PHYSICAL CHEMISTRY

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1964

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Abstract

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STATISTICAL THEORY OF NONEQUILIBRIUM PROCESSES AT THE METAL–SOLUTION INTERFACE

STATISTICAL THEORY OF A NONEQUILIBRIUM DOUBLE LAYER

1. The electrical double layer has a substantial influence on the character of nonequilibrium processes occurring at the metal—solution interface (^{1}). In (^{2}) it was noted that disregarding the discrete structure of charge in the double layer, which is characteristic of the Gouy—Chapman—Stern theory, leads in a number of cases to discrepancies between that theory and experiment. The need to take into account the discrete structure of charge in the double layer also arises in problems concerned with the investigation of nonequilibrium processes at the metal—solution interface.

In previous works (^{2}), a statistical theory of the equilibrium double layer at interphase boundaries metal—solution and dielectric (gas)—solution was considered.

In the present work, questions of the statistical theory of nonequilibrium processes at the metal—solution interface are considered. The introduction of the method of correlation functions (^{3}) makes it possible to carry out a statistical formulation of the problem of a nonequilibrium double layer and to take into account the discrete structure of charge in the double layer, as well as correlation effects in the interaction of ions, which is impossible within the framework of model representations. The work also discusses the question of the influence of image forces on the kinetics of electrode processes.

By applying the apparatus of generalized correlation functions (^{4}), which makes it possible to consider in the general case not only Markov-type processes but also stochastic processes with aftereffect, the conditions of applicability of the self-consistent-field approximation in the theory of the nonequilibrium double layer (^{5}) are clarified, as are ways of improving this approximation on the basis of a statistical description of nonequilibrium processes at the metal—solution interface.

2. The system under consideration is a metallic phase and an electrolyte solution that are in interaction with one another. In the case where exchange of charges between the phases is impossible, the system represents an ideally polarizable interphase boundary. The opposite limiting case of large exchange currents characterizes a reversible electrode.

In what follows we are interested in the behavior of the ionic subsystem of the solution, the ions interacting both with one another and with the solvent, as well as with the metallic phase.

The motion of the ions, caused by their interaction with the solvent, will be described by a certain stochastic process,* making use for this purpose of the apparatus of generalized correlation functions (^{4}).

If $\mathbf{r}_i$ are the coordinates of the ions, then the equations of motion of the ionic subsystem under these assumptions may be written in the form

$$d\mathbf{r}_i/dt = \mathbf{f}_i(\mathbf{r}_1, \dots, \mathbf{r}_N), \qquad i = 1, 2, \dots, N, \tag{1}$$

where in a system with an unchanged (specified) number of particles N it is constant, while $\mathbf{f}_i$ are random functions, also including prescribed components of the interionic interaction and the interaction of the particles with the metallic phase.

* A rigorous formulation of the problem would include a general scheme of the kinetic equation for the entire system as a whole, including the solvent. However, in view of the complexity of the analysis of such a problem, which has not been solved even for the equilibrium case, it is expedient first to consider the indicated approximate scheme for describing this interaction.

Let, further, $\eta_{a_1 \dots a_s}(\mathbf{r}_1, \dots; t_1, \dots, t_s)$ be the correlation functions defining the stochastic process under consideration, and $K_{a_1 \dots a_s}(x_1, \dots, x_N)$ the structural numbers (in the general case, functions of the coordinates)

$$K_{a_1 \dots a_s}(x_1, \dots, x_s) = \int \eta_{a_1 \dots a_s}(\mathbf{r}_1, \dots; t'_1, \dots, t'_{s-1})\, dt'_1 \dots dt'_{s-1}. \tag{2}$$

The correlation time τ_{corr} is defined as the largest of the times

$$\tau^{(k)}_{a_1 \dots a_s} \simeq \frac{s!}{K_s} \int \sigma_1\, d\sigma_1 \int_{(\sigma_1)} d\sigma_2 \dots \int_{(\sigma_{s-2})} \eta_{a_1 \dots a_s}(\mathbf{r}_1, \dots; \sigma_1, \dots, \sigma_{s-1})\, d\sigma_{s-1}. \tag{3}$$

If, in particular, the characteristic times of the system $\tau_c \sim (\partial f/\partial x)^{-1}$ are much greater than τ_{corr}, then for time intervals $\Delta t \gg \tau_{\text{corr}}$ a generalized Fokker–Planck equation holds.

Let, further, U_N be the interaction energy of the ionic subsystem at time t. In what follows we shall assume that at each instant t the value of U_N is determined by the corresponding equilibrium value of this energy for the given instantaneous configuration of the ionic subsystem in the nonequilibrium state.

We shall further take into account, as in the equilibrium case (^{2}), the effect of polarization of the compact layer by the electric field (ε is the dielectric permittivity of the compact layer, depending, generally speaking, on the field strength and on the magnitude of adsorption of surface-active substances). The latter circumstance, as was shown earlier in (^{2}), substantially changes the character of the interaction of ions with the metal.

Denote by ε_0 the dielectric permittivity of the homogeneous phase of the solvent, and let d be the thickness of the compact layer (the thickness of the "dielectric interlayer," in the terminology of (^{2})).

Using the results of the preceding work (^{2}), for U_N we obtain (in the limiting case $\lambda \to \infty$, the latter meaning the transition to consideration of the double layer at a single electrode)

$$U_N^t(\mathbf{r}_1, \dots, \mathbf{r}_N) =$$

$$= \frac{2\pi\lambda}{\varepsilon S} q_M^2 + \sum_{a,i} e_a \Phi_a^{(\mathrm{im})}(x_i) + \sum_{(a,b;\, i<j)} \tilde{u}_{ab}(\mathbf{r}_i, \mathbf{r}_j), \tag{4}$$

where q_M is the charge of the metal, $\Phi_a^{(\mathrm{im})}$ is the interaction energy of a charge e_a with the metal, and $\tilde{u}_{ab}(\mathbf{r}_i, \mathbf{r}_j)$ is the binary potential of the Coulomb interaction, modified owing to the presence of image forces,

$$\Phi_a^{(\mathrm{im})}(x) = -\frac{e_a}{2\varepsilon_0} \int_0^\infty e^{-2kx} \left(\frac{\varepsilon}{\varepsilon_0} - \mathrm{th}\, kd\right) \left(\frac{\varepsilon}{\varepsilon_0} + \mathrm{th}\, kd\right)^{-1} dk, \tag{5}$$

$$\tilde{u}_{ab}(\mathbf{r}_i, \mathbf{r}_j) = \frac{e_a e_b}{\varepsilon_0} \int_0^\infty J_0(k\rho_{r_i \mathbf{r}_j}) \left\{ e^{-k|x_i - x_j|} - \left(\frac{\varepsilon/\varepsilon_0 - \mathrm{th}\, kd}{\varepsilon/\varepsilon_0 + \mathrm{th}\, kd} \right) e^{-k(x_i + x_j)} \right\} dk. \tag{6}$$

Here $J_0(x)$ is the Bessel function of zeroth order; the summation in (4) is carried out over all species of ions a ($a_1 = 1, 2, \dots, M$) and particle coordinates $\mathbf{r}_i = (x_i, y_i, z_i)$, where in (6) $\rho_{r_i \mathbf{r}_j} = [(y_i - y_j)^2 + (z_i + z_j)^2]^{1/2}$, while the x_i are measured from the outer Helmholtz plane ($x = 0$). If the motion of ions, caused by the presence of their interaction with the solvent, is described by a stochastic process of Markov type, then the probability distribution of space-time configurations of the sys-

of the system, $\widetilde{D}_N(t, \mathbf{r}_1, \dots, \mathbf{r}_N)$, satisfies the equation*

$$\frac{\partial \widetilde{D}_N(t,\mathbf{r}_1,\dots,\mathbf{r}_N)}{\partial t} = \sum_{(a,\alpha,i)} D_a \frac{\partial}{\partial r_i^\alpha}\left(\frac{\partial \widetilde{D}_N(t,\mathbf{r}_1,\dots,\mathbf{r}_N)}{\partial r_i^\alpha} + \frac{1}{\theta}\frac{\partial U_N}{\partial r_i^\alpha}\widetilde{D}_N(t,\mathbf{r}_1,\dots,\mathbf{r}_N)\right), \tag{7}$$

where $\alpha = 1,2,3$; $r_i^\alpha = x_i, y_i, z_i$ for $\alpha = 1,2,3$, and D_a is the diffusion coefficient of ions of species a, related to the structure number $K_2^{(a)}$ by the relation $K_2^{(a)} = 2D_a$. Note that in the equilibrium case $\left(\frac{\partial}{\partial t}\cdots = 0\right)$, from (7) for $\widetilde{D}_N$ we obtain the Gibbs distribution $\widetilde{D}_N = Q_N^{-1}e^{-U_N/\theta}$. The latter means, according to (7), that in this case the particle flux in the isothermal system is absent.

Characterizing the probability density $\widetilde{D}_N(t,\mathbf{r}_1,\dots,\mathbf{r}_N)$ by a sequence of nonequilibrium distribution functions $F_{a_1\dots a_s}$ pertaining to complexes of s particles of the system, we obtain for these functions, analogously to the equilibrium case, the chain of coupled equations

$$\frac{\partial F_{a_1\dots a_s}(t,\mathbf{r}_1,\dots,\mathbf{r}_s)}{\partial t} = \sum_{\substack{1\le\alpha\le3\\1\le j\le s}} D_{a_j}\frac{\partial}{\partial r_j^\alpha}\left\{\frac{\partial F_{a_1\dots a_s}}{\partial r_j^\alpha} + \frac{1}{\theta}F_{a_1\dots a_s}\frac{\partial}{\partial r_j^\alpha}\left(\tilde{u}_{a_1\dots a_s} + \Psi^{(\mathrm{ex})}_{a_1\dots a_s}\right)\right\} +$$

$$+ \sum_{\substack{1\le\alpha\le3\\1\le j\le s;\ 1\le a_{s+1}\le M}} \frac{n_{a_{s+1}}}{\theta v} D_{a_j}\frac{\partial}{\partial r_j^\alpha}\int \frac{\partial}{\partial r_j^\alpha}\tilde{u}_{a_j a_{s+1}}(\mathbf{r}_j,\mathbf{r}_{s+1})F_{a_1\dots a_s a_{s+1}}\,d\mathbf{r}_{s+1}; \tag{8}$$

$$\tilde{u}_{a_1\dots a_s} = \sum_{\substack{a_i,a_j\\1\le i<j\le s}} \tilde{u}_{a_i a_j}(\mathbf{r}_i,\mathbf{r}_j); \qquad \Psi^{(\mathrm{ex})}_{a_1\dots a_s} = \sum_{\substack{a_i\\1\le i\le s}} e_{a_i}\Phi_i^{(\mathrm{ex})}(x_i). \tag{9}$$

Approximate methods for solving the system of equations (8) in the general case of arbitrary electrolyte concentrations are evidently reduced to obtaining, by one or another approximate method, closed equations (i.e., to truncating the chain) for the unknown functions.

At not too large volume concentrations of the electrolyte, it is expedient to use expansions in the Debye (plasma) parameter v/r_d^3, where $v = V/N$ is the specific volume, and r_d is the Debye characteristic length. To this end, instead of $F_{a_1\dots a_s}$, introduce new unknown functions according to the relation

$$F_{a_1\dots a_s} = \chi_{a_1\dots a_s}\exp\left\{-v\sum_{(1\le i<j\le s)} g_{a_i a_j}(t,\mathbf{r}_i,\mathbf{r}_j)\right\}. \tag{10}$$

Further putting

$$\chi_a = g_a(t, \mathbf{r}); \qquad \chi_{ab} = g_a(t, \mathbf{r})\, g_b(t, \mathbf{r}') + (v/r_b^3)\xi_{ab}(t, \mathbf{r}, \mathbf{r}') \tag{11}$$

and so on, and expanding the functions g_a, $\xi_{a_1 \ldots a_s}$ in power series in the parameter v/r_d^3, for the one-particle function of the first approximation we obtain closed equations which, being written in the form of continuity equations, take the form

$$\frac{\partial g_a^{(0)}(t,x)}{\partial t} = -\frac{\partial j_a^{(0)}(t,x)}{\partial x}; \qquad j_a^{(0)} = -D_a \frac{\partial g_a^{(0)}}{\partial x} - \frac{D_a}{\theta} e_a \frac{\partial \varphi^{(0)}}{\partial x} g_a^{(0)},$$

$$\frac{\partial^2 \varphi^{(0)}(t,x)}{\partial x^2} = -\frac{4\pi}{\varepsilon_0} \sum_{(a)} r_a \frac{e_a}{v} g_a^{(0)}(t,x). \tag{12}$$

These are the usual equations of the nonequilibrium double layer in the approximation of a self-consistent field (5).

Subsequent approximations are obtained from the original system of equations (8) by taking into account higher approximations in the parameter v/r_d^3. However, as was already noted earlier with reference to questions of equilibrium, the self-consistent-field approximation is strictly valid in the region of distances $r > r_d$. At small distances ($r \ll r_d$) the discrete structure of the layer charge is manifested, and taking it into account by the small-parameter method in standard form is not entirely legitimate here. It is therefore expedient, in order to improve the initial approximation in equation (8), to put $g_{ab} = g_a g_b$ for $s = 1$. If, following also our previous works (2), one takes into account the influence on the structure of the diffuse double layer of the polarization of the dense layer, which changes the character of the interaction of ions with the metal, then the approximate equations of the nonequilibrium double layer, having an interpolational character, take the form

$$\frac{\partial g_a(t,x)}{\partial t} = -\frac{\partial i_a(t,x)}{\partial x}; \qquad \frac{\partial^2 \varphi(t,x)}{\partial x^2} = -\frac{4\pi}{\varepsilon_0} \sum_{(a)} \frac{n_a}{v} e_a g_a(t,x); \tag{13}$$

$$j_a(t,x) = -D_a \frac{\partial g_a}{\partial x} + \frac{D_a}{\theta} \frac{\partial \Psi_a^{(\mathrm{iz})}(x)}{\partial x} g_a - \frac{D_a}{\theta} e_a g_a \frac{\partial \varphi}{\partial x}; \tag{14}$$

$$\Psi_a^{(\mathrm{iz})}(x) = \left(\frac{e_a^2 \chi}{2\varepsilon_0}\right) \int_0^\infty \left\{ \frac{(\varepsilon/\varepsilon_0)\sqrt{\lambda^2 - 1} - \lambda \,\mathrm{th}\left(\chi d \sqrt{\lambda^2 - 1}\right)}{(\varepsilon/\varepsilon_0)\sqrt{\lambda^2 - 1} + \lambda \,\mathrm{th}\left(\chi d \sqrt{\lambda^2 - 1}\right)} \right\} e^{-2(\chi x)\lambda}\, d\lambda. \tag{15}$$

* Equation (7) is the Fokker–Planck equation in the configuration space of the system.

The obtained equations of the double layer (13)–(15), in contrast to (12), take into account the discrete charge structure of the diffuse double layer. It can be shown that the equations of the nonequilibrium double layer (12) characterize the asymptotic behavior of the one-particle distribution function, which gives complete information on the structure of the charge and field in the double layer.

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Received
1 VIII 1964

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