KINETICS OF ELECTRODE PROCESSES

III. QUANTUM-MECHANICAL THEORY. THE POLAR SOLVENT MODEL

R. R. Dogonadze and A. M. Kuznetsov

UDC 541.138

On the basis of permittivity $\varepsilon(\mathbf{k}, \omega)$, a model Hamiltonian was constructed correctly describing the polarization characteristics of a medium. The classification of polarization into fast and slow polarization types is discussed. The Hamiltonian for the medium describes excitations whose spectrum is determined by the absorption of longitudinal electromagnetic waves in the medium. Summation rules and expressions for the space-time correlation function of the fluctuations of the polarization of the medium were obtained.

On the basis of analysis of numerous experimental data, it has been found that the polarity of the medium exhibits a significant influence upon the elementary act of a chemical reaction which is accompanied by a new distribution of charge densities of the reagents. From the physical point of view, this effect is caused by a strong interaction of the charge with solvent dipoles. As far as the calculation of the reaction rate is concerned, it means that the interaction of reagents with the solvent polarization has to be taken into account in zero approximation without using the usual perturbation theory. It is known [1-3] that the most efficient method of solving such problems is the adiabatic perturbation theory (Born-Oppenheimer approximation). This theory requires that the entire system be divided into a series of subsystems which differ noticeably from each other by motion velocities or, more accurately, by "vibrational" frequencies. In order to analyze the possibility of dividing the overall polarization into the "slow" and "fast" components, the present paper discusses a pure solvent without the presence of any outside particles (e.g., ions). The state of the liquid will be described by the fluctuation (or dynamic) polarization $\mathscr{P}(\mathbf{r}, t)$ which is equal to the dipole moment of a unit volume of the medium. In the absence of external fields, the mean polarization $\langle\mathscr{P}(\mathbf{r}, t)\rangle$ is naturally zero. However, when one applies an external field described by the induction of electric field $\mathbf{D}(\mathbf{r}, t)$ the mean polarization formed in the liquid is different from zero. Within the framework of the linear theory, when the induction $\mathbf{D}$ is not too high and one can neglect the effects of dielectric saturation, there is a linear correlation between $\langle\mathscr{P}(\mathbf{r}, t)\rangle$ and $\mathbf{D}(\mathbf{r}, t)$ [4]. Since later we shall be interested in the interaction of polarization with dissolved particles, $\mathbf{D}(\mathbf{r}, t)$ may be considered to be an induction generated by a fictitious charge with a density $\rho_{\text{ext}}(\mathbf{r}, t)$ placed in the medium. Taking into consideration the relationship between polarization and the charge densities of the liquid, $\rho_{\text{med}}(\mathbf{r}, t) = -\operatorname{div} \mathscr{P}(\mathbf{r}, t)$, the interaction of the external field with the medium can be written as

$$V(t) = -\iint \frac{\rho_{\text{ext}}(\mathbf{r}', t)\operatorname{div}\mathscr{P}(\mathbf{r}, t)}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'. \tag{1}$$

If $\mathscr{P}(\mathbf{r}, t)$ is represented as a set of planar monochromatic waves which may be resolved into longitudinal and transverse components,

$$\mathscr{P}(\mathbf{r}, t) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\frac{\mathbf{k}}{|\mathbf{k}|}P_{\mathbf{k}}(t)\,e^{i\mathbf{k}\mathbf{r}} + \frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\boldsymbol{\tau}_{\mathbf{k}}P_{\mathbf{k}}^{\perp}(t)\,e^{i\mathbf{k}\mathbf{r}} \equiv \mathbf{P}(\mathbf{r}, t) + \mathbf{P}^{\perp}(\mathbf{r}, t), \tag{2}$$

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 7, No. 6, pp. 763-770, June, 1971. Original article submitted June 11, 1969.

where V is the volume of the fundamental periodicity region for the medium ($V \to \infty$), τ_k is the unit vector perpendicular to the wave vector **k**, then we obtain from Eq. (1) that the external charge interacts only with the longitudinal polarization $\mathbf{P}(\mathbf{r}, t)$ since div $\mathbf{P}^{\perp}(\mathbf{r}, t) = 0$. Using the Ostrogradskii–Gauss theorem, we can finally write for V(t) [2]

$$V(t) = -\int \mathbf{D}(\mathbf{r}, t)\,\mathbf{P}(\mathbf{r}, t)\,d\mathbf{r}. \tag{1a}$$

It is known from the quantum theory of irreversible processes [5] that

$$\langle P(\mathbf{k}, \omega)\rangle = G(k, \omega)\,D(\mathbf{k}, \omega) \equiv \frac{1}{4\pi}\left\{1 - \frac{1}{\varepsilon(k, \omega)}\right\} D(\mathbf{k}, \omega), \tag{3}$$

where

$$\begin{gathered}\langle P(\mathbf{k}, \omega)\rangle = \left\langle \frac{\mathbf{k}}{|\mathbf{k}|}\,\mathbf{P}(\mathbf{k}, \omega)\right\rangle = \int_{-\infty}^{\infty} dt\,\langle P_{\mathbf{k}}(t)\rangle\,e^{i\omega t};\\ \mathbf{D}(\mathbf{k}, \omega) = \frac{1}{\sqrt{V}}\int d\mathbf{r}\int_{-\infty}^{\infty} dt\,\mathbf{D}(\mathbf{r}, t)\,e^{-i(\mathbf{k}\mathbf{r} - \omega t)};\quad D(\mathbf{k}, \omega) = \frac{\mathbf{k}}{|\mathbf{k}|}\,\mathbf{D}(\mathbf{k}, \omega),\end{gathered} \tag{4}$$

and the longitudinal component of permittivity may be found from the equation [5]

$$\begin{gathered}G(k, \omega) = \frac{i}{\hbar}\int_{-\infty}^{\infty} \theta(t - t')\,\langle P_{\mathbf{k}}(t)\,P_{\mathbf{k}}^{+}(t') - P_{\mathbf{k}}^{+}(t')\,P_{\mathbf{k}}(t)\rangle\,e^{i\omega(t - t')}\,d(t - t');\\ \theta(\tau) = \begin{cases} 1, & \tau > 0\\ 0, & \tau \leqslant 0\end{cases}.\end{gathered} \tag{5}$$

Here the brackets denote the quantum-statistical average and the operators P_k and P_k^{+} are taken in the Heisenberg representation. From the practical point of view, the calculation of the complex functions $G(k, \omega)$ and $\varepsilon(k, \omega)$ according to the Eq. (5) presents difficulties which lie in the theory of liquids. Because of this, we shall try to derive a formalism within which a reverse problem will be given, i.e., to construct the model Hamiltonian for a liquid which would correctly describe the dielectric properties of the medium. From the formal viewpoint, such a possibility exists when one uses Eqs. (3) and (5) unequivocally relating the permittivity $\varepsilon(k, \omega)$ and the retarded Green's function (the propagation function) for longitudinal polarization waves $G(k, \omega)$ since

$$\begin{aligned}G_{\alpha\beta}(\mathbf{r} - \mathbf{r}'; t - t') &= \frac{i}{\hbar}\,\theta(t - t')\,\langle[P_{\alpha}(\mathbf{r}, t), P_{\beta}^{+}(\mathbf{r}', t')]_{-}\rangle\\ &= \frac{1}{2\pi V}\sum_{\mathbf{k}}\int_{-\infty}^{\infty} d\omega\,e^{-i[\omega(t - t') - \mathbf{k}(\mathbf{r} - \mathbf{r}')]}\,\frac{k_{\alpha}k_{\beta}}{|\mathbf{k}|^{2}}\,G(k, \omega),\end{aligned} \tag{6}$$

where the symbol [,] denotes a commutator and $\alpha, \beta = x, y, z$. From the physical viewpoint, the same expression follows from a relation of δ-like characteristics (poles) of imaginary parts Im $G(k, \omega)$ and Im $\varepsilon(k, \omega)$ with the excitation spectrum $\omega_{n'n} = E_{n'} - E_n$ (E_n are energy levels of the medium). To prove this, we may rewrite Eq. (5) in the form

$$G(k, \omega) = \sum_{n, n'} \rho_n \frac{(1 - e^{\hbar\omega_{nn'}/kT})\,|(P_{\mathbf{k}})_{nn'}|^{2}}{\hbar(\omega_{n'n} - \omega) - i\delta},\quad \delta \to +0, \tag{7}$$

where ρ_n is the Gibbs partition function. If we introduce the spectral function

$$J(k, \omega) = \sum_{n, n'} \rho_n\,|(P_{\mathbf{k}})_{nn'}|^{2}\,\delta(\hbar\omega - \hbar\omega'_{nn}) > 0, \tag{8}$$

we may write Eq. (7) in its integrated form

$$G(k, \omega) = \int_{-\infty}^{\infty} \left(1 - e^{-\frac{\hbar\omega'}{kT}}\right)\frac{J(k, \omega')}{\omega' - \omega - i\delta}\,d\omega' = \int_{0}^{\infty} \frac{2\omega'\left(1 - e^{-\frac{\hbar\omega'}{kT}}\right) J(k, \omega')}{\omega'^{2} - \omega^{2} - i\delta\,\frac{\omega}{|\omega|}}\,d\omega'. \tag{9}$$

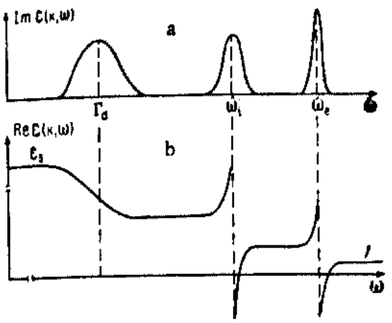

Fig. 1.

After separating out the imaginary parts in Eqs. (7) and (9), we obtain

$$\operatorname{Im} G(k,\omega)=\frac{\operatorname{Im}\varepsilon(k,\omega)}{4\pi\,|\varepsilon(k,\omega)|^2}=\pi\sum_{n,n'}\rho_n\left(1-e^{-\frac{\hbar\omega}{kT}}\right)|(P_k)_{nn'}|^2 \times\delta(\hbar\omega-\hbar\omega_{n'n})=\pi\left(1-e^{-\frac{\hbar\omega}{kT}}\right)J(k,\omega). \tag{10}$$

From (10) one can see the above-mentioned relation between Im ε (k, ω) and $\omega_{nn'}$.

Starting from the general qualitative information on the structure of liquids, one can schematically describe a characteristic course of the dependence of permittivity upon the frequency using Eqs. (7)-(10). First of all, it should be pointed out that at very high frequencies when ω is larger than any $\omega_{nn'} = E_n - E_{n'}$, it follows from (8) and (9) that G(k, ω) ≈ 0 and ε (k, ω) ≈ 1, respectively. From the physical viewpoint it is caused by the fact that the polarization of the medium is not able to adjust itself to the change of the external field when the external field frequencies are considerably higher than frequencies corresponding to the motion of all particles in the liquid; thus $\langle \mathbf{P}(\mathbf{r}, t)\rangle \simeq 0$. According to Eq. (10), at a frequency ω whose magnitude is comparable to the "frequency" ω_e of the fastest particles in the liquid, i.e., electrons, the imaginary part Im ε (k, ω) begins to increase (cf. the portion in the vicinity of ω_e, Fig. 1a). In this frequency region, there is a strong absorption of the longitudinal electromagnetic waves due to transitions between various electronic levels $\omega^e_{nn'}$. A further decrease of the frequency leads to continuous decrease of Im ε (k, ω) until ω is comparable with the highest value of intramolecular frequency of the solvent ω_i. There is practically no absorption of electromagnetic waves in the $\omega_i < \omega < \omega_e$ range and thus Im ε (k, ω) ≈ 0. Figure 1a shows only one peak for Im ε (k, ω); as a matter of fact, several such peaks (including overlaps) corresponding to the excitation of different electronic levels are possible. Also, in the vicinity of $\omega = \omega_e$ one observes a sharp change of the real part of permittivity Re ε (k, ω) which may be calculated from the dispersion relation for G(k, ω) [cf. Eqs. (9), (10)],

$$\operatorname{Re} G(k,\omega)=\frac{1}{4\pi}\left\{1-\frac{\operatorname{Re}\varepsilon(k,\omega)}{|\varepsilon(k,\omega)|^2}\right\}=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\operatorname{Im}(G(k,\omega')\,d\omega'}{\omega'-\omega} =\frac{1}{4\pi^2}\int_{-\infty}^{\infty}\frac{\operatorname{Im}\varepsilon(k,\omega')\,d\omega'}{(\omega'-\omega)\,|\varepsilon(k,\omega')|^2}=\frac{1}{2\pi^2}\int_{0}^{\infty}\frac{\omega'\operatorname{Im}\varepsilon(k,\omega')\,d\omega'}{(\omega'^2-\omega^2)\,|\varepsilon(k,\omega')|^2}. \tag{11}$$

The shape of the Re ε (k, ω) curve in the optical absorption region ($\omega \approx \omega_e$) depends on the actual form of the function Im ε (k, ω). Because of this, Fig. 1b shows only a qualitative picture which is easily obtained from Eq. (11) for a δ-like character of the spectral function J(k, ω) [and, consequently, also of Im ε (k, ω)] in the vicinity of $\omega = \omega_e$. However, the only important fact for our future discussion will be the presence of the "transparency" zone in the frequency interval $\omega_i < \omega < \omega_e$ where Im ε (k, ω) ≈ 0 and Re ε (k, ω) ≈ const = ε_0(k). From the physical viewpoint, this region is expressed by such frequencies of the external field ω at which the electrons of the medium adiabatically (without inertia) "follow" the external field while the other particles of the liquid (nuclei) "do not have time" to adjust themselves with respect to the charges of external field. In the infrared region ($\omega \sim \omega_i$) Im ε (k, ω) will exhibit one or several peaks (possibly overlapping) corresponding to the transitions between different vibrational levels of the molecules of the solvent. In all the above-described cases the absorption has a resonance character (somewhat diffuse) and the behavior of ε (k, ω) between two nearest "transparency" zones is satisfactorily approximated by the empirical equation [6]

$$\varepsilon_r(\omega)=\varepsilon_r^{+}+(\varepsilon_r^{-}-\varepsilon_r^{+})\,\frac{\omega_r^2+\Gamma_r^2-i\Gamma_r\omega}{\omega_r^2-(\omega+i\Gamma_r)^2}, \tag{12}$$

where ε_r^+ and ε_r^- are the constant values of permittivity to the right and to the left from the resonance frequency ω_r, respectively, and Γ_r determines the width of the absorption region and physically characterizes the decay time ($\tau_r = 1/\Gamma_r$) of the polarization waves possessing energy close to $\hbar\omega_r$. Finally, in the region of even lower frequencies ($\omega < \omega_i$), the excitation of rotational degrees of freedom of solvent molecules becomes important. In contrast to dipolar gases, in the case of liquids one cannot consider free rotation of molecules because of strong friction (viscosity). In other words, the decay Γ for vibrational "levels" $\hbar\omega_0$ is high ($\Gamma \gg \omega_0$). The empirical expression for $\varepsilon(\omega)$ in this region can be formally obtained from Eq. (12) assuming that $\Gamma_r \gg \omega_r, \omega$

$$\varepsilon_d(\omega) = \varepsilon_d^+ + (\varepsilon_s - \varepsilon_d^+)\frac{1}{1 - 2i\omega/\Gamma_d} \tag{13}$$

where ε_s is the statistical permittivity, and ε_d^+ is the permittivity in the nearest right-side "transparency" zone. Equation (13) coincides with the relation obtained by Debye [6] when $2/\Gamma_d$ is identified with the relaxation time ($\tau_d = 2/\Gamma_d$). The above empirical expressions (12) and (13) are in good agreement with the experimental data for water, if one uses the following basic parameter values [7]: $\varepsilon_s = 78$; $\varepsilon_d^+ = \varepsilon_r^- = 4.9$; $\varepsilon_r^+ = 1.8$; $\Gamma_d = 2.35 \cdot 10^{11}$ sec^{-1}; $\Gamma_r = 2.60 \cdot 10^{13}$ sec^{-1}; $\omega_r = 6.67 \cdot 10^{12}$ sec^{-1}.

In order to construct the model Hamiltonian for a liquid we shall proceed from the physical fact that the formation of a polarization wave P_k may be due to the excitation of various types of particle motion in the medium (electronic, nuclear, or translational)

$$P_k = \sum_\nu A_{k\nu} P_{k\nu}. \tag{14}$$

The physical meaning of the "weighting" factors $A_{k\nu}$ will be explained later. Here we shall make the fundamental assumption of the theory: we shall assume that quasi-particles $P_{k\nu}$ are nondecaying quasi-particles with energies $\hbar\omega_{k\nu}$. Introducing the origination and decay operators of the Bose type, we obtain

$$P_{k\nu} = -i\sqrt{\frac{\hbar\omega_{k\nu}}{2\Phi_{k\nu}}}(b^+_{-k\nu} + b_{k\nu}), \tag{15}$$

where $\Phi_{k\nu}$ are constants, and the Hamiltonian of the medium may be written in the form

$$H = \frac{1}{2}\sum_{k,\nu} \hbar\omega_{k\nu}(b^+_{k\nu}b_{k\nu} + b_{k\nu}b^+_{k\nu}). \tag{16}$$

In order to determine the physical meaning of the parameters $A_{k\nu}$, we shall use the Hamiltonian (16) and Eqs. (9) and (10) to calculate the functions Im $\varepsilon(k, \omega)$ and $G(k, \omega)$, respectively:

$$\frac{\mathrm{Im}\,\varepsilon(k,\omega)}{|\varepsilon(k,\omega)|^2} = 4\pi^2\omega \sum_\nu \frac{|A_{k\nu}|^2}{2\Phi_{k\nu}}\{\delta(\omega - \omega_{k\nu}) + \delta(\omega + \omega_{k\nu})\}, \tag{17}$$

$$G(k,\omega) = \sum_\nu |A_{k\nu}|^2 \frac{\omega^2_{k\nu}}{\Phi} \frac{1}{\omega_{k\nu}^2 - \omega^2 - i\delta\frac{\omega}{|\omega|}}. \tag{18}$$

As can be seen from Eqs. (16)-(18), in the adopted approximation the medium is described by a set of harmonic oscillators with frequencies $\omega_{k\nu}$ which coincide with those frequencies of the external electromagnetic field that are absorbed by the liquid. $|A_{k\nu}|^2 \cdot \omega_{k\nu}^2/e_2\Phi_{k\nu}$ plays the role of the "oscillator number" (oscillator strength) possessing the energy $\hbar\omega_{k\nu}$. It has to be stressed that, in contrast to ideal crystals in which, within the harmonic approximation, the absorption of electromagnetic waves with a given wavelength $\lambda = 2\pi/k$ occurs only at several discrete frequencies $\omega = \omega_{k\nu}$ where ν has discrete values, in liquids optically active frequency ranges are continuous, i.e., ν goes through a continuous range of values. This observation is connected with the properties of the translational symmetry of the medium. In ideal crystals containing a finite number of particles N in an elementary unit, the energy spectrum of elementary excitations breaks up into a finite number of 3N branches describing the spectrum of elementary excitations of the corresponding quasi-particles. In liquids and also in nonideal crystals (including solid solutions), where the elementary excitations are not described by planar waves because of the absence of translational symmetry, an "elementary" unit may formally comprise $N \to \infty$ particles corresponding to an infinite number of branches ν. This leads to the diffusion of the resonance and to a weak absorption in the whole frequency region [8].

In our above discussion we have derived the Hamiltonian (16) from a purely formal point of view. Here we shall present a physically more descriptive derivation based (with necessary generalizations) on the method worked out by Pitaevskii [9] in the phenomenological theory of liquid helium (He^4). For this purpose, along with the classical polarization field $\mathscr{P}(\mathbf{r})$ we shall introduce a canonically conjugate field $\mathscr{G}(\mathbf{r})$ which is directly related to the polarization current $\dot{\mathscr{P}}(\mathbf{r})$, i.e., to the rate of change of polarization in time. Considering the Hamiltonian of the medium as a functional of $\mathscr{P}_\nu(\mathbf{r})$ and $\mathscr{G}_\nu(\mathbf{r})$ where ν is the number of the branch [cf. (14)], in a harmonic approximation $\mathscr{H}$ may be represented as a functional expansion

$$\mathscr{H} = \frac{1}{2}\sum_{\substack{\nu\\ \alpha,\beta}} \iint d\mathbf{r}\, d\mathbf{r}' \{F^{\nu}_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\,\mathscr{G}_{\alpha\nu}(\mathbf{r})\,\mathscr{G}_{\beta\nu}(\mathbf{r}') + \Phi^{\nu}_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\,\mathscr{P}_{\alpha\nu}(\mathbf{r})\,\mathscr{P}_{\beta\nu}(\mathbf{r}')\}. \tag{19}$$

Here we have taken into account that, because of the homogeneity of the medium, the terms which are linear with respect to $\mathscr{P}_{\alpha\nu}$ and $\mathscr{G}_{\alpha\nu}$ must be missing in $\mathscr{H}$ and thus the functions $F_{\alpha\beta}{}^\nu$ and $\Phi_{\alpha\beta}{}^\nu$ characterizing dielectric properties of a liquid may depend only on the coordinate difference $\mathbf{r}-\mathbf{r}'$. The absence of mixed terms $\mathscr{P}_{\alpha\nu}\mathscr{G}_{\beta\nu}$ in Eq. (19) is due to invariance of $\mathscr{H}$ with respect to the inversion of the time symbol. It is worth mentioning that the nonlocal character of the Hamiltonian (19), i.e., the absence of the assumption $\Phi(\mathbf{r}-\mathbf{r}')$, $F(\mathbf{r}-\mathbf{r}') \sim \delta(\mathbf{r}-\mathbf{r}')$ is formally equivalent to taking into account directional derivatives of $\mathscr{P}$ and $\mathscr{G}$ of any order and, as we shall see later, it enables us to phenomenologically described the directional dispersion of permittivity (i.e., the dependence of ε on $\mathbf{k}$). Going to Fourier components [cf. (2)]

$$\mathscr{G}_\nu(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}} \mathscr{G}_{\mathbf{k}\nu} e^{-i\mathbf{k}\mathbf{r}};\quad F^{\nu}_{\alpha\beta}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} F^{\nu}_{\alpha\beta}(\mathbf{k})\, e^{i\mathbf{k}\mathbf{r}};$$
$$\Phi^{\nu}_{\alpha\beta}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} \Phi^{\nu}_{\alpha\beta}(\mathbf{k})\, e^{i\mathbf{k}\mathbf{r}} \tag{20}$$

and taking into consideration that for a homogeneous system the tensors $F_{\alpha\beta}{}^\nu(\mathbf{k})$ and $\Phi_{\alpha\beta}{}^\nu(\mathbf{k})$ may be expressed by scalar functions [10]

$$F^{\nu}_{\alpha\beta}(\mathbf{k}) = \frac{k_\alpha k_\beta}{k^2} F_{k\nu} + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) F^{\perp}_{k\nu};\quad \Phi^{\nu}_{\alpha\beta}(\mathbf{k}) = \frac{k_\alpha k_\beta}{k^2}\Phi_{k\nu} + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right)\Phi^{\perp}_{k\nu}, \tag{21}$$

we obtain the Hamiltonian (19) in a modified form

$$\mathscr{H} = \frac{1}{2}\sum_{\mathbf{k},\nu}\{F_{k\nu}|G_{\mathbf{k}\nu}|^2 + \Phi_{k\nu}|P_{\mathbf{k}\nu}|^2\} + \frac{1}{2}\sum_{\mathbf{k},\nu}\{F^{\perp}_{k\nu}|G^{\perp}_{\mathbf{k}\nu}|^2 + \Phi^{\perp}_{k\nu}|P^{\perp}_{\mathbf{k}\nu}|^2\} \equiv H + H^{\perp}, \tag{22}$$

where the index ⊥ corresponds to transverse components. In order to obtain the quantum Hamiltonian (16), it is sufficient to perform substitution in Eq. (22) [cf. (15)]

$$G_{\mathbf{k}\nu} = \sqrt{\hbar\Phi_{k\nu}/2\omega_{k\nu}}\,(b^-_{\mathbf{k}\nu} - b^+_{\mathbf{k}\nu});\quad \omega_{k\nu} \equiv \sqrt{F_{k\nu}\Phi_{k\nu}}. \tag{23}$$

Among all the parameters the physical meaning of $\Phi_{\mathbf{k}\nu}$ remains to be explained. In order to do this, we first calculate the space-time correlation function for the polarization

$$S_{\alpha\beta}(\mathbf{r}-\mathbf{r}';\, t-t') = \langle P_\alpha(\mathbf{r},t)\, P_\beta(\mathbf{r}',t')\rangle = 1/(2\pi)^4 \iint d\mathbf{k}\, d\omega e^{i[\mathbf{k}(\mathbf{r}-\mathbf{r}')-\omega(t-t')]}\, k_\alpha k_\beta/k^2 S(k,\omega). \tag{24}$$

It is easy to ascertain on the basis of simple calculations that $S(k,\omega)$ coincides with $J(k,\omega)$ with the accuracy up to the factor $2\pi\hbar$

$$S(k,\omega) = 2\pi\hbar J(k,\omega) = \pi\sum_{\nu}|A_{\mathbf{k}\nu}|^2 \frac{\hbar\omega_{k\nu}}{\Phi_{k\nu}}\, 1/(1 - e^{-\frac{\hbar\omega}{kT}})\{\delta(\omega-\omega_{k\nu}) - \delta(\omega+\omega_{k\nu})\}. \tag{25}$$

Thus for the Fourier component of the directional correlation function

$$S(\mathbf{r}-\mathbf{r}') = \sum_{\alpha,\beta} S_{\alpha\beta}(\mathbf{r}-\mathbf{r}';\, 0) = \langle \mathbf{P}(\mathbf{r})\,\mathbf{P}(\mathbf{r}')\rangle = \frac{1}{(2\pi)^3}\int d\mathbf{k} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\, S(k) \tag{26}$$

one obtains

$$S(k)=\frac{1}{2\pi}\int S(k,\omega)\,d\omega=\sum_{\nu}|A_{k\nu}|^{2}\frac{\hbar\omega_{k\nu}}{2\Phi_{k\nu}}\operatorname{cth}\frac{\hbar\omega_{k\nu}}{2kT}. \tag{27}$$

When the system contains only one branch, i.e., $A_{k\nu}=\delta_{\nu,\nu_0}$, $\omega_{k\nu}=\omega_k$ and $\Phi_{k\nu}=\Phi_k$, then $\Phi_k=[\hbar\omega_k/2S(k)]$ $\coth(\hbar\omega_k/2kT)$ or, for classical oscillators, $(\hbar\omega_k \ll kT)$ $\Phi_k\approx kT/S(k)$. This determines the physical meaning of the parameter $\Phi_{k\nu}$. In order to analyze Eq. (27) in more detail, we shall obtain certain summation rules following from (18). First of all, let us note that at $\omega\to 0$ Eq. (18) has the form

$$G(k,0)=\frac{1}{4\pi}\left(1-\frac{1}{\varepsilon(k,0)}\right)=\sum_{\nu}\frac{|A_{k\nu}|^{2}}{\Phi_{k\nu}}. \tag{28}$$

Along with this exact summation rule, one can write a series of approximate summation rules which will be useful in our future discussion. We will introduce

$$c_i(k)=4\pi\sum_{\nu_i}\frac{|A_{k\nu}|^{2}}{\Phi_{k\nu}}, \tag{29}$$

where the summation is over all "branches" ν lying in the i-th region of absorption [in the vicinity of the peak at the frequency ω_i, on the curve $\operatorname{Im}\varepsilon(\omega)$]. These regions will be numbered from the left to the right, i.e., $i=1$ will correspond to the Debye region of absorption, and $i=2$ to the first infrared region etc. Similarly, the permittivities in the transparency zones (where $\operatorname{Im}\varepsilon(\omega)\approx 0$) will also be numbered from the left to the right, i.e., ε_i will coincide with the statistical permittivity ε_s, and in the last transparency zone $\varepsilon_N=1$. Let us put $\omega_{i-1}\ll\omega\ll\omega_i$ in Eq. (18)

$$1-1/\varepsilon_i(k)\simeq\sum_{n=i}^{N-1}c_n(k)-\sum_{n=1}^{i-1}\sum_{\nu_n}\omega^{2}_{k\nu}/\omega^{2}\frac{|A_{k\nu}|^{2}}{\Phi_{k\nu}}=\sum_{n=i}^{N-1}c_n(k)-\sum_{n=1}^{i-1}\frac{\overleftarrow{\omega^{2}_{n}}}{\omega^{2}}c_n(k)$$

or, neglecting the last term (this can be done when $\varepsilon(k)$ exhibits only weak dependence on the frequency within the zone), we obtain

$$1-\frac{1}{\varepsilon_i(k)}=\sum_{n=i}^{N-1}c_n(k).$$

The solution of this system of equations for $c_n(k)$ has the form

$$c_n(k)=4\pi\sum_{\nu_n}\frac{|A_{k\nu}|^{2}}{\Phi_{k\nu}}=\frac{1}{\varepsilon_{n+1}(k)}-\frac{1}{\varepsilon_n(k)},\quad n=1,2,\ldots,N-1. \tag{30}$$

Let us note that the following equality follows directly from Eq. (30):

$$\sum_{i=1}^{n-1}c_i(k)=4\pi\sum_{\nu<\nu_n}\frac{|A_{k\nu}|^{2}}{\Phi_{k\nu}}=1/\varepsilon_n(k)-1/\varepsilon_s(k);\ \varepsilon_1(k)\equiv\varepsilon_s(k). \tag{31}$$

Comparing Eqs. (27) and (29), we can see that there is a close relationship between the directional correlation function S(k) and the permittivity. We may rewrite Eq. (27) in the form

$$S(k)=\sum_i S_i(k);\ S_i(k)=\sum_{\nu_i}|A_{k\nu}|^{2}\frac{\hbar\omega_{k\nu}}{2\Phi_{k\nu}}\operatorname{cth}\frac{\hbar\omega_{k\nu}}{2kT}, \tag{32}$$

where $S_i(k)$ determines the directional correlation of that part of the overall polarization which is characterized by frequencies $\omega_{k\nu_i}$. Let us first discuss the classical subsystem of full polarization ($\hbar\omega_{k\nu}\ll kT$) consisting, first of all, of the orientation part ($\omega_{k\nu}\sim\Gamma_d\sim 10^{11}$ sec^{-1}) and possibly also (partly) of infrared polarization.

$$S_i(k) = kT\frac{c_i(k)}{4\pi} = \frac{kT}{4\pi}\left[\frac{1}{\varepsilon_{i+1}(k)} - \frac{1}{\varepsilon_i(k)}\right]; \quad \hbar\omega_{k\nu} \ll kT. \tag{33}$$

If one neglects the directional dispersion of permittivity which holds in the long-wavelength approximation ($\lambda = 2\pi/k \to \infty$), i.e., if we assume $c_i(k) \approx c_i(0)$, using Eqs. (26) and (33), we obtain

$$S_i(\mathbf{r} - \mathbf{r}') \simeq \frac{kT}{4\pi} c_i(0)\,\delta(\mathbf{r} - \mathbf{r}'). \tag{34}$$

However, from the practical point of view it seems more reasonable to try to find the correlation function $S(\mathbf{r} - \mathbf{r}')$ either from experimental data or from general physical considerations and to use it to establish the dependence $c_i(k)$. Thus, substituting the δ-function in Eq. (34) by a diffuse function with a characteristic correlation radius r_0

$$S_i(\mathbf{r} - \mathbf{r}') \sim e^{-|\mathbf{r}-\mathbf{r}'|/r_0}/|\mathbf{r} - \mathbf{r}'|, \tag{35}$$

we obtain

$$c_i(k) = c_i(0) \,/\, (1 + k^2 r_0^2).$$

On the other hand, such an emprirical method may prove to be useful for checking the correctness of various approximations of correlation functions used in the theory of liquids.

For a quantum subsystem of polarization ($\hbar\omega_{k\nu} > kT$) including the electronic and partly also the infrared parts

$$S_i(k) = \sum_{\nu_i} |A_{k\nu}|^2/2\Phi_{k\nu} \cdot \hbar\omega_{k\nu}. \tag{36}$$

This means that it is possible to directly relate $S_i(k)$ and $c_i(k)$ if $\omega_{k\nu} \approx$ const. However, using general concepts, one can assume that correlation effects should be less significant for the quantum part and that, in this case, the dependence of c_i on k will be weak.

It seems necessary to make the following general comments concerning the formalism developed in the the present work. As has been shown above, all parameters of the model Hamiltonian of a liquid (16) are determined by the complex permittivity $\varepsilon(k, \omega)$ which is related to the binary correlation function of polarization [cf. Eqs. (3), (5), (9), and (25)]. On the other hand, all higher correlation functions are necessary for the calculation of kinetic parameters (e.g., rate constants) [11, 12]. Hence it is necessary to make an additional assumption that higher correlation functions "break up" into products of binary functions and in the final calculation are expressed by $\varepsilon(k, \omega)$. Such an "uncoupling" can be strictly justified only in the long-wavelength ($k \to 0$) approximation [13]. However, in subsequent papers we shall not make the assumption that $k = 0$ and shall consider the obtained results as extrapolations [9]. On the other hand, it has to be noted that in the contemporary theory of liquids various variation methods are used which are based on "decoupling" of older correlation moments (e.g., superposition approximation [14]).

LITERATURE CITED

1. W. Pauli, Exclusion Principle and Quantum Mechanics, Griffon, Neuchâtel (1947).
2. S. I. Pekar, Investigations on the Electronic Theory of Crystals [in Russian], Gostekhizdat, Moscow (1951).
3. R. R. Dogonadze and A. M. Kuznetsov, Results of Science. Electrochemistry [in Russian], All-Union Institute of Scientific and Technical Information, Moscow (1969).
4. L. D. Landau and E. M. Lifshits, Electrodynamics of Continuous Media [in Russian], Gostekhizdat, Moscow (1957).
5. V. L. Bonch-Bruevich and S. V. Tyablikov, The Method of Green's Functions in Statistical Mechanics [in Russian], Fizmatgiz, Moscow (1961).
6. H. Fröhlich, Theory of Dielectrics; Dielectric Constant and Dielectric Loss, Clarendon Press, Oxford (1949).
7. R. Saxton, Proc. Roy. Soc. (London), A213, 473 (1952).
8. I. M. Lifshits, Zh. Éksp. Teor. Fiz., 12, 117 (1942).
9. L. P. Pitaevskii, Zh. Éksp. Teor. Fiz., 31, 536 (1956).

10. M. E. Gertsenshtein, Zh. Éksp. Teor. Fiz., 22, 303 (1952).
11. A. M. Kuznetsov, Dissertation, Moscow Engineering-Physics Institute (1964).
12. A. A. Ovchinnikov and M. Ya. Ovchinnikova, Zh. Éksp. Teor. Fiz., 56, 1278 (1969).
13. A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, Methods of Quantum Field Theory in Statistical Physics [in Russian], Fizmatgiz, Moscow (1962).
14. N. N. Bogolyubov, Problems of Dynamics Theory in Statistical Physics [in Russian], Gostekhizdat, Moscow (1946).