STATISTICAL THEORY OF NONEQUILIBRIUM PROCESSES AT A METAL – SOLUTION BOUNDARY

STATISTICAL THEORY OF THE NONEQUILIBRIUM DOUBLE LAYER

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1. The electric double layer exerts a substantial effect on the nature of the nonequilibrium processes taking place at a metal–solution boundary [1]. It was pointed out in [2] that ignoring the discrete structure of the charge in the double layer, as is characteristic of the Guy–Chapman–Stern theory, leads, in a number of cases, to a difference between theory and experiment. The need to take account of the discrete structure of the charge in the double layer also occurs in problems dealing with the nonequilibrium processes occurring at a metal–solution boundary.

A discussion has been given in previous papers [2] of the statistical theory of the equilibrium double layer at metal–solution and dielectric (gas)–solution interphase boundaries.

In this paper, we deal with problems in the statistical theory of the nonequilibrium processes occurring at a metal–solution boundary. Introducing the method of correlative functions [3] makes possible a statistical formulation of the problem of the nonequilibrium double layer, including the discrete structure of the charge in the double layer, as well as the correlation effects in the interaction between ions, which is impossible within the framework of model representations. The paper also discusses the problem of what effect the image forces have on the kinetics of the electrode processes.

By using the apparatus of generalized correlation functions [4], which makes it possible in the general case to treat both processes of Markov type and stochastic processes with an after-effect, it becomes clear what the conditions are for the applicability of the self-consistent field approximation in the theory of the nonequilibrium double layer [5], and reveals methods of improving this approximation, based on a statistical description of the nonequilibrium processes at a metal–solution boundary.

2. The system under discussion consists of a metallic phase and a solution of an electrolyte, that are interacting with one another. In the case where charge exchange between the phases is impossible, the system represents an ideally polarizable interphase boundary. The opposite limiting case of large exchange currents is characteristic of a reversible electrode.

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

The motion of the ions, due to their interaction with the solvent, will be described by a definite stochastic process† invoking for the purpose the apparatus of generalized correlation functions [4].

If r_i are the coordinates of the ions, the equations of motion of the ionic subsystem under these assumptions may be written in the form:

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†An exact formulation of the problem would include the general scheme of the kinetic equation for the system as a whole, including the solvent. However, in view of the complexity involved in analyzing such a problem, which cannot be solved even for the equilibrium case, it is well to consider first the above approximate scheme for describing the interaction.

$$dr_i/dt = f_i(r_1, \ldots, r_N), \quad i = 1, 2, \ldots, N, \tag{1}$$

where, in a system with a constant (given) number of particles, N is constant, and f_i are stochastic functions, including also the given components of the interionic interaction, and the interaction of the particles with the metallic phase.

Further, let $\eta a_1 \ldots a_s(r_1, \ldots; \quad t_1, \ldots, t_s)$ be the correlation functions determining the stochastic process under discussion, and let $K_{a_1 \ldots a_s}(\chi_1 \ldots, \chi_N)$ be the structure numbers (functions of the coordinates in the general case):

$$K_{a_1 \ldots a_s}(x_1, \ldots, x_s) = \int \eta_{a_1 \ldots a_s}(\mathbf{r}_1, \ldots; t'_1, \ldots, t'_{s-1})\, dt_1' \ldots dt'_{s-1}. \tag{2}$$

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

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

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

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

Further, as in the equilibrium case [2], we take account of the polarization effect of the dense layer by the electric field (ε is the dielectric constant of the dense layer, which, generally speaking, depends on the field intensity and the amount of adsorption of surface active substances). This last effect, as shown previously in [2], produces a substantial change in the nature of the interaction between the ions and the metal.

Let ε_0 be the dielectric constant of the homogeneous solvent phase, and let d be the thickness of the dense layer (the thickness of the "dielectric layer", in the terminology of [2]).

Using the results of the previous paper [2], we find for U_N (in the limiting case $\lambda \to \infty$, which means going to a discussion of the double layer at one electrode):

$$U_N^t(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{2\pi\lambda}{\varepsilon S} q_{\text{M}}^2 + \sum_{a,i} e_a \Phi_a^{(\text{im})}(x_i) + \sum_{(a,b;\; i<j)} \tilde{u}_{ab}(\mathbf{r}_i, \mathbf{r}_j), \tag{4}$$

where q_M is the charge on the metal $\Phi_a^{(\text{im})}$ is the interaction energy between the charge e_a and the metal, and a $u_{ab}(r_i, r_j)$ is the binary Coulomb interaction potential, as modified by the presence of the image forces:

$$\Phi_a^{(\text{im})}(x) = -\frac{e_a}{2\varepsilon_0} \int\limits_0^\infty e^{-2kx} \left(\frac{\varepsilon}{\varepsilon_0} - \text{th}\, kd\right) \left(\frac{\varepsilon}{\varepsilon_0} + \text{th}\, kd\right)^{-1} dk, \tag{5}$$

$$\tilde{u}_{ab}(\mathbf{r}_i \;\; \mathbf{r}_j) = \frac{e_a e_b}{\varepsilon_0} \int\limits_0^\infty J_0(k\rho_{\mathbf{r}_i \mathbf{r}_j}) \left\{ e^{-k|x_i - x_j|} - \left(\frac{\varepsilon/\varepsilon_0 - \text{th}\, kd}{\varepsilon/\varepsilon_0 + \text{th}\, kd}\right) e^{-k(x_i + x_j)} \right\} dk. \tag{6}$$

Here, $J_0(\chi)$ is the zero order Bessel function, the summation in (4) is extended over all the sorts of ions a ($a_1 = 1, 2 \ldots, M$) and the coordinates of the particles $r_i = (\chi_i, y_i, z_i)$, with, in (6) $\rho_{r_i r_j} = [(y_i - y_i)^2 + (z_i + z_j)^2]^{1/2}$ and the values of χ_i are read from the external Helmholtz plane ($\chi = 0$). If the motion of the ions due to interaction between the ions in the solvent is described by a stochastic process of Markov type, the probability distribution of the space-time configurations of the system $D_N(t, r_1, \ldots, r_N)$ satisfies the equation*:

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

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

where $\alpha = 1, 2, 3$, $r_i^\alpha = \chi_i, y_i, z_i$ for $\alpha = 1, 2, 3$, and D_a is the diffusion coefficient of the ions of sort $\underline{a}$, which is related to the structure number $K_2^{(a)}$ by the equation $K_2^{(a)} = 2D_a$. Note that in the equilibrium case $(\partial/\partial t \ldots = 0)$, we obtain from (7) for D_N the Gibbs distribution $D_N = Q_N^{-1} e^{-U_N/\theta}$. This means, in accordance with (7), that in this case there is no particle flux in the isothermal system.

Characterizing the probability density $D_N(t, r_1, \ldots, r_N)$ by the sequence of nonequilibrium distribution function $F_{a_1 \ldots a_s}$, referring to complexes of $\underline{s}$ particles of the system, we obtain for these functions, as in the equilibrium case, the system of coupled equations:

$$\frac{\partial F_{a_1\ldots a_s}(t, \mathbf{r}_1, \ldots, \mathbf{r}_s)}{\partial t} = \sum_{\left(\substack{1\leqslant\alpha\leqslant 3\\ 1\leqslant j\leqslant s}\right)} D_{a_j}\frac{\partial}{\partial r_j^\alpha}\left\{\frac{\partial F_{a_1\ldots a_s}}{\partial r_j^\alpha} + \frac{1}{\theta}F_{a_1\ldots a_s}\frac{\partial}{\partial r_j^\alpha}\left(\widetilde{u}_{a_1\ldots a_s} + \Psi_{a_1\ldots a_s}^{(\mathrm{im})}\right)\right\}$$
$$+ \sum_{\left(\substack{1\leqslant\alpha\leqslant 3\\ 1\leqslant j\leqslant s;\ 1\leqslant a_{s+1}\leqslant M}\right)} \frac{n_{a_{s+1}}}{\theta v} D_{a_j}\frac{\partial}{\partial r_j^\alpha}\int\frac{\partial}{\partial r_j^\alpha}\widetilde{u}_{a_j a_{s+1}}(\mathbf{r}_j, \mathbf{r}_{s+1})F_{a_1\ldots a_s a_{s+1}}d\mathbf{r}_{s+1}; \tag{8}$$

$$\widetilde{u}_{a_1\ldots a_s} = \sum_{\left(\substack{a_i,\, a_j\\ 1\leqslant i<j\leqslant s}\right)} \widetilde{u}_{a_i a_j}(\mathbf{r}_i, \mathbf{r}_j); \quad \Psi_{a_1\ldots a_s}^{(\mathrm{im})} = \sum_{\left(\substack{a_i\\ 1\leqslant i\leqslant s}\right)} e_{a_i}\Phi_{a_i}^{(\mathrm{im})}(x_i). \tag{9}$$

Approximate methods of solving the system of equations (8) in the general case of arbitrary electrolyte concentrations obviously reduce to using some approximate method of finding closed equations (i. e., breaking the chain) for the desired functions.

For not too large volume electrolyte concentrations, it is well to use an expansion in the Debye (plasma) parameter v/r_d^3, where $v = V/N$ is the specific volume, and r_d is the characteristic Debye length. For this purpose, we introduce instead of $F_{a_1 \ldots a_s}$, the new unknown functions as given by the relation:

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

Assuming further:

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

etc., and expanding the functions $g_a, \xi_{a_1 \ldots a_s}$ in power series in the parameter v/r_d^3, we obtain closed equations for the unary first approximation function, which, when written in the form of continuity equations, takes the form:

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

These are the usual equations of the nonequilibrium double layer in the self-consistent field approximation [5].

Subsequent approximations are found from the original system of equations (8) by taking account of the higher approximations in the parameter v/r_d^3. However, as has already been pointed out in connection with equilibrium problems, a self-consistent field approximation is rigorously correct in the range of distances $r > r_d$. But at small distances ($r \ll r_d$) and discrete structure of the charge in the layer shows up, which it is not completely legitimate to take account of here by the small parameter method in the standard form. It is therefore well for the purpose of improving the initial approximation in Eq. (8) for $s = 1$ to set $g_{ab} = g_a g_b$. If, still following our previous paper [2], we take account of the effect exerted on the structure of the diffuse double layer by polarization of the dense layer, which changes the nature of the interaction between the ions and the metal, the approximate equations of the nonequilibrium double layer, which are of an interpolational nature, take the form:

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

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

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

Unlike (12), the resulting double layer Eqs. (13)–(15) take account of the discrete structure of the charge in the diffuse double layer. It may be shown that the equations of the nonequilibrium double layer (12) characterize the asymptotic behavior of the unary distribution function, which gives complete information on the structure of the charge and the field in the double layer.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.