species. Since the solution is neutral we have

$$\sum_{\alpha=1}^{s} Q^{(\alpha)} c^{(\alpha)} = 0 \tag{2.1}$$

where $Q^{(\alpha)}$ is the ionic charge belonging to the αth ionic component and $c^{(\alpha)}$ is the number concentration of the species. We assume that the solution was in thermal equilibrium prior to the application of the spatially homogeneous electric field $E(t) = \mathrm{Re}\, E^0 \exp(i\omega t)$ in the infinite past. According to the standard hydrodynamic model, the ions are treated as Brownian particles moving in an unbounded continuous medium. The motion of ions under the influence of the external field is correlated due to their mutual interaction. The position distribution function of all ions in the system is determined by the multiparticle Smoluchowski diffusion equation, which in the linear response approximation can be expressed in the following form:

$$\partial_t P(\{\boldsymbol{R}^{(\gamma)}\}, t) = S(\{\boldsymbol{R}^{(\gamma)}\})P + S^{\mathrm{ext}}(\{\boldsymbol{R}^{(\gamma)}\}, t)P^{\mathrm{eq}}(\{\boldsymbol{R}^{(\gamma)}\}). \tag{2.2}$$

$P(\{\boldsymbol{R}^{(\gamma)}\}, t)$ is the time-dependent position distribution function of all the ionic particles, $P^{\mathrm{eq}}(\{\boldsymbol{R}^{(\gamma)}\})$ is the appropriate equilibrium distribution, we denote by $\{R^{\gamma}\}$ a complete set of all the position vectors of the ionic particles and $S(\{\boldsymbol{R}^{(\gamma)}\})$ is the unperturbed part of the Smoluchowski diffusion operator which can be expressed in the form

$$S(\{\boldsymbol{R}^{(\gamma)}\}) = \sum_{\alpha,\beta=1}^{s} \sum_{i=1}^{N^{(\alpha)}} \sum_{j=1}^{N^{(\beta)}} \frac{\partial}{\partial \boldsymbol{R}_i^{(\alpha)}} \cdot \boldsymbol{D}_{ij}^{(\alpha)(\beta)} \cdot \left(\frac{\partial}{\partial \boldsymbol{R}_j^{(\beta)}} - \frac{1}{kT} \boldsymbol{F}_j^{(\beta)} \right). \tag{2.3}$$

Where kT is the Boltzmann factor, $N^{(\alpha)}$ is the number of ionic particles of the αth species, $\boldsymbol{F}_i^{(\alpha)}$ is the force acting on the ith ion belonging to the αth species,

$$\boldsymbol{F}_i^{(\alpha)} = \sum_{\beta=1}^{s} \sum_{j=1}^{N^{(\beta)}} \boldsymbol{\Phi}_{ij}^{(\alpha)(\beta)}(|\boldsymbol{R}_i^{(\alpha)} - \boldsymbol{R}_j^{(\beta)}|), \tag{2.4}$$

and $\boldsymbol{\Phi}_{ij}^{(\alpha)(\beta)}$ is the interionic force which includes both Coulombic and short-range interactions. By $\boldsymbol{D}_{ij}^{(\alpha)(\beta)}$ we denote the diffusion tensor whose form depends on the assumed model of the hydrodynamic interaction between the medium and Brownian particles (see e.g. Felderhof 1977, 1978). If one treats an ion as a point source of the friction force (as we do in the remaining part of this paper), this tensor can be expressed by the well known Kirkwood formula

$$\boldsymbol{D}_{ij}^{(\alpha)(\beta)} = kT[(1/\xi^{(\alpha)})\delta_{\alpha\beta}\delta_{ij}\boldsymbol{I} + \boldsymbol{T}_{ij}^{(\alpha)(\beta)}] \tag{2.5}$$

where $\xi^{(\alpha)}$ is the ionic friction coefficient and $T_{ij}^{(\alpha)(\beta)}$ is the Oseen tensor of the hydrodynamic interaction,

$$T_{ij}^{(\alpha)(\beta)}(r) = \frac{1}{8\pi\eta_0 r}\left(I + \frac{rr}{r^2}\right), \qquad r = R_i^{(\alpha)} - R_j^{(\beta)}. \tag{2.6}$$

η_0 is the solvent viscosity.

The perturbation part of the equation (2.2) can be expressed in the form

$$S^{\text{ext}}(\{R^\gamma\}, t)P^{\text{eq}}(\{R^{(\gamma)}\})$$

$$= -\frac{1}{kT}\sum_{\alpha\beta}\sum_{ij}\frac{\partial}{\partial R_i^{(\alpha)}} \cdot D_{ij}^{(\alpha)(\beta)} \cdot E(t)Q^{(\beta)}P^{\text{eq}}$$

$$= -\left(\frac{1}{kT}\right)^2 \sum_{\alpha\beta}\sum_{ij} Q^{(\beta)}P^{\text{eq}}F_i^{(\alpha)} \cdot D_{ij}^{(\alpha)(\beta)} \cdot E(t). \tag{2.7}$$

The method of derivation of the Smoluchowski diffusion equation and its limitations are well known. In the present paper we restrict ourselves to the theory of electrolytic conductance in a low-frequency external field fulfilling the conditions

$$\omega \ll \xi^{(\alpha)}/m^{(\alpha)} \tag{2.8}$$

and

$$\omega \ll \nu_0 \varkappa^2 \tag{2.9}$$

where $m^{(\alpha)}$ is the mass of an ion belonging to the αth species, ν_0 is the kinematic viscosity of the solvent and $\varkappa^2$ is the inverse of the square of the Debye length,

$$\varkappa^2 = \frac{4\pi}{\epsilon_0 kT}\sum_\alpha Q^{(\alpha)2}c^{(\alpha)}. \tag{2.10}$$

where ϵ_0 is the dielectric permittivity of the solvent.

Condition (2.8) ensures that the inertial effects of the ionic motion can be neglected, and (2.9) allows us to neglect inertial effects related to the hydrodynamic interaction between the ionic particles. Since here we also neglect the dielectric dispersion of the solvent, the external field frequency should be kept in the region in which this effect does not contribute. Usually, for a dilute aqueous solution containing small inorganic ions, $\xi^{(\alpha)}/m^{(\alpha)}$ is of order 10^{13} Hz and $\nu_0\varkappa^2$ is of order 10^{11} Hz. The dielectric dispersion of the solvent appears at about 10^{11} Hz. Since most of the conductivity measurements are performed in the range 10^2–10^4 Hz, conditions (2.8) and (2.9) are very well satisfied and the dielectric dispersion of the solvent can also be neglected. It should also be mentioned here that, following a standard approach to the theory of ionic conduction (see e.g. Falkenhagen 1971), we have neglected all 'electrode effects', such as concentration polarisation of electrodes, double layer formation and specific adsorption, which would lead in principle to the appearance of spatial inhomogeneities in the ionic distribution in the immediate neighbourhood of the electrodes.

The scalar electric current density is defined by the relation

$$i(t) = \frac{1}{V}\int \mathrm{d}\{R^{(\gamma)}\}\sum_{\alpha,i} Q^{(\alpha)} j_i^{(\alpha)}(\{R^{(\gamma)}\}, t) \cdot \hat{E} \tag{2.11}$$

where E is the versor of the external field ($\hat{\boldsymbol{E}} = \boldsymbol{E}^0/E^0$), $\boldsymbol{j}_i^{(\alpha)}$ is the particle current given by

$$\boldsymbol{j}_i^{(\alpha)}(\{\boldsymbol{R}^{(\gamma)}\}, t) = -\sum_{\beta,j} \boldsymbol{D}_{ij}^{(\alpha)(\beta)} \cdot \left(\frac{\partial}{\partial \boldsymbol{R}_j^{(\beta)}} - \frac{1}{kT} \boldsymbol{F}_j^{(\beta)}\right) P(\{\boldsymbol{R}^{(\gamma)}\}, t)$$

$$+ \frac{1}{kT} \sum_{\beta,j} \boldsymbol{D}_{ij}^{(\alpha)(\beta)} \cdot \boldsymbol{E}(t) Q^{(\beta)} P^{\text{eq}} \tag{2.12}$$

and $\int \mathrm{d}\{\boldsymbol{R}^{(\gamma)}\} \ldots$ means integration over all position variables. V is the volume of the system.

The generalised Ohm law for our problem can be expressed in the form (see e.g. Silin and Rukhathe 1961, Ebeling 1964, Falkenhagen 1971)

$$i(t) = \int_{-\infty}^{t} \mathrm{d}t' \, \sigma(t - t') E(t') \tag{2.13}$$

where $\sigma(t)$ is the scalar conductivity and $E(t)$ is the time-dependent magnitude of the external field acting on ions immersed in the solvent. Using the formal solution of equation (2), we obtain

$$\sigma(t) = (\sigma^{\text{id}} + \sigma^{\text{el}})\delta(t) + \sigma^{\text{rel}}(t) \tag{2.14}$$

where

$$\sigma^{\text{id}} = \sum_{\alpha} \frac{Q^{(\alpha)2}}{\xi^{(\alpha)}} c^{(\alpha)} \tag{2.15}$$

is the conductivity of non-interacting ions,

$$\sigma^{\text{ef}} = \sum_{\alpha,\beta} Q^{(\alpha)} c^{(\alpha)} Q^{(\beta)} c^{(\beta)} \int \mathrm{d}\boldsymbol{R} \, \hat{\boldsymbol{E}} \cdot \boldsymbol{T}(\boldsymbol{R}) \cdot \hat{\boldsymbol{E}} (g_{\text{eq}}^{(\alpha)(\beta)}(R) - 1) \tag{2.16}$$

is the electrophoretic correction and

$$\sigma^{\text{rel}}(t) = \frac{-1}{kT} \frac{1}{V} \int \mathrm{d}\{R^{(\gamma)}\} I(0) \, \mathrm{e}^{tS} I(0) P^{\text{eq}}(\{\boldsymbol{R}^{(\gamma)}\})$$

$$= \frac{(-1)}{kT} \frac{1}{V} \int \mathrm{d}\{\boldsymbol{R}^{(\gamma)}\} P^{\text{eq}}(\{\boldsymbol{R}^{(\gamma)}\}) I(0) \, \mathrm{e}^{tS^*} I(0), \tag{2.17}$$

where

$$I(0) = I_2(0) + I_3(0), \tag{2.18}$$

$$I_2(0) = \frac{1}{2} \sum_{\alpha,\beta} \sum_{ij} \left(\frac{Q^{(\alpha)}}{\xi^{(\alpha)}} - \frac{Q^{(\beta)}}{\xi^{(\beta)}}\right) \hat{\boldsymbol{E}} \cdot \boldsymbol{\Phi}_{ij}^{(\alpha)(\beta)}$$

$$- \frac{1}{2} \sum_{\alpha,\beta} \sum_{ij} (Q^{(\alpha)} - Q^{(\beta)}) \hat{\boldsymbol{E}} \cdot \boldsymbol{T}_{ij}^{(\alpha)(\beta)} \cdot \boldsymbol{\Phi}_{ij}^{(\alpha)(\beta)}, \tag{2.19}$$

$$I_3(0) = \sum_{\alpha,\beta,\gamma} \sum_{i,j,k} (1 - \delta_{\alpha\gamma}\delta_{ik}) Q^{(\alpha)} \hat{\boldsymbol{E}} \cdot \boldsymbol{T}_{ij}^{(\alpha)(\beta)} \cdot \boldsymbol{\Phi}_{jk}^{(\beta)(\gamma)}, \tag{2.20}$$

is the contribution of the relaxation effect to the conductivity.

It should be noted here that our definition of the relaxation effect contribution differs from that which is used by Ebeling *et al* (1978). These authors tend to classify all

terms involving the hydrodynamic interaction tensor as an electrophoretic contribution. In our opinion, the relaxation effect manifests as a time-dependent perturbation of the interionic irreducible correlation functions, which can be more visually interpreted as a time-dependent distortion of the ionic atmosphere around a given ion. It is not important which type of interaction (direct or direct and hydrodynamic) contributed to this effect. Ebeling and collaborators studied only the response to a static external field, and did not use the correlation function formalism in which the difference between the time-dependent and static contributions to the conductivity is more clearly pronounced.

By $g_{eq}^{(\alpha)(\beta)}(R)$ we denote in the expression (2.16) the equilibrium interionic pair distribution function, and by the operator S^* in (2.17) the adjoint to the Smoluchowski operator (2.3) which is defined by

$$S^* \ldots = (P^{eq})^{-1} S P^{eq} \ldots . \tag{2.21}$$

Equations (2.13) and (2.14), which describe the generalised Ohm law for our system, mean that in the frequency range considered in this paper the response of the electric current to the external field is not immediate. The presence of the finite relaxation time of the ionic atmosphere leads to the appearance of the 'delay' effect. This effect can be observed in the form of the frequency dispersion of the conductivity which appears at the external field frequencies of order $\omega \propto \varkappa^2 \bar{D}$. The coefficient $\bar{D}$ is the relative diffusion coefficient, and $\varkappa^2 \bar{D}$ is roughly equal to the inverse of the relaxation time of the ionic atmosphere. It is also possible to introduce an effective, time-dependent dielectric permittivity of the electrolyte solution. The dielectric permittivity can be defined by the relation between the magnitude of the external field and the charge surface density on the plates of electrodes:

$$q(t) = \frac{1}{4\pi} \int_{-\infty}^{t} dt' \, \epsilon(t-t')E(t'). \tag{2.22}$$

Since the surface charge density satisfies the relation

$$q(t) = \frac{\epsilon_0}{4\pi} E(t) + \int_{-\infty}^{t} dt' \, i(t'), \tag{2.23}$$

we also have the following well known relation between the dielectric permittivity of the electrolyte solution and its conductivity:

$$\epsilon(t) = \epsilon_0 \delta(t) + 4\pi \int_{-\infty}^{t} dt' \, \sigma(t'). \tag{2.24}$$

The linear response to the periodic external field $E(t) = E^\circ \exp(i\omega t)$ leads to the relations

$$i(t) = \text{Re}\,\sigma(\omega)E(t), \tag{2.25}$$

$$q(t) = (1/4\pi) \, \text{Re} \, \epsilon(\omega)E(t), \tag{2.26}$$

where $\sigma(\omega)$ and $\epsilon(\omega)$ are the Fourier–Laplace transforms of $\sigma(t)$ and $\epsilon(t)$ defined by

$$\sigma(\omega) = \int_0^\infty dt \, \exp(-i\omega t)\sigma(t), \tag{2.27}$$

$$\epsilon(\omega) = \int_0^\infty dt \, \exp(-i\omega t)\epsilon(t). \tag{2.28}$$

From the previous results it follows that the conductivity of the system is characterised by

$$\text{Re } \sigma(\omega) = \sigma^{\text{id}} + \sigma^{\text{el}} + \text{Re } \sigma^{\text{rel}}(\omega) \tag{2.29}$$

and the dielectric properties by

$$\text{Re } \epsilon(\omega) = \epsilon_0 + (4\pi/\omega) \text{ Im } \sigma^{\text{rel}}(\omega) \tag{2.30}$$

where $\sigma^{\text{rel}}(\omega)$ is given by

$$\sigma^{\text{rel}}(\omega) = \frac{-1}{kT} \frac{1}{V} \int_0^\infty dt \, \langle I(0)I(t)\rangle_{\text{eq}} \, e^{-i\omega t}, \tag{2.31}$$

$$I(t) = \exp(tS^*)I(0), \tag{2.32}$$

and the bracket denotes averaging over the complete ionic equilibrium distribution function.

The correlation function expressions for the frequency-dependent conductivity and dielectric permittivity of the electrolyte solution are the first (as far as we are aware) to have been proposed in the quasihydrodynamic theory of electrolytic conductivity. By the application of linear response theory, we obtained a very convenient, general expression for the contribution of the relaxation effect to the complex conductivity whose determination is a central problem of the theory. Though there is little hope of calculating the time correlation function directly from the definition (2.31), the formula can be used as a starting point for some approximation methods which are now very well developed in non-equilibrium statistical mechanics.

The expression (2.17), can also be considered as a non-equilibrium average

$$\sigma^{\text{rel}}(t) = -\frac{1}{V} \int d\{\boldsymbol{R}^{(\gamma)}\} P'(\{\boldsymbol{R}^{(\gamma)}\}, t) I(0) \tag{2.33}$$

where $P'(t)$ is the solution of the unperturbed Smoluchowski equation

$$\partial_t P'(t) = SP'(t) \tag{2.34}$$

with the initial condition $P'(0) = I(0)P^{\text{eq}}(1/kT)$. Taking into account the identity of ionic particles, we can express (2.33) as a sum of two terms,

$$\sigma^{\text{rel}}(t) = \sigma_2^{\text{rel}}(t) + \sigma_3^{\text{rel}}(t), \tag{2.35}$$

which involve respectively two- and three-particle correlations

$$\sigma_2^{\text{rel}}(t) = \frac{-1}{2} \sum_{\alpha,\beta} c^{(\alpha)} c^{(\beta)} \int d\boldsymbol{r} \left[\left(\frac{Q^{(\alpha)}}{\xi^{(\alpha)}} - \frac{Q^{(\beta)}}{\xi^{(\beta)}} \right) \hat{\boldsymbol{E}} \cdot \boldsymbol{\Phi}^{(\alpha)(\beta)}(\boldsymbol{r}) \right.$$

$$\left. - (Q^{(\alpha)} - Q^{(\beta)}) \hat{\boldsymbol{E}} \cdot \boldsymbol{T}(\boldsymbol{r}) \cdot \boldsymbol{\Phi}^{(\alpha)(\beta)}(\boldsymbol{r}) \right] \delta h^{(\alpha)(\beta)}(\boldsymbol{r}, t), \tag{2.36}$$

$$\sigma_3^{\text{rel}}(t) = - \sum_{\alpha,\beta,\gamma} c^{(\alpha)} Q^{(\alpha)} c^{(\beta)} c^{(\gamma)} \int d\boldsymbol{r} \int d\boldsymbol{r}' \, \hat{\boldsymbol{E}} \cdot \boldsymbol{T}(\boldsymbol{r} - \boldsymbol{r}') \cdot \boldsymbol{\Phi}^{(\beta)(\gamma)}(\boldsymbol{r}') \delta h^{(\alpha)(\beta)(\gamma)}(\boldsymbol{r}, \boldsymbol{r}', t). \tag{2.37}$$

By $\delta h^{(\alpha)(\beta)}(t)$ and $\delta h^{(\alpha)(\beta)(\gamma)}(t)$ we denote the linear perturbations of the irreducible pair and triple ionic correlation functions related to the function $P'(t)$. This is an important result. In the first place it indicates that the conductivity is not only related to the pair correlations, as was always assumed in the Debye–Onsager–Falkenhagen theory, but

that it also involves triple ionic correlations. Besides, it suggests a possible method of calculation of the relaxation effect contribution—through the solution of the linearised evolution equations for the ionic irreducible correlation functions.

3. The dynamics of ionic correlations

The reduced generic distribution functions of ionic species can be conveniently defined with the help of generating functionals introduced by Bogoliubov (1962). If we define the functional $A(t; \{u^{(\gamma)}\})$ by

$$A(t; \{u^{(\gamma)}\}) = \int d\{\boldsymbol{R}^{(\gamma)}\} P(\{\boldsymbol{R}^{(\gamma)}\}, t) \prod_{\alpha=1}^{s} \prod_{i=1}^{N^{(\alpha)}} [1 + u^{(\alpha)}(\boldsymbol{R}_i)] \tag{3.1}$$

where $u^{(\alpha)}(\boldsymbol{R})$ are arbitrary regular functions, then the reduced distribution functions are defined by

$$p^{(\alpha_1)\dots(\alpha_n)}(\boldsymbol{R}_1, \dots, \boldsymbol{R}_n, t) = \frac{\delta^n A}{\delta u^{(\alpha_1)}(\boldsymbol{R}_1) \dots \delta u^{(\alpha_n)}(\boldsymbol{R}_n)}\bigg|_{\{u^{(\gamma)}\}=0}. \tag{3.2}$$

For a spatially homogeneous system we have

$$p^{(\alpha)}(\boldsymbol{R}, t) = c^{(\alpha)}, \tag{3.3}$$

$$p^{(\alpha_1)\dots(\alpha_n)}(\boldsymbol{R}_1, \dots, \boldsymbol{R}_n, t) = \prod_{i=1}^{n} c^{(\alpha_i)} g^{(\alpha_1)\dots(\alpha_n)}(\boldsymbol{R}_1, \dots, \boldsymbol{R}_n, t), \tag{3.4}$$

where the last relation defines the n-particle correlation functions $g^{(\alpha_1)\dots(\alpha_n)}(t)$.

The irreducible correlation functions can be defined with the help of the functional $\Omega(t; \{u^{(\gamma)}\})$, which is related to the functional $A(t; \{u^{(\gamma)}\})$ by

$$\Omega(t; \{u^{(\gamma)}\}) = \ln A(t; \{u^{(\gamma)}\}). \tag{3.5}$$

By the functional differentiation of Ω, we obtain that for a spatially homogeneous system

$$\delta\Omega/\delta u^{(\alpha)}(\boldsymbol{R})|_0 = c^{(\alpha)}, \tag{3.6}$$

$$\frac{\delta^n \Omega}{\delta u^{(\alpha_1)}(\boldsymbol{R}_1) \dots \delta u^{(\alpha_n)}(\boldsymbol{R}_n)}\bigg|_0 = \prod_{i=1}^{n} c^{(\alpha_i)} h^{(\alpha_1)\dots(\alpha_n)}(t). \tag{3.7}$$

Relations between the correlation functions $g^{(\alpha_1\dots(\alpha_n)}(t)$ and irreducible correlation functions $h^{(\alpha_1)\dots(\alpha_n)}(t)$ can be found from (3.5). In particular, we have

$$g^{(\alpha_1)(\alpha_2)}(\boldsymbol{R}_1, \boldsymbol{R}_2, t) = 1 + h^{(\alpha_1)(\alpha_2)}(\boldsymbol{R}_1, \boldsymbol{R}_2, t), \tag{3.8}$$

$$g^{(\alpha_1)(\alpha_2)(\alpha_3)}(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, t) = 1 + h^{(\alpha_1)(\alpha_2)}(\boldsymbol{R}_1, \boldsymbol{R}_2, t) + h^{(\alpha_1)(\alpha_3)}(\boldsymbol{R}_1, \boldsymbol{R}_3, t)$$
$$+ h^{(\alpha_2)(\alpha_3)}(\boldsymbol{R}_2, \boldsymbol{R}_3, t) + h^{(\alpha_1)(\alpha_2)(\alpha_3)}(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, t). \tag{3.9}$$

An hierarchy of evolution equations for the correlation functions can be easily obtained by functional differentiation of the evolution equations for the functionals $A(t)$ and $\Omega(t)$, which in turn follow from the equations (2.2) and (3.1). However, in our problem we are interested only in a small, linear deviation of the irreducible correlation functions from their equilibrium forms,

$$\delta h^{(\alpha_1)\dots(\alpha_n)}(t) = h^{(\alpha_1)\dots(\alpha_n)}(t) - h_{eq}^{(\alpha_1)\dots(\alpha_n)}, \tag{3.10}$$

which appears in the relations (2.36) and (2.37). One should note here that, in the problem of determination of the relaxation effect contribution from the formulae (2.36) and (2.37), we are interested not in the complete Smoluchowski equation (2.2) but only in the unperturbed form of this equation (2.34), with a suitable initial condition for the function $P'(t = 0)$. This initial condition can be treated formally as a perturbation of the equilibrium distribution P^{eq} at time $t = 0$. It can be shown that the linearised evolution equations for the $\delta h(t)$ functions can be obtained by functional differentiation of the equation

$$\partial_t \Omega'(t; \{u^{(\gamma)}\}) = \oint_\alpha u^{(\alpha)} S^{(\alpha)} \frac{\delta \Omega'}{\delta u^{(\alpha)}} + \oiint_{\alpha, \beta} u^{(\alpha)} (1 + u^{(\beta)}) S^{(\alpha)(\beta)} \left(\frac{\delta^2 \Omega'}{\delta u^{(\alpha)} \delta u^{(\beta)}} \right.$$

$$+ (1 + T^{(\alpha)(\beta)}) \frac{\delta \Omega'}{\delta u^{(\alpha)}} \frac{\delta \Omega^{eq}}{\delta u^{(\beta)}} \right) + \int \oiint_{\alpha \beta \gamma} u^{(\alpha)} (1 + u^{(\beta)}) (1 + u^{(\gamma)})$$

$$\times S^{(\alpha)(\beta)(\gamma)} \left[\frac{\delta^3 \Omega'}{\delta u^{(\alpha)} \delta u^{(\beta)} \delta u^{(\gamma)}} + (1 + T^{(\alpha)(\gamma)} + T^{(\beta)(\gamma)}) \right.$$

$$\times \left(\frac{\delta^2 \Omega'}{\delta u^{(\alpha)} \delta u^{(\beta)}} \frac{\delta \Omega^{eq}}{\delta u^{(\gamma)}} + \frac{\delta^2 \Omega^{eq}}{(\delta u^{(\alpha)} \delta u^{(\beta)}} \frac{\delta \Omega'}{\delta u^{(\gamma)}} \right)$$

$$+ (1 + T^{(\alpha)(\gamma)} + T^{(\alpha)(\beta)}) \frac{\delta \Omega'}{\delta u^{(\alpha)}} \frac{\delta \Omega^{eq}}{\delta u^{(\beta)}} \frac{\delta \Omega^{eq}}{\delta u^{(\gamma)}} \right] \tag{3.11}$$

where the notation $\oint_\alpha \ldots$ denotes summation over the species index α and integration over the appropriate variable of the function $u^{(\alpha)}$, e.g.

$$\oint_\alpha f^{(\alpha)} = \sum_\alpha \int dr f^{(\alpha)}(r). \tag{3.12}$$

$T^{(\alpha)(\beta)}$ is the transposition operator interchanging species indexes with the arguments of appropriate functions

$$T^{(\alpha)(\beta)} f^{(\alpha)(\beta)}(r^{(\alpha)}, r^{(\beta)}) = f^{(\beta)(\alpha)}(r^{(\beta)}, r^{(\alpha)}) \tag{3.13}$$

and we have (for a spatially homogeneous system)

$$\delta \Omega' / \delta u^{(\alpha)} |_0 = 0,$$

$$\left. \frac{\delta^n \Omega'}{\delta u^{(\alpha_1)} \ldots \delta u^{(\alpha_n)}} \right|_0 = \prod_{i=1}^n c^{(\alpha_i)} \delta h^{(\alpha_1) \ldots (\alpha_n)}(t). \tag{3.14}$$

By $S^{(\alpha)}, S^{(\alpha)(\beta)}$ and $S^{(\alpha)(\beta)(\gamma)}$ we denote respectively one-, two- and three-particle components of the Smoluchowski operator:

$$S^{(\alpha)}(\boldsymbol{R}) = (kT/\xi^{(\alpha)}) \partial^2 / \partial \boldsymbol{R}^2, \tag{3.15}$$

$$S^{(\alpha)(\beta)}(\boldsymbol{R}, \boldsymbol{R}') = kT \partial / \partial \boldsymbol{R} . \boldsymbol{T}(\boldsymbol{R} - \boldsymbol{R}') . (\partial / \partial \boldsymbol{R}' + (1/kT) \Phi^{(\alpha)(\beta)}(\boldsymbol{R} - \boldsymbol{R}'))$$

$$- \frac{1}{\xi^{(\alpha)}} \partial / \partial \boldsymbol{R} . \Phi^{(\alpha)(\beta)}(\boldsymbol{R} - \boldsymbol{R}'), \tag{3.16}$$

$$S^{(\alpha)(\beta)(\gamma)}(\boldsymbol{R}, \boldsymbol{R}', \boldsymbol{R}'') = -\partial / \partial \boldsymbol{R} . \boldsymbol{T}(\boldsymbol{R} - \boldsymbol{R}') . \Phi^{(\beta)\gamma}(\boldsymbol{R}' - \boldsymbol{R}''). \tag{3.17}$$

The initial value of the functional Ω' is given by

$$\Omega'(t=0) = \oint_{\alpha} u^{(\alpha)} \delta S^{(\alpha)} \frac{\delta \Omega^{\mathrm{eq}}}{\delta u^{(\alpha)}}$$

$$+ \oiint_{\alpha\beta} u^{(\alpha)}(1+u^{(\beta)}) \delta S^{(\alpha)(\beta)} \left(\frac{\delta^2 \Omega^{\mathrm{eq}}}{\delta u^{(\alpha)} \delta u^{(\beta)}} + \frac{\delta \Omega^{\mathrm{eq}}}{\delta u^{(\alpha)}} \frac{\delta \Omega^{\mathrm{eq}}}{\delta u^{(\beta)}} \right) \qquad (3.18)$$

where

$$\delta S^{(\alpha)}(\boldsymbol{R}) = (Q^{(\alpha)}/\xi^{(\alpha)}) \hat{\boldsymbol{E}} \cdot \partial/\partial \boldsymbol{R}, \qquad (3.19)$$

$$\delta S^{(\alpha)(\beta)}(\boldsymbol{R}, \boldsymbol{R}') = Q^{(\beta)} \hat{\boldsymbol{E}} \cdot \boldsymbol{T}(\boldsymbol{R} - \boldsymbol{R}') \cdot \partial/\partial \boldsymbol{R}, \qquad (3.20)$$

represent perturbation caused by the external field.

For spatially homogeneous solutions there is no perturbation of the one-particle distribution, and the two-particle correlation functions depend only on the relative distance between the ionic particles. Besides, the linear correction to the self-type correlation function $\delta h^{(\alpha)(\alpha)}(t)$ vanishes for reasons of symmetry (see e.g. Ebeling *et al* 1978). Thus for the pair correlation function $\delta h^{(\alpha)(\beta)}(t)$ we obtain, by double functional differentiation of (3.11), the following equation:

$$\partial_t \delta h^{(\alpha)(\beta)}(t) = (1 + T^{(\alpha)(\beta)}) \Big(S^{(\alpha)} \delta h^{(\alpha)(\beta)}(t) + S^{(\alpha)(\beta)} \delta h^{(\alpha)(\beta)}(t)$$

$$+ \oint_{\gamma} c^{(\gamma)} S^{(\alpha)(\gamma)} [\delta h^{(\alpha)(\beta)(\gamma)}(t) + \delta h^{(\beta)(\gamma)}(t)]$$

$$+ \oint_{\gamma} c^{(\gamma)} S^{(\alpha)(\beta)(\gamma)} [\delta h^{(\alpha)(\beta)(\gamma)}(t) + \delta h^{(\alpha)(\gamma)}(t)]$$

$$+ \oint_{\gamma} c^{(\gamma)} S^{(\alpha)(\gamma)(\beta)} [\delta h^{(\alpha)(\gamma)(\beta)}(t) + \delta h^{(\alpha)(\gamma)}(t) + \delta h^{(\alpha)(\beta)}(t)]$$

$$+ \oiint_{\gamma\delta} c^{(\gamma)} c^{(\delta)} S^{(\alpha)(\gamma)(\delta)} [\delta h^{(\alpha)(\beta)(\gamma)(\delta)}(t) + \delta h^{(\alpha)(\gamma)}(t) h_{\mathrm{eq}}^{(\beta)(\delta)}$$

$$+ h_{\mathrm{eq}}^{(\alpha)(\gamma)} \delta h^{(\beta)(\delta)}(t) + \delta h^{(\alpha)(\delta)}(t) h_{\mathrm{eq}}^{(\gamma)(\beta)} + h_{\mathrm{eq}}^{(\alpha)(\delta)} \delta h^{(\gamma)(\beta)}(t)] \Big). \qquad (3.21)$$

Terms which give a vanishing contribution have been eliminated.

4. The mean field approximation

In the previous section we derived the first equation of the hierarchy which determines the time evolution of irreducible correlation functions in spatially homogeneous solutions. Since, as is usual in sets of equations of the BBGKY type, the lower-order correlation functions are coupled with those of higher order, practical application of these equations requires the introduction of additional simplifications which would allow us to close the set on a manageable level. In this section we use what may be called

a mean field approximation, in which only the first equation of the hierarchy is kept and all higher-order perturbations of the irreducible correlation functions are assumed to be equal to zero. The mean field approximation is in fact the only one used so far in the hydrodynamic theory of transport processes in electrolyte solutions. The contribution of the relaxation effect to the conductivity is in this approximation given solely by the expression (2.36), and the pair irreducible correlation function is determined by the following equation

$$
\partial_t \delta h^{(\alpha)(\beta)}(r, t) = (1 + T^{(\alpha)(\beta)}) \left[\frac{kT}{\xi^{(\alpha)}} \partial/\partial r \cdot [I - \xi^{(\alpha)} T(r)] (\partial/\partial r - 1/kT \, \Phi^{(\alpha)(\beta)}(r)) \right.
$$

$$
\times \delta h^{(\alpha)(\beta)}(r, t)
$$

$$
- \frac{1}{\xi^{(\alpha)}} \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} \int dr' \, \Phi^{(\alpha)(\gamma)}(r - r') \delta h^{(\gamma)(\beta)}(r', t)
$$

$$
+ \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} \int dr' \, T(r') \cdot \Phi^{(\alpha)(\gamma)}(r') \delta h^{(\gamma)(\beta)}(r - r', t)
$$

$$
+ \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} T(r) \cdot \int dr' \, \Phi^{(\beta)\gamma}(r') \delta h^{(\gamma)(\alpha)}(r - r', t)
$$

$$
- \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} \int dr' \, T(r') \cdot \Phi^{(\beta)(\gamma)}(r - r') \delta h^{(\gamma))\alpha}(r', t)
$$

$$
- \partial/\partial r \cdot \sum_{\gamma, \delta} c^{(\gamma)} c^{(\delta)} \int dr' \int dr'' T(r') \cdot \Phi^{(\gamma)(\delta)}(r'')
$$

$$
\times [h_{eq}^{(\delta)(\beta)}(r - r' - r'') \cdot \delta h^{(\alpha)(\gamma)}(r', t) + h_{eq}^{(\alpha)(\gamma)}(r') \delta h^{(\beta)(\delta)}(r - r' - r'', t)
$$

$$
\left. + h_{eq}^{(\gamma)(\beta)}(r - r') \delta h^{(\alpha)(\delta)}(r' + r'', t) + h_{eq}^{(\alpha)(\delta)}(r' + r'') \delta h^{(\beta)(\gamma)}(r - r'), t) \right] \right].
$$

$$
(4.1)
$$

This is an exact, linearised equation for the ionic irreducible pair correlation function, which is valid within the limits of the mean field approach for arbitrary concentrations and strengths of the ionic interaction. The initial condition is given by

$$
\delta h^{(\alpha)(\beta)}(r, t = 0) = \left(\frac{Q^{(\alpha)}}{\xi^{(\alpha)}} - \frac{Q^{(\beta)}}{\xi^{(\beta)}} \right) \hat{E} \cdot \partial/\partial r \, h_{eq}^{(\alpha)(\beta)}(r)
$$

$$
- (Q^{(\alpha)} - Q^{(\beta)}) \hat{E} \cdot T(r) \cdot \partial/\partial r \, h_{eq}^{(\alpha)(\beta)}(r). \tag{4.2}
$$

The relative importance of the interaction terms in (4.1) can be most conveniently estimated if one introduces a dimensionless variable defining the unit of time scale, τ, by

$$
\tau^{-1} = \varkappa^2 \bar{D} = \varkappa^2 kT (1/\xi^{(\alpha)} + 1/\xi^{(\beta)}) \tag{4.3}
$$

and the unit of the length scale, l, by

$$
l^{-1} = \varkappa. \tag{4.4}
$$

Then it can be easily seen that every appearence of the Coulombic interaction potential is connected with the dimensionless coupling parameter

$$
\lambda^{Coul} = e^2 \varkappa / (kT \epsilon_0) \tag{4.5}
$$

which is known as a plasma parameter. The hydrodynamic interaction contribution is manifested by the appearence of the Ossen tensor, which introduces another characteristic dimensionless coupling parameter

$$\lambda^{\text{Hydr}} = kT\varkappa/(8\pi\eta_0\bar{D}).$$
(4.6)

The form of the coupling parameter related to the short-range direct interionic interaction depends on its assumed form. For example, for a short-range repulsive potential

$$U^{\text{SR}}(r) = \epsilon(a/r)^n, \qquad n \sim 6 \div 15,$$
(4.7)

where ϵ and a are constants, the coupling parameter takes the form

$$\lambda^{\text{SR}} = \epsilon(a\varkappa)^n/kT,$$
(4.8)

while for the hard-core interaction, for which the interionic force can be assumed to be

$$\Phi^{\text{HC}}(r) = kT\hat{r}\delta(r-a),$$
(4.9)

the coupling parameter is

$$\lambda^{\text{HC}} = 1.$$
(4.10)

It should be also noted that every integration over superfluous variables leads to the additional parameter which is related both to the ionic concentration and the range of screened electric interaction $\varkappa^{-1}$. This parameter ϕ, is defined by

$$\phi = c\varkappa^{-3}.$$
(4.11)

For a binary 1 : 1 electrolyte at 298 K these parameters are roughly of order

$$\lambda^{\text{Coul}} \propto 0.74c^{0.5}, \qquad \lambda^{\text{Hydr}} \propto 0.16c^{0.5}, \qquad \phi \propto 0.52c^{-0.5},$$
(4.12)

where c is the salt concentration in mol dm^{-3}.

Let us now consider a limiting conductance problem, assuming a short-range potential of the form (4.7). In the limit $c \to 0$, and taking into account that

$$\lim_{c \to 0} \left\{ \begin{array}{c} \lambda^{\text{Coul}}\phi \\ \lambda^{\text{Hydr}}\phi \end{array} \right\} = \text{finite quantity},$$
(4.13)

we obtain the following asymptotic form of equation (4.1)

$$\partial_t \delta h^{(\alpha)(\beta)}(\mathbf{r}, t) = (1 + T^{(\alpha)(\beta)})\left(\frac{kT}{\xi^{(\alpha)}} \partial^2/\partial r^2 \, \delta h^{(\alpha)(\beta)}(\mathbf{r}, t) \right.$$

$$\left. - \frac{1}{\xi^{(\alpha)}} \partial/\partial\mathbf{r} \cdot \sum_\gamma c^{(\gamma)} \int d\mathbf{r}' \Phi_{\text{Coul}}^{(\alpha)(\gamma)}(\mathbf{r} - \mathbf{r}')\delta h^{(\gamma)(\beta)}(\mathbf{r}', t) \right)$$
(4.14)

with the initial condition

$$\delta h^{(\alpha)(\beta)}(\mathbf{r}, t = 0) = \left(\frac{Q^{(\alpha)}}{\xi^{(\alpha)}} - \frac{Q^{(\beta)}}{\xi^{(\beta)}} \right)\hat{\mathbf{E}} \cdot \frac{\partial}{\partial\mathbf{r}} h_{\text{eq}}^{(\alpha)(\beta)}(\mathbf{r})$$
(4.15)

which is exactly the well known equation of the Debye–Onsager–Falkenhagen theory used for the determination of the limiting conductance, which in this case reduces to the following expression:

$$\sigma(t) = \delta(t)(\sigma^{\text{id}} + \sigma^{\text{el}}) - \frac{1}{2}\sum_{\alpha,\beta} c^{(\alpha)}c^{(\beta)} \int d\mathbf{r} \, \hat{\mathbf{E}} \cdot \Phi_{\text{Coul}}^{(\alpha)(\beta)}(\mathbf{r})\left(\frac{Q^{(\alpha)}}{\xi^{(\alpha)}} - \frac{Q^{(\beta)}}{\xi^{(\beta)}} \right)\delta h^{(\alpha)(\beta)}(\mathbf{r}, t)$$
(4.16)

where the asymptotic form of the pair correlation is determined by (4.14), and the linearised form of the equilibrium Debye–Hückel pair distribution is used.

The Onsager formula (4.16) is in good agreement with the experimental data at very low concentrations; however, already for values of the coupling parameters $\lambda \sim 10^{-3}$ a clear deviation of the predicted and experimental values is observed, which indicates that some other effect should be taken into account. Most of the later attempts to improve the theory are based on the assumption that the excluded volume effects are responsible for the observed discrepancies. Usually the so-called restricted primitive model of interionic interaction was applied, in which excluded volume effects were taken into account through the introduction of the hard-core short-range interaction between the ionic particles (see e.g. Falkenhagen 1971, Falkenhagen *et al* 1971, Fuoss *et al* 1962, 1963, 1964, Pitts 1953, Pitts *et al* 1969, 1970, Murphy *et al* 1970). So far, only corrections to the limiting conductance have been calculated. In view of our general mean field equation (4.1), these attempts were not entirely consequent. Although we do not intend to consider here the specific model of electrolytic conductance, it seems useful to present the equation which follows in this case from (4.1) in the infinite dilution limit.

Assuming that

$$\Phi^{(\alpha)(\beta)}(r) = kT\hat{r}\delta(r - a^{(\alpha)(\beta)}) - (Q^{(\alpha)}Q^{(\beta)}/\epsilon_0 r^2)\hat{r} \tag{4.17}$$

where $a^{(\alpha)(\beta)}$ is the repulsion distance, we obtain, in the limit of low concentrations,

$$\partial_t \delta h^{(\alpha)(\beta)}(r, t) = (1 + T^{(\alpha)(\beta)}) \left\{ \frac{kT}{\xi^{(\alpha)}} \partial/\partial r \cdot \left(\frac{\partial}{\partial r} - \frac{1}{kT} \Phi_{\text{HC}}^{(\alpha)(\beta)}(r) \right) \delta h^{(\alpha)(\beta)}(r, t) \right.$$

$$- \frac{1}{\xi^{(\alpha)}} \frac{\partial}{\partial r} \cdot \sum_\gamma c^{(\gamma)} \int dr' \, \Phi_{\text{Coul}}^{(\alpha)(\gamma)}(r - r')\delta h^{(\gamma)(\beta)}(r', t)$$

$$- \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} \int dr' \, T(r') \cdot \Phi_{HC}^{(\alpha)(\gamma)}(r')\delta h^{(\gamma)(\beta)}(r - r', t)$$

$$+ \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} T(r) \cdot \int dr' \, \Phi_{HC}^{(\beta)(\gamma)}(r')\delta h^{(\gamma)(\alpha)}(r - r', t)$$

$$- \partial/\partial r \cdot \sum_\gamma c^{(\gamma)} \int dr' \, T(r') \cdot \Phi_{HC}^{(\beta)(\gamma)}(r - r')\delta h^{(\gamma)(\alpha)}(r', t)$$

$$- \partial/\partial r \cdot \sum_{\gamma,\delta} c^{(\gamma)}c^{(\delta)} \int dr' \int dr'' \, T(r') \cdot \Phi_{HC}^{(\gamma)(\delta)}(r'')$$

$$\times [\overset{0}{h}_{\text{eqHC}}^{(\gamma)(\beta)}(r - r' - r'')\delta h^{(\alpha)(\delta)}(r', t) + \overset{0}{h}_{\text{eqHC}}^{(\alpha)(\gamma)}(r')\delta h^{(\beta)(\delta)}(r - r' - r'', t)$$

$$\left. + \overset{0}{h}_{\text{eqHC}}^{(\gamma)(\beta)}(r - r')\delta h^{(\alpha)(\delta)}(r' + r'', t) + \overset{0}{h}_{\text{eqHC}}^{(\alpha)(\delta)}(r' + r'')\delta h^{(\beta)(\gamma)}(r - r', t)] \right\}$$

$$\tag{4.18}$$

where $\overset{0}{h}_{\text{eqHC}}^{(\alpha)(\beta)}(r)$ we denote the low-density, hard-core pair correlation function given by

$$\overset{0}{h}_{\text{eqHC}}^{(\alpha)(\beta)}(r) = -H(a^{(\alpha)(\beta)} - r) \tag{4.19}$$

where $H(x)$ is the Heaviside step function.

5. Summary and conclusions

In the present paper we have given a general formulation of the quasihydrodynamic theory of electrolytic conductance in an isothermal, spatially homogeneous solution of strong electrolyte. Our formulation was based on the Brownian particle model of ionic conductance, with the multiparticle Smoluchowski equation playing the role of the fundamental equation of evolution for the ionic probability distribution function. By the application of the linear response method, we obtained new, convenient, correlation function type expressions for the contributions of the relaxation effect to the conductivity and dielectric permittivity of the electrolyte solution. We also found that the relaxation effect can be directly related to the linear perturbations of the non-equilibrium pair and triple irreducible correlation functions of the ionic particles. These functions can in principle be determined from the hierarchy of coupled equations of the BBGKY type. The hierarchy is infinite, and additional assumptions are necessary in order to close the set on a level which would be of some practical significance. Since the mean field approximation is of special importance for the theory, we discussed it in some detail, and proposed the first exact mean field equation for the time-dependent irreducible ionic pair correlation function. Our theory is applied here only to the problem of electrolytic conductance. It can, however, be easily generalised and modified to the problem of determination of other transport coefficients (e.g. intrinsic viscosity or thermal conductivity) of the electrolyte solution. Extensions to spatially inhomogeneous external fields and to nonlinear response are also possible.

Acknowledgments

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