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## STRUCTURAL RELAXATION AND THERMOELASTIC PROPERTIES OF ELECTROLYTIC SOLUTIONS

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On the basis of the kinetic equations for the one- and two-particle distribution functions accounting the contributions of the spatial correlations of density and the correlations of velocities, we study the thermoelastic properties of electrolytic solutions. We obtained the formulas for the dynamical heat conduction coefficient  $\lambda(\omega)$  and the thermal modulus of elasticity  $Z(\omega)$  which include the contributions of the translational and structural relaxations. We studied the asymptotic behavior of the latter at low and high frequencies which completely agrees with the result obtained by the method of molecular dynamics for classical liquids. At low frequencies,  $\lambda(\omega)$  tends to its static value by the law  $\sim \omega^{1/2}$ , and  $Z(\omega)$  tends to zero as  $\sim \omega^{3/2}$ . It is established that, at high-frequency mode, the thermal modulus of elasticity does not depend on the frequency, which corresponds to the Zwanzig high-frequency modulus of elasticity for liquids, and  $\lambda(\omega)$  tends to zero proportionally to  $\omega^{-1}$ .

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### 1. Noindent

The study of the structure, the phenomenon of transfer, and elastic properties of electrolytic solutions with regard for the contributions of the internal relaxation processes, in particular of the structural relaxation, has important meaning in the theory of liquid state. In view of the wide application of solutions in various fields, especially actual are the knowledge of and the possibility to predict their thermophysical parameters describing the viscoelastic, thermoelastic, electroconductive, and acoustic properties in wide intervals of variation of the density, temperature, concentration, and frequency of the external action. A lot of experimental and theoretical works is devoted to the study of the thermoelastic properties of liquids and solutions and the nature of the thermal motion of their structural units [1–6]. The

necessary element of these studies is the determination of macroscopic parameters revealing the appearance of the thermal motion and an rearrangement of the structure in the presence of irreducible processes in liquids and their solutions. In particular, the thermoelastic properties of electrolytic solutions reflect, to the essential degree, the character of the individual and collective motions of their particles. However, only a static value of the heat conduction coefficient is measured in experiments, which does not allow one to determine the contributions of the relaxation processes, in particular that of the structural relaxation, which are significant in liquids. Moreover, it is impossible to experimentally measure the thermal modulus of elasticity of solutions which appears at high frequencies and ensures the propagation of the second sound. According to [4], few experimental results on the heat conduction are available, and no reliable theoretical model for their description is known. In works [6, 7], the formulas for the heat conduction coefficient and the high-frequency thermal modulus of elasticity in terms of the autocorrelation functions of the relevant flows are obtained. It is necessary to indicate that, namely due to the generality of autocorrelation functions, the explicit calculation of the kinetic coefficients and the high-frequency thermal modulus of elasticity in such a form is extremely difficult, because one must deal with the full  $N$ -particle problem. In works [8, 9], the phenomena of transfer in non-Newton fluids were studied by the method of molecular dynamics. In particular, the heat conduction coefficient of a Lennard-Jones fluid and the frequency dependence of the dynamical heat conduction coefficient were studied in [9]. The complex-valued heat

conduction coefficient was determined from the Fourier-transform of the correlator of a heat flow vector, whose real part is the dynamical heat conduction coefficient. It was shown that, at low frequencies, the real part of the complex-valued heat conduction coefficient obeys the law  $\omega^{1/2}$ . The main achievement of the nonequilibrium statistical theory of transfer and elastic properties of electrolytic solutions is the determination of the kinetic coefficients and the moduli of elasticity in two limiting cases of slow and fast processes. Hence, the study of the dynamical thermoelastic properties of liquids and their solutions in a wide interval of frequencies remains open. In works [10–12] on the basis of the kinetic equations for the one- and two-particle distribution functions, the thermoelastic properties of classical liquids were studied with the most complete regard for the contributions of the translational and structural relaxation processes. The analytic formulas for the dynamical heat conduction coefficient and the thermal modulus of elasticity, as well as the high-frequency propagation velocity of heat waves and the spectrum of thermal modes in simple liquids, are obtained. The goal of the present work is a generalization of those results, in particular, the search for the formulas for the heat conduction coefficient and the thermal modulus of elasticity of electrolytic solutions.

## 2. Description of the System and the Starting Kinetic Equations

The solutions of electrolytes are referred to mixed ion-molecular systems. The characteristic peculiarities of the latter consisting of ions and polar molecules are related to the mutual screening of electrostatic interactions. The most traditional approach to the description of electrolytic solutions is based on the osmos formalism, within which the study of a solution is reduced to the explicit consideration of only the ion subsystem and the elimination of the molecular one. A microscopic description of ion-molecular systems, which would be suitable in a wide interval of ion concentrations, should be based on the successive account of all possible types of interaction of all structural units forming a solution. The study of the equilibrium structure of solutions, the choice of ion-molecular potentials, and the determination of binary distribution functions of electrolytic solutions in various approximations are presented in [13]. Hence, while studying the thermoelastic properties of electrolytic solutions, the interaction potentials between structural units of a solution in various models and the equilibrium radial distribution function are considered to be known.

Let us consider the one-phase and electrically neutral inhomogeneous system of particles of three sorts: positive and negative ions of the sorts  $i, j$ , and dipole molecules of a solvent  $s$ . In the general form, we denote that by using the indices  $a$  and  $b$ . The number of the structural particles of solutions, their mass and diameter are denoted as  $N_a, m_a, d_a$  and  $N_b, m_b, d_b$ , respectively. The structural units of a solution interact through the potential  $\Phi_{ab}(|\vec{r}|, \Omega_s)$  which consists of the sum of interionic  $\Phi_{ij}$ , ion-molecular  $\Phi_{is}$  and  $\Phi_{js}$ , and intermolecular  $\Phi_{ss}$  interactions. Here,  $\vec{r} = \vec{r}_{ab}/d_{ab}$  is the reduced distance,  $\vec{r}_{ab} = \vec{q}_b - \vec{q}_a = \vec{q}_2 - \vec{q}_1$  is the interparticle distance,  $d_{ab} = (d_a + d_b)/2$  is the mean diameter of the particles of a solution,  $\Omega_s = (\vartheta_s, \alpha_s)$  are the polar angles describing the orientation of a dipole relative to the axis passing through the centers of masses of the interacting particles. The neutral medium of a solvent renders a drag to moving ions of the dissolved substance and leads to the hydration.

It is worth noting that the well-measured thermophysical parameters are the first heat conduction coefficient and the thermal modulus of elasticity conditioned by the presence of the temperature gradient in a solution. This enforces us to neglect the terms proportional to the pressure gradient (or the density gradient) in the formula for a heat flow. According to [14], this becomes possible in the case where the motion velocity of a liquid will be small in comparison with the sound velocity. Then the pressure variations arising as a result of the motion of a liquid will be so small that we can neglect the variations in the density (and in other thermodynamical quantities) induced by them. Therefore in what follows, like in [12], we restrict ourselves to the study of the dynamical thermoelastic properties of electrolytic solutions at a constant pressure with regard for the contributions of the translational and structural relaxations. In the case of a small deviation of a state of the solution from the equilibrium one, the radial symmetry, and the small spatial inhomogeneity, the components of the heat flow vector  $S^\alpha(\vec{q}_1, t)$ , which enter the equations of generalized hydrodynamics, can be microscopically presented in the form [12]

$$S^\alpha(\vec{q}_1, t) = \sum_a S_a^{k\alpha}(\vec{q}_1, t) + \sum_{a,b} \frac{d_{ab}^3}{4} \int \left( \Phi_{ab} \delta^{\alpha\beta} - \frac{r^\alpha r^\beta}{r} \frac{\partial \Phi_{ab}}{\partial r} \right) J_{ab}^\beta(\vec{q}_1, \vec{r}, t) d\vec{r}, \quad (1)$$

where

$$S_a^{k\alpha}(\vec{q}_1, t) = \frac{1}{2} \int \frac{\tilde{p}_a^2 \tilde{p}_a^\alpha}{m_a^2} f_a(\vec{x}_a, t) d\vec{p}_a \quad (2)$$

is the kinetic part of a component of the heat flow vector;  $p_a^\alpha, \tilde{p}_a^\alpha = p_a^\alpha - m_a v^\alpha(1)$  are the components of the momentum and the relative momentum of particles of the sort  $a$ ;  $v^\alpha(1) = v^\alpha(\vec{q}_1, t)$  is the mean velocity of particles;  $J_{ab}^\alpha(\vec{q}_1, \vec{r}, t) = J_{ab}^\alpha(a) + J_{ab}^\alpha(b)$  is the nonequilibrium binary flow of particles of the sorts  $a$  and  $b$ ,

$$J_{ab}^\alpha(a) = \int \frac{\tilde{p}_a^\alpha}{m_a} f_{ab}(\vec{x}_a, \vec{x}_b, t) d\vec{p}_a d\vec{p}_b, \quad (3)$$

and  $\vec{x} = (\vec{q}, \vec{p})$ . For the determination of  $J_{ab}^\alpha(b)$ , it is necessary to replace  $a$  by  $b$  in (3). Here and below, we set for convenience that the coordinates of particles  $\vec{q}_a = \vec{q}_1, \vec{q}_b = \vec{q}_2, \vec{q}_c = \vec{q}_3$ , and so on. The kinetic and potential parts in (3) are, according to (2) and (3), are the momentum moments of the one-particle  $f_a(\vec{x}_a, t)$  and two-particle  $f_{ab}(\vec{x}_a, \vec{x}_b, t)$  distribution functions of the structural units of a solution. Hence, it is necessary to have the kinetic equations for  $f_a$  and  $f_{ab}$  describing the irreducible processes running in electrolytic solutions. As the starting kinetic equations for  $f_a$  and  $f_{ab}$ , we take the equations given in [15] in order to study the viscoelastic properties of electrolytic solutions:

$$\begin{aligned} \hat{L}_1 f_a + e_a E^\alpha \frac{\partial f_a}{\partial p_a^\alpha} - \sum_b \int \Theta_{ab} f_{ab} d\vec{x}_b = \\ = \beta_a \frac{\partial}{\partial p_a^\alpha} \left[ \frac{\tilde{p}_a^\alpha}{m_a} f_a + kT \frac{\partial f_a}{\partial p_a^\alpha} \right], \end{aligned} \quad (4)$$

$$\begin{aligned} \hat{L}_{12} f_{ab} + \left( e_a \frac{\partial f_{ab}}{\partial p_a^\alpha} + e_b \frac{\partial f_{ab}}{\partial p_b^\alpha} \right) E^\alpha - \Theta_{12} f_{ab} - \\ - \sum_c \int (\hat{\Theta}_{ac} + \hat{\Theta}_{bc}) f_{abc} d\vec{x}_c = \beta_a \frac{\partial}{\partial p_a^\alpha} \left[ \frac{\tilde{p}_a^\alpha}{m_a} + \right. \\ \left. + kT \frac{\partial}{\partial p_a^\alpha} \right] f_{ab} + \beta_b \frac{\partial}{\partial p_b^\alpha} \left[ \frac{\tilde{p}_b^\alpha}{m_b} + kT \frac{\partial}{\partial p_b^\alpha} \right] f_{ab}, \end{aligned} \quad (5)$$

where

$$L_1 = \frac{\partial}{\partial t} + \frac{p_a^\alpha}{m_a} \frac{\partial}{\partial q_1^\alpha}; \quad \hat{L}_{12} = \frac{\partial}{\partial t} + \frac{p_a^\alpha}{m_a} \frac{\partial}{\partial q_1^\alpha} + \frac{p_b^\alpha}{m_b} \frac{\partial}{\partial q_2^\alpha},$$

$\hat{\Theta}_{ab} = \frac{\partial \Phi_{ab}}{\partial q_1^\alpha} \frac{\partial}{\partial p_1^\alpha} + \frac{\partial \Phi_{ab}}{\partial q_2^\alpha} \frac{\partial}{\partial p_2^\alpha}$  is the Uhlenbeck interaction operator,  $e_a = z_a e$ ,  $e_b = z_b e$ ,  $e$  is the elementary charge;  $z_a, z_b, \beta_a, \beta_b$  are the valency and the friction coefficients of particles of the sorts  $a$  and  $b$ , and  $E^\alpha = E^\alpha(\vec{q}_1, t)$  are the components of the electric field intensity. The integral terms on the left-hand sides of (4) and (5) describe the contributions of large-scale fluctuations

to relaxation processes and are the consequence of collective phenomena observed in electrolytic solutions. The right-hand sides of these equations are obtained in the approximation of pairwise interactions. They ensure the irreversibility of these equations in time, i.e., the possibility to describe the dissipative processes running in solutions. These equations are not closed in such a form. In order to close the equations for  $f_a$  and  $f_{ab}$ , it is necessary to use an additional approximation on the decomposition of the three-particle distribution function  $f_{abc}(\vec{x}_a, \vec{x}_b, \vec{x}_c, t)$ . Therefore, we take the Kirkwood superposition approximation for it, in which  $f_{abc}$  is expressed in terms of  $f_a$  and  $f_{ab}$  in the form

$$\begin{aligned} f_{abc}(\vec{x}_a, \vec{x}_b, \vec{x}_c, t) = \\ = \frac{f_{ab}(\vec{x}_a, \vec{x}_b, t) f_{ac}(\vec{x}_a, \vec{x}_c, t) f_{bc}(\vec{x}_b, \vec{x}_c, t)}{f_a(\vec{x}_a, t) f_b(\vec{x}_b, t) f_c(\vec{x}_c, t)}. \end{aligned} \quad (6)$$

The joint solution of Eqs. (4)–(6) ensures the closedness of the kinetic equations for  $f_a(\vec{x}_a, t)$  and  $f_{ab}(\vec{x}_a, \vec{x}_b, t)$ , which allows us to study of the thermoelastic properties of solutions. Multiplying Eq. (4) by  $\frac{\tilde{p}_a^\alpha \tilde{p}_a^\alpha}{2m_a^2}$ , integrating over all values of the momenta  $\vec{p}_a$ , and taking definition (2) into account, we get the equation

$$\frac{\partial S_a^{k\alpha}}{\partial t} + \frac{5 n_a k^2 T_0}{2 m_a} \frac{\partial T}{\partial q_1^\alpha} + \frac{5 k T_0}{2 m_a} \frac{\partial K_a^{\alpha\beta}}{\partial q_1^\beta} = -\frac{3\beta_a}{m_a} S_a^{k\alpha} \quad (7)$$

for the kinetic part of the component of the heat flow vector  $S_a^{k\alpha}(\vec{q}_1, t)$ . For the nonequilibrium binary flow of particles  $J_{ab}^\alpha(\vec{q}_1, \vec{r}, t)$ , we obtain the Smoluchowski equation in view of (5) with regard for definition (3) in [16]:

$$\frac{\partial J_{ab}^\alpha(\vec{q}_1, \vec{r}, t)}{\partial t} + \omega_1 J_{ab}^\alpha + \omega_2 \hat{L} J_{ab}^\alpha = Q_{ab}^\alpha(\vec{q}_1, \vec{r}, t). \quad (8)$$

Here,

$$\omega_1 = \frac{3\beta_a}{m_a}, \quad \omega_2 = \tau_{ab}^{-1} = \frac{1}{2} \frac{kT_0(\beta_a + \beta_b)}{\beta_a \beta_b d_{ab}^2},$$

$$\hat{L} = -\frac{\partial}{\partial r^\alpha} \left[ \frac{\partial}{\partial r^\alpha} - \frac{\partial}{\partial r^\alpha} \ln n_{ab}^0(r) \right]$$

is the Smoluchowski operator,

$$Q_{ab}^\alpha(\vec{q}_1, \vec{r}, t) = \omega_1 \tilde{J}_{ab}^\alpha(\vec{q}_1, \vec{r}, t),$$

$$\tilde{J}_{ab}^\alpha(\vec{q}_1, \vec{r}, t) =$$

$$= \frac{kT_0(\beta_a + \beta_b)}{\beta_a \beta_b} n_a^2 g_{ab}^0(r) \frac{r^\alpha r^\beta}{r} \frac{\partial}{\partial r} \left( \frac{\partial \ln g_{ab}^0(r)}{\partial T} \right)_p \frac{\partial T(1)}{\partial q_1^\beta} -$$

$$-\frac{kT_0(\beta_a + \beta_b)}{\beta_a\beta_b}n_a^2g_{ab}^0(r)\left(\frac{\partial \ln g_{ab}^0(r)}{\partial T}\right)_p \frac{\partial T(1)}{\partial q_1^\alpha},$$

$k$  is the Boltzmann constant,  $n_a$  and  $\beta_a$  are the density and the friction coefficient of particles of the sort  $a$ ;  $T_0$  and  $T(1) = T(\vec{q}_1, t)$  are the equilibrium and nonequilibrium temperatures, respectively,  $n_{ab}^0(r)$  is the equilibrium binary density,  $g_{ab}^0(r)$  is the radial distribution function describing the equilibrium structure of a solution. The definition of  $K_a^{\alpha\beta}(\vec{q}_1, t)$  and other parameters in (7) and (8) are given in [12]. Equation (8) is a generalized Smoluchowski equation for the binary flow of structural units of the solutions of electrolytes in the configurational space. The second term on the left-hand side of this equation describes the relaxation  $J_{ab}^\alpha$  in the momentum space. The last term on the left-hand side of (8), which is defined by the interaction of particles of a solution, is a ‘‘collision’’ term of the Smoluchowski type for the binary flow of particles. The presence of this term allows us to study the process of rearrangement of the structure of a solution under the action of a thermal deformation and ensures the account of the contribution of the structural relaxation to the thermoelastic properties of the solutions of electrolytes.

Following [12,16], we present the general solution of Eq. (8) as

$$J_{ab}^\alpha(\vec{q}_1, \vec{r}, t) = \int_0^t dt_1 \int_{-\infty}^{\infty} \Theta(r, r_1, t - t_1) Q^\alpha(\vec{q}_1, \vec{r}_1, t) d\vec{r}_1, \quad (9)$$

where  $\Theta(r, r_1, t - t_1)$  is the fundamental solution (the Green function) of Eq. (8) which describes completely the space-time behavior of the binary flow  $J_{ab}^\alpha(\vec{q}_1, \vec{r}, t)$  in the configurational space. The explicit form of the function  $\Theta(r, r_1, t - t_1)$  and its asymptotic behavior is given in [12] via the Bessel and Neumann functions defined in the space of the equilibrium radial distribution function  $g_{ab}^0(r)$ , as well as via the associated Legendre polynomials. In the case of spherical symmetry, the function  $\Theta(r, r_1, t - t_1)$  is as follows [16]:

$$\begin{aligned} \Theta(r, r_1, t - t_1) &= \frac{2(rr_1)^{-1}}{(2\pi)^3} \left( \frac{\pi}{\omega_2(t - t_1)} \right)^{1/2} \times \\ &\times \left\{ \exp\left[-\frac{(r - r_1)^2}{4\omega_2(t - t_1)}\right] - \right. \\ &\left. - \exp\left[-\frac{(r + r_1)^2}{4\omega_2(t - t_1)}\right] \right\} \exp[-\omega_1(t - t_1)]. \end{aligned} \quad (10)$$

According to (10), the fundamental solution of Eq. (8) in the case of spherical symmetry contains, besides of the diffusive part describing the process of structural relaxation, the exponentially decaying term with a characteristic frequency  $\omega_1$  conditioned by the translational relaxation. By definition (1), the components of the heat flow vector  $S^\alpha(\vec{q}_1, t)$  consist of two parts. The first part is conditioned by the transfer of the kinetic energy, and the second one by the interaction of structural units of a solution. The relaxation  $S_a^{k\alpha}(\vec{q}_1, t)$  is translational. The second part of the heat flow is defined through  $J_{ab}^\alpha(\vec{q}_1, \vec{r}, t)$ . According to (10), in addition to the structural relaxation, there is also the translational one. The exponential behavior of the decay indicates that the translational relaxation with a characteristic frequency  $\omega_1$  is a more rapid process as compared with the structural relaxation with the frequency  $\omega_2$  decaying by the law of diffusion. In order to determine only the contribution of the process of rearrangement of the structure of a solution to the potential part  $S^\alpha(\vec{q}_1, t)$ , we must average (10) over the time interval of the translational relaxation. Then the kinetic and potential parts of the heat flow are described, respectively, by the translational and structural relaxations. Hence, by averaging (10) over the characteristic time interval of the translational relaxation, we get a smoothed quantity  $\tilde{\Theta}(r, r_1, t - t_1)$  in the following form:

$$\begin{aligned} \tilde{\Theta}(r, r_1, t - t_1) &= \frac{2(rr_1)^{-1}}{(2\pi)^3} \left( \frac{\pi}{\omega_2(t - t_1)} \right)^{1/2} \times \\ &\times \left\{ \exp\left[-\frac{(r - r_1)^2}{4\omega_2(t - t_1)}\right] - \exp\left[-\frac{(r + r_1)^2}{4\omega_2(t - t_1)}\right] \right\}. \end{aligned} \quad (11)$$

At great times  $t - t_1 \rightarrow \infty$ , on the basis of (11), we obtain the long-term asymptotics of the fundamental solution of the Smoluchowski equation,

$$\tilde{\Theta}_0(r, r_1, t - t_1) = \frac{1}{4\pi} \left( \frac{\beta_a\beta_b d_{ab}^2}{2\pi k T_0(\beta_a + \beta_b)} \right)^{3/2} (t - t_1)^{-3/2}, \quad (12)$$

which coincides with the long-term asymptotics of the autocorrelation functions [9, 17, 18]. Thus, definition (1) with regard for relations (7)-(11) allows us to study the dynamical process of heat transfer in electrolytic solutions.

### 3. Thermoelastic Properties

With regard for (10), we substitute (9) and the solution of Eq. (7) for independent flows in (1) and carry out the Fourier-transformation with respect to time. Then the dynamical thermal modulus of elasticity  $Z(\omega)$  and the dynamical heat conduction coefficient  $\lambda(\omega)$  look as

$$Z(\omega) = \sum_a \frac{\frac{5}{2}\rho_a(\frac{k}{m_a})^2 T_0(\omega\tau_a)^2}{1 + (\omega\tau_a)^2} + \sum_{a,b} \frac{4\pi}{3} n_a n_b d_{ab}^3 \omega \left[ \int_0^\infty \Phi_{ab}^{(1)} r^2 dr \times \int_0^r \Theta_2(r, r_1, \omega) A_1(r_1) r_1^2 dr_1 + \int_0^\infty \Phi_{ab}^{(2)} r^2 dr \int_0^r \Theta_2(r, r_1, \omega) A_2(r_1) r_1^3 dr_1 \right], \quad (13)$$

$$\lambda(\omega) = \sum_a \frac{\frac{5}{2}\rho_a(\frac{k}{m_a})^2 T_0 \tau_a}{1 + (\omega\tau_a)^2} + \sum_{a,b} \frac{4\pi}{3} n_a n_b d_{ab}^3 \left[ \int_0^\infty \Phi_{ab}^{(1)} r^2 dr \times \int_0^r \Theta_1(r, r_1, \omega) A_1(r_1) r_1^2 dr_1 + \int_0^\infty \Phi_{ab}^{(2)} r^2 dr \int_0^r \Theta_1(r, r_1, \omega) A_2(r_1) r_1^3 dr_1 \right], \quad (14)$$

where

$$\begin{aligned} \Phi_{ab}(1) &= 3 \left( \Phi_{ab}(r) - \frac{1}{3} r \frac{d\Phi_{ab}}{dr} \right); \\ \Phi_{ab}(2) &= \Phi_{ab}(r) - r \frac{d\Phi_{ab}}{dr}; \\ \Theta_1(r, r_1, \omega) &= \\ &= A(\omega) \left[ (V(\omega) \sin \varphi_1 - U(\omega) \cos \varphi_1) e^{-\psi_1(\omega)} - \right. \\ &\left. - (V(\omega) \sin \varphi_2 - U(\omega) \cos \varphi_2) e^{-\psi_2(\omega)} \right], \\ \Theta_2(r, r_1, \omega) &= \end{aligned} \quad (15)$$

$$= -A(\omega) \left[ (U(\omega) \sin \varphi_1 + V(\omega) \cos \varphi_1) e^{-\psi_1(\omega)} - (U(\omega) \sin \varphi_2 + V(\omega) \cos \varphi_2) e^{-\psi_2(\omega)} \right], \quad (16)$$

$$A(\omega) = (4\pi r r_1)^{-1} \left[ (\omega_2/2)(\omega^2 - \omega_1^2) \right]^{-1/2};$$

$$U(\omega) = \left[ \frac{\sqrt{\omega^2 - \omega_1^2} + \omega_1}{2} \right]^{1/2};$$

$$V(\omega) = \left[ \frac{\sqrt{\omega^2 - \omega_1^2} - \omega_1}{2} \right]^{1/2};$$

$$\varphi_{1,2} = \left( \frac{2}{\omega_2} \right)^{1/2} V(\omega) (r \mp r_1);$$

$$\psi_{1,2} = \left( \frac{2}{\omega_2} \right)^{1/2} U(\omega) (r \mp r_1),$$

$$A_1(r_1) = \frac{kT_0(\beta_a + \beta_b)}{\beta_b \beta_a} \left( \frac{\partial g(r_1)}{\partial T} \right)_p;$$

$$A_2(r_1) = -\frac{kT_0(\beta_a + \beta_b)}{\beta_b \beta_a} g_{ab}^0(r_1) \frac{\partial}{\partial r_1} \left( \frac{\partial \ln g_{ab}^0(r_1)}{\partial T} \right)_p$$

$$\omega_2 = \omega_{ab} = \tau_{ab}^{-1} = \frac{kT_0(\beta_a + \beta_b)}{2\beta_b \beta_a d_{ab}^2}; \quad \omega_1 = \tau_a^{-1} = \frac{3\beta_a}{m_a};$$

and  $\Phi_{ab}(r)$  is the potential energy of the interaction of particles of a solution. Formulas (13) and (14) describe the dynamical behavior of the thermoelastic properties of electrolytic solutions in a wide range of frequencies with regard for the contributions of the collective and individual motion of particles of a solution. The frequency dependences of the dynamical heat conduction coefficient  $\lambda(\omega)$  and the dynamical thermal modulus of elasticity  $Z(\omega)$  are mainly described by the functions  $\Theta_1(r, r_1, \omega)$  and  $\Theta_2(r, r_1, \omega)$  which are defined, in turn, by formulas (15) and (16) and have a very complicated form. Consider some limiting case. Let us restrict ourselves by the region of frequencies  $\omega$  below the characteristic frequency of the translational relaxation  $\omega_1$ . Then, in all dynamical formulas, the contribution of the exponential term conditioned by the translational relaxation to  $\Theta_1(r, r_1, \omega)$  and  $\Theta_2(r, r_1, \omega)$  will be small as compared with that of the term describing the structural relaxation. This is equivalent to that we use the Fourier-transform  $\tilde{\Theta}(r, r_1, \omega)$  describing, according to (11), only the process of structural relaxation. Then we get

$$U(\omega) = V(\omega) = (\omega/2)^{1/2};$$

$$\psi_{1,2} = \varphi_{1,2} = (\omega\tau_{ab})^{1/2} (r \mp r_1),$$

$$\tilde{\Theta}_{1,2}(r, r_1, \omega) = \pm \frac{(\omega\tau_{ab})^{-1/2}}{4\pi r r_1} \times \\ \times \left[ (\sin \varphi_1 \mp \cos \varphi_1) e^{-\varphi_1} - (\sin \varphi_2 \mp \cos \varphi_2) e^{-\varphi_2} \right] \quad (17)$$

With regard for (17), formulas (13) and (14) describe the dynamical behavior of the thermoelastic properties of electrolytic solutions, which is mainly conditioned by the process of structural relaxation, in a wide range of frequencies and coincide with the earlier obtained results for classical simple liquids by the form [12]. At low frequencies, when  $\omega \rightarrow 0$ , formulas (13) and (14) with regard for (17) yield the low-frequency asymptotics of the heat conduction coefficient and the thermal modulus of elasticity for solutions as

$$\lambda(\omega) - \lambda = \omega^{1/2} \Lambda_1, \quad Z(\omega) = \omega^{3/2} \Lambda_2, \quad (18)$$

where

$$\Lambda_{1,2} = \mp \sum_{a,b} \frac{4\pi}{3} n_a n_b d_{ab}^3 \tau_{ab}^{3/2} \times \\ \times \left[ \int_0^\infty \Phi_{ab}^{(1)} r^2 dr \int_0^r A_1(r_1) r_1^2 dr_1 + \right. \\ \left. + \int_0^\infty \Phi_{ab}^{(2)} r^2 dr \int_0^r A_2(r_1) r_1^3 dr_1 \right], \\ \lambda = \sum_a \frac{5}{2} \rho_a \left( \frac{k}{m_a} \right)^2 T_0 \tau_a + \sum_{a,b} \frac{\pi k T_0}{3} \frac{\beta_a + \beta_b}{\beta_a \beta_b} n_a n_b d_{ab}^3 \times \\ \times \left\{ \int_0^\infty \Phi_{ab}^{(1)} \left( \frac{\partial g_{ab}^0}{\partial T} \right)_p r^2 dr - \right. \\ \left. - \int_0^\infty \Phi_{ab}^{(2)} \frac{\partial}{\partial r} \left[ \frac{\partial \ln g_{ab}^0(r)}{\partial T} \right]_p g_{ab}^0(r) r^3 dr \right\},$$

Here, the static heat conduction coefficient  $\lambda$  coincides with the formula obtained by J. Kirkwood and his co-authors. Relations (18) indicate that, at low frequencies, the dynamical heat conduction coefficient  $\lambda(\omega)$  tends to its static value  $\lambda$  by the law  $\omega^{1/2}$ , whereas the thermal modulus of elasticity  $Z(\omega)$  tends asymptotically to zero by the law  $\omega^{3/2}$ , which coincides with the results in [8, 9, 18]. In the other limiting case where  $\omega \rightarrow \infty$ , formulas (13) and (14) with regard for (17) yield the following high-frequency asymptotics for  $Z(\omega)$  and  $\lambda(\omega)$ :

$$Z_\infty = \sum_a \frac{5}{2} \rho_a \left( \frac{k}{m_a} \right)^2 T_0 +$$

$$+ \sum_{a,b} \frac{\pi n_a n_b}{3} d_{ab}^3 \left\{ \int_0^\infty \Phi_{ab}^{(1)} A_1(r) r^2 dr + \int_0^\infty \Phi_{ab}^{(2)} A_2(r) r^3 dr \right\},$$

$$\lambda(\omega \rightarrow \infty) = \omega^{-1} \left[ Z_\infty - \sum_a \frac{5}{2} \rho_a \left( \frac{k}{m_a} \right)^2 T_0 \right]. \quad (19)$$

According to (19), the thermal modulus of elasticity at high frequencies has a finite limiting value independent of the frequency, and the heat conduction coefficient decays by a slower law,  $\omega^{-1}$ , than that by the general relaxation theory, ( $\sim \omega^{-2}$ ). The first formula in (19) shows that, at extremely high frequencies, the solutions (liquids) possess, together with the high-frequency moduli of bulk and shear elasticities, the high-frequency thermal modulus of elasticity. Thus, formulas (13) and (14) with regard for (17) describe the frequency dispersion of the thermoelastic properties of electrolytic solutions with regard for the contributions of the relaxation processes, mainly that of the structural relaxation, and are in full agreement with the general conclusions of statistical theory.

#### 4. Choice of a Model of Solution and Execution of Numerical Calculations

The execution of numerical calculations requires the determination of the explicit form of the potential energy  $\Phi_{ab}(r)$  and the radial distribution function  $g_{ab}(r)$ . According to [13], the potential energy of a pairwise interaction between structural units of a solution has the form

$$\Phi_{ab}(r) = \sum_{i < j} \Phi_{ij}(r_{ij}) + \sum_{i,j} \Phi_s(r_{ij}) + \sum_{i < j} \Phi_{ss}(r_{ij}), \quad (20)$$

where  $\Phi_{ij}(r_{ij})$ ,  $\Phi_{is}(r_{ij})$ , and  $\Phi_{ss}(r_{ij})$  are, respectively, interionic, ion-molecular, and intermolecular interaction potentials. The determination of  $\Phi_{ab}(r)$  in the form (20) is a very difficult problem which can be solved only in some approximations on the basis of quantum-mechanical calculations.

We restrict ourselves by the case of spherical symmetry and choose the simplest semiphenomenological model of solution which is based on the osmos theory of solutions [13]. In this case, a solvent is assumed structureless (i.e., the thermal motion of the ion subsystem occurs in it). The contribution of the solvent is taken into account in the coefficients of

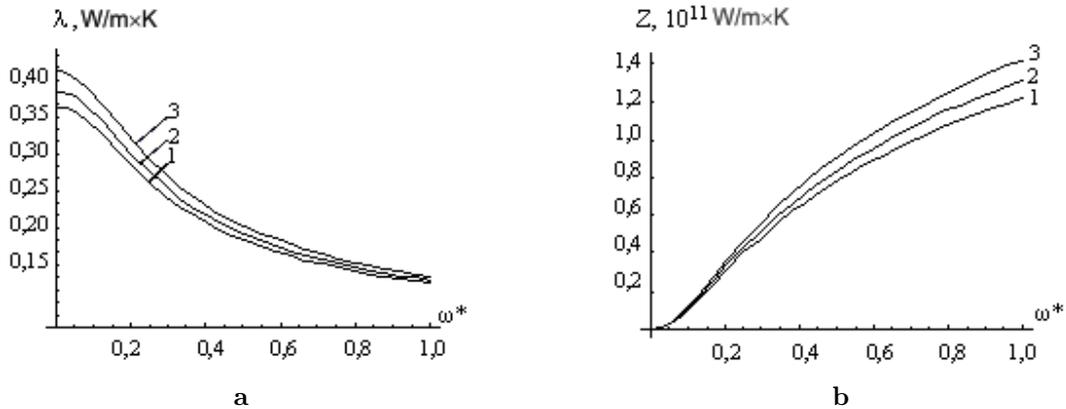


Fig. 1. Frequency dispersion of the heat conduction coefficient (a) and the thermal modulus of elasticity (b) of an aqueous solution of NaCl at  $c=0.25$  and at temperatures  $t_1 = 20$  °C,  $t_2 = 55$  °C, and  $t_3 = 90$  °C

dielectric permittivities ( $\epsilon$ ) and the friction coefficients ( $\beta_a, \beta_b$ ) of ions of the sorts  $a$  and  $b$ . The interparticle interaction potential is chosen in the form

$$\Phi_{ab}(r) = \Phi_{ab}^L(r) + \Phi_{ab}^C(r), \tag{21}$$

where  $\Phi_{ab}^L(r) = 4\epsilon_{ab} \left[ \left(\frac{d_{ab}}{r}\right)^{12} - \left(\frac{d_{ab}}{r}\right)^6 \right]$ ;  $\Phi_{ab}^C(r) = \frac{R_{ab}}{r} e^{-\kappa^* r}$ ,  $R_{ab} = \frac{f z_a z_b e^2}{kT \epsilon d_{ab}} \frac{\exp(\kappa^*)}{1 + \kappa^*}$ ;  $f = 9 \times 10^9$  F/m;  $\kappa^* = \frac{d_{ab}}{1.4 \times 10^{-12} (kT/c_a)^{1/2}}$  is the dimensionless reciprocal Debye radius;  $\vec{r} = \frac{\vec{r}_{ab}}{d_{ab}}$  is the reduced interparticle distance,  $\vec{r}_{ab} = \vec{q}_b - \vec{q}_a$  is the distance between ions,  $\epsilon$  is the dielectric permittivity of a solvent,  $e$  is the elementary charge,  $z_a$  and  $z_b$  are the valencies of ions of the sorts  $a$  and  $b$ ,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $c_a$  is the concentration of ions of the sort  $a$ .

Following [13], we write the radial distribution function of the ion subsystem in the form

$$g_{ab}(r) = y(r, \rho^*) \exp[-\Phi_{ab}(r)/kT]. \tag{22}$$

Here, for the function  $y(r, \rho^*)$ , we limited ourselves in the first approximation by its contact value obtained by Carnahan and Starling,

$$y(\rho^*) = (2 - \rho^*) / 2(1 - \rho^*)^3.$$

Here,  $\rho^* = \frac{\pi}{6} n d_{ab}^3 = \frac{\pi}{6} \frac{\rho d_{ab}^3 N_0}{M}$  is the reduced density,  $\rho$  is the solution density,  $N_0$  is the Avogadro number, and  $M$  is the molar mass.

Based on formulas (13) and (14) with regard for (17), we carried out numerical calculations in a wide range of the reduced frequency in a particular case of an

aqueous solution of NaCl. We used experimental values for the concentration  $c$  at temperatures (15 – 90) °C and the corresponding densities of a solution  $\rho$  given in [19]. The dependences of the dynamical heat conduction coefficient  $\lambda(\omega)$  and the thermal modulus of elasticity  $Z(\omega)$  on the reduced frequency  $\omega^* = \omega \tau_1 = 10^{-7} \div 1$  (at  $\tau_1 \sim 10^{-12}$  c,  $\omega \sim 10^5 \div 10^{12}$  Hz) for three temperatures  $t_1=20$  °C,  $t_2=55$  °C, and  $t_3=90$  °C and for the fixed concentration  $c=25\%$  are given in Fig. 1. It is worth to note that the behavior of all the dependences  $\lambda(\omega)$  and  $Z(\omega)$  and their order agree with the general conclusions of the statistical theory of the coefficients of transfer and the elastic properties of liquids and their solutions. However, due to the absence of experimental data, we cannot perform the quantitative comparison of the dynamical quantities  $\lambda(\omega)$  and  $Z(\omega)$ .

The results of calculations of the heat conduction coefficient  $\lambda$  at  $\omega \sim 10^7$  Hz ( $\omega^* = 10^{-5}$ ), the concentration  $c = 0.25$ , six temperatures  $t$ , and the corresponding densities  $\rho$  are given in the Table (the last column) and are compared with static values of  $\lambda$  presented in [20, 21].

On the whole, the calculated dependences of  $\lambda$  on the temperature and density are in satisfactory agreement with experiments. Apparently, a certain disagreement

$\rho$ , $10^3$ kg/m <sup>3</sup>	$t$ , °C	$\lambda$ , W/(m×K) [20]	$\lambda$ , W/(m×K) [21]	$\lambda$ , W/(m×K)
1.1661	20	0.578	0.570	0.358
1.1635	30	0.590	0.588	0.369
1.1609	35	—	0.597	0.374
1.1099	55	—	0.625	0.398
1.0937	80	—	0.645	0.409
1.0871	90	—	0.651	0.415

is conditioned by the accepted osmos approximation, since we neglected the contributions of ion-molecular and intermolecular interactions in a solution. The improvement of the model of solution and the execution of real numerical calculations by the obtained formulas describing the thermoelastic properties of electrolytic solutions will be a purpose of our further studies. We note that if the Smoluchowski "collision" term in Eq. (8) is neglected, then the nonequilibrium flow of particles  $J_{ab}^\alpha$  decays by the exponential law with a characteristic frequency  $\omega_1$ , and the formulas for the frequency dispersion of the heat conduction coefficient  $\lambda(\omega)$  and the thermal modulus of elasticity  $Z(\omega)$  are conditioned only by the contribution of the translational relaxation and coincide completely with results of the general relaxation theory.

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#### СТРУКТУРНА РЕЛАКСАЦІЯ ТА ТЕРМОПРУЖНІ ВЛАСТИВОСТІ РОЗЧИНІВ ЕЛЕКТРОЛІТІВ

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#### Резюме

На основі кінетичних рівнянь для одно- та двочастинкових функцій розподілу, які враховують внески просторової кореляції густини та кореляції швидкостей, досліджено термопружні властивості розчинів електролітів. Отримано вирази для динамічного коефіцієнта теплопровідності і термічного модуля пружності  $Z(\omega)$ , який містить внески як трансляційної, так і структурної релаксації. Досліджено асимптотичні поведінки останніх на низьких та високих частотах. Отримані результати повністю збігаються з результатами, одержаними методом молекулярної динаміки для класичних рідин. На низьких частотах  $\lambda(\omega)$  прямує до свого статичного значення за законом  $\sim \omega^{1/2}$ , а  $Z(\omega)$  — до нуля за законом  $\sim \omega^{3/2}$ . Встановлено, що у височастотному режимі термічний модуль пружності не залежить від частоти, що відповідає височастотному модулю пружності Цванціга для рідин, а  $\lambda(\omega)$  прямує до нуля пропорційно  $\omega^{-1}$ .