QUANTUM-MECHANICAL MODEL OF A POLAR LIQUID

R. R. Dogonadze, A. M. Kuznetsov,
and V. G. Levich*

UDC 541.13

Analysis of a vast amount of experimental data on processes of charge transfer in polar liquids shows that the surrounding medium has a significant influence on the elementary stage of a chemical reaction accompanied by a redistribution of the charge of the reagents. Physically, this is due to the strong interaction of the charge with the polarization of the dipolar solvent. The lack of a theory of liquids at the present time makes it very difficult to carry out a detailed calculation of the kinetics of chemical reactions in solutions. As shown in [1-3], however, the calculation of the elementary stage of charge transfer in polar liquids makes possible a completely regorous quantitative description, if use is made of the continuous model of a dipolar medium. The aim of the present work was to develop a dielectric formalism within which all the properties of a polar liquid could be described by the complex dielectric constant $\varepsilon(\mathbf{k}, \omega)$, determining the nature of the propagation, in the medium, of polarization waves with wavelength $\lambda = 2\pi/|\mathbf{k}|$ and frequency ω. To obtain the classical Hamiltonian function H we use the procedure developed by Pitaevskii [4]. We shall assume that H is a function of the dynamic polarization $\mathbf{P}(\mathbf{r})$ and the canonically conjugate field $\mathbf{G}(\mathbf{r})$. In a homogeneous liquid the functional expansion of H with an accuracy up to quadratic terms may be written in the form

$$H = {}^1/_2 \int \{F_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\,G_\alpha(\mathbf{r})\,G_\beta(\mathbf{r}') + \Phi_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\,P_\alpha(\mathbf{r})\,P_\beta(\mathbf{r}')\}\,d\mathbf{r}\,d\mathbf{r}', \tag{1}$$

where the recurrent subscripts $\alpha, \beta = x, y, z$ correspond to summation and the functions $F(\mathbf{r})$ and $\Phi(\mathbf{r})$ are determined by the dielectric properties of the medium. In Eq. (1) we have omitted the constant term $H_0(\langle\mathbf{G}\rangle, \langle\mathbf{P}\rangle)$ and have taken account of the fact that the mean values $\langle\mathbf{G}\rangle = \langle\mathbf{P}\rangle = 0$. We proceed to the Fourier components:

$$\mathbf{P}(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}} \mathbf{P}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}; \quad \mathbf{G}(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}} \mathbf{G}_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{r}},$$

$$F_{\alpha\beta}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} F_{\alpha\beta}(\mathbf{k})\, e^{i\mathbf{k}\mathbf{r}}; \quad \Phi_{\alpha\beta}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} \Phi_{\alpha\beta}(\mathbf{k})\, e^{i\mathbf{k}\mathbf{r}}. \tag{2}$$

For H we obtain

$$H = \frac{1}{2}\sum_{\mathbf{k}} \{F_{\alpha\beta}(\mathbf{k})\, G_{\alpha\mathbf{k}} G^*_{\beta\mathbf{k}} + \Phi_{\alpha\beta}(\mathbf{k})\, P_{\alpha\mathbf{k}} P^*_{\beta\mathbf{k}}\}. \tag{3}$$

For a homogeneous liquid [5]

$$F_{\alpha\beta}(\mathbf{k}) = \frac{k_\alpha k_\beta}{k^2} F_\parallel(k) + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) F_\perp(k); \quad \Phi_{\alpha\beta}(\mathbf{k}) = \frac{k_\alpha k_\beta}{k^2} \Phi_\parallel(k) + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) \Phi_\perp(k), \tag{4}$$

where $F_\parallel(k)$, $\Phi_\parallel(k)$ and $F_\perp(k)$, $\Phi_\perp(k)$ determine the dielectric properties of the liquid for longitudinal ($G_k^\parallel$, $P_k^\parallel$) and transverse ($G_k^\perp$, $P_k^\perp$) polarization waves. Substitution of Eq. (4) in Eq. (3) gives

$$H = H^\parallel + H^\perp = {}^1/_2 \sum_{\mathbf{k}} \{F_\parallel(k)\,|G_{\mathbf{k}}^\parallel|^2 + \Phi_\parallel(k)\,|P_{\mathbf{k}}^\parallel|^2\} + {}^1/_2 \sum_{\mathbf{k}} \{F_\perp(k)\,|G_{\mathbf{k}}^\perp|^2 + \Phi_\perp(k)\,|P_{\mathbf{k}}^\perp|^2\}. \tag{5}$$

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*Corresponding Member, Academy of Sciences of the USSR.

Institute of Electrochemistry, Academy of Sciences of the USSR. Translated from Doklady Akademii Nauk SSSR, Vol. 188, No. 2, pp. 383-386, September, 1969. Original article submitted May 6, 1969.

Since a charge introduced into the liquid from outside reacts only with the longitudinal polarization, we shall subsequently consider only $H^{\parallel}$. The change from the classical Hamiltonian (5) to the quantum-mechanical Hamiltonian is brought about by replacing $P_k^{\parallel}$ and $G_k^{\parallel}$ by generation and annihilation operators of the Bose type:

$$P_{\mathbf{k}}^{\parallel} \to -i\left(\frac{\hbar}{2}\sqrt{\frac{F_{\parallel}(k)}{\Phi_{\parallel}(k)}}\right)^{1/2}(b_{-k}^{+}+b_k);\; G_{\mathbf{k}}^{\parallel} \to \left(\frac{\hbar}{2}\sqrt{\frac{\Phi_{\parallel}(k)}{F_{\parallel}(k)}}\right)^{1/2}(b_{-k}-b_k^{+}). \tag{6}$$

For $H^{\parallel}$ we finally obtain

$$H^{\parallel} = \frac{1}{2}\sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}}^{\parallel}(b_{\mathbf{k}}b_{\mathbf{k}}^{+}+b_{\mathbf{k}}^{+}b_{\mathbf{k}}); \quad (\omega_{\mathbf{k}}^{\parallel})^2 \equiv F_{\parallel}(k)\,\Phi_{\parallel}(k). \tag{7}$$

In order to relate the phenomenological parameters of the theory $F_{\parallel}(k)$ and $\Phi_{\parallel}(k)$ with the properties of the liquid, we calculate the complex dielectric constant $\varepsilon(\mathbf{k}, \omega)$. The functional expansion of Eq. (1) means physically that we use the linear theory for the medium. In this approximation the reaction of the medium with the induction of the external field $\mathbf{D}(\mathbf{r}, t)$ can be written in the form

$$H' = -\int \mathbf{P}^{\parallel}(\mathbf{r})\,\mathbf{D}^{\parallel}(\mathbf{r}, t)\,d\mathbf{r}. \tag{8}$$

The dielectric constant can be determined by the standard method, by calculating $<P_k^{\parallel}(\omega)> = \chi_{\parallel}(\mathbf{k}, \omega) \cdot D''(\mathbf{k}, \omega)$, where $<\ldots>$ denotes the quantum-statistical mean, and $\chi_{\parallel}(\mathbf{k}, \omega)$ is found from Eq. (6)

$$\chi_{\parallel}(k, \omega) = \frac{1}{4\pi}\left\{1-\frac{1}{\varepsilon_{\parallel}(\mathbf{k}, \omega)}\right\} = +\int_{-\infty}^{+\infty} \frac{i}{\hbar}\theta(t-t')\langle[\hat{P}_k^{\parallel}(t), \hat{P}_k^{\parallel +}(t')]_{-}\rangle$$
$$\times\, e^{i\omega(t-t_1)}\,d(t-t') = \frac{-F_{\parallel}(k)}{\omega^2-(\omega_k^{\parallel})^2+i\delta\,\mathrm{sign}\,\omega}. \tag{9}$$

From this formula it can be seen that if the function $\chi_{\parallel}(\mathbf{k}, \omega)$ (or $\varepsilon_{\parallel}(\mathbf{k}, \omega)$), is known, it is possible to find $F_{\parallel}(k)$ and $\Phi_{\parallel}(k)$. For example, by substituting $\omega = 0$ in Eq. (9), we obtain

$$\Phi_{\parallel}(k) = \frac{1}{\chi_{\parallel}(\mathbf{k}, 0)} = \frac{4\pi\varepsilon_{\parallel}(\mathbf{k}, 0)}{\varepsilon_{\parallel}(\mathbf{k}, 0)-1}. \tag{10}$$

The values of $F_{\parallel}(k)$ are found from the poles $\chi_{\parallel}(\mathbf{k}, \omega)$.

Relationship (9) makes it possible to establish criteria for the applicability of the phenomenological theory developed above. We first of all note that according to Eq. (9) in the approximation used, there is no attenuation of the polarization waves. In real liquids, the polarization waves will naturally always be attenuated. If, however, the absorption of light is resonance absorption with small width $\Gamma_r = \hbar/\tau_r$, we can still use Hamiltonian (7) in the calculation of kinetic problems. For this purpose it is necessary that the "collision" time [7] $\tau_c = \hbar(\hbar^2\omega_0^2 kTE_s)^{-1/4}$ be less than the attenuation time τ_r.

In order to make correct allowance for the attenuation of the polarization waves in Hamiltonian (7) it is necessary to include the interaction H_i between the polarization coordinates $\{P_k^{\parallel}, G_k^{\parallel}\}$ and the other internal degrees of freedom of the liquid. Within framework of the phenomenological theory this difficulty can be avoided if it is assumed that the Hamiltonian $H^{\parallel} + H_i$ can be approximately diagonalized by changing to new normal coordinates $P_{k\nu}^{\parallel}$, related to the old variables $P_k^{\parallel}$ by the linear relationship

$$P_{\mathbf{k}}^{\parallel} = \sum_{\nu} P_{\mathbf{k}\nu}A_{\mathbf{k}\nu}. \tag{11}$$

In order to understand the physical significance of the transformation (11), let us first consider the case of an ideal crystal whose unit cell contains several atoms. In this case, several optical branches arise in the frequency spectrum. In accordance with this, the function $\chi_{\parallel}(\mathbf{k}, \omega)$ should have a number of poles for a given value of $\mathbf{k}$.

This result can be obtained formally if the functional expansion of H is carried out not with respect to a single function $\mathbf{P}(\mathbf{r})$ but with respect to several functions $\mathbf{P}_\nu(\mathbf{r})$, where ν runs over as many values as there are optical branches. Thus in Eq. (11), ν in this case is taken to mean the number of the optical branch. In the examination of a liquid it can formally be assumed that the unit cell will contain $N \to \infty$ atoms, so that the number of branches should be a continuous large number. It should be emphasized that the above interpretation is justified only if nonlinear effects (subsequent terms in expansion (1)) are unimportant in the system.

For new quasiparticles, in accordance with the above condition, the Hamiltonian has the form

$$H = {}^1/_2 \sum_{\mathbf{k}\nu} \hbar\omega_{\mathbf{k}\nu} (b_{\mathbf{k}\nu} b^+_{\mathbf{k}\nu} + b^+_{\mathbf{k}\nu} b_{\mathbf{k}\nu}), \tag{12}$$

where the new operators $b_{k\nu}$ and $b_{k\nu}+$ are also Bose operators. Formally, Hamiltonian (12) is obtained most simply from the functional expansion of H with respect to $P_\nu(\mathbf{r})$ and $\mathbf{G}_\nu(\mathbf{r})$; all the above equations remain applicable, if the suffix $\mathbf{k}$ is replaced by $(\mathbf{k}, \nu)$ and summation over ν is added in the required places. In particular, in place of Eq. (9) we obtain

$$\chi_{\parallel}(\mathbf{k}, \omega) = \sum_{\nu} \frac{|A_{\mathbf{k}\nu}|^2 F_\nu(k)}{\omega^2_{\mathbf{k}\nu} - \omega^2 - i\delta \operatorname{sign}\omega}. \tag{13}$$

In this equation we change from summation over ν to integration. For this purpose we introduce the function

$$\sum_{\substack{\nu \\ (\lambda < \omega^2_{\mathbf{k}\nu} < \lambda + d\lambda)}} |A_{\mathbf{k}\nu}|^2 F_\nu(k) =: |B(\mathbf{k}, \lambda)|^2 d\lambda. \tag{14}$$

Equation (13) can then be rewritten in the form

$$\chi_{\parallel}(\mathbf{k}, \omega) = \int_0^\infty \frac{|B(\mathbf{k}, \lambda)|^2 d\lambda}{\lambda - \omega^2 - i\delta \operatorname{sign}\omega}, \tag{15}$$

or, by equating the imaginary parts, we obtain

$$\operatorname{Im}\chi_{\parallel}(\mathbf{k}, \omega) = \pi |B(\mathbf{k}, \omega^2)|^2, \qquad \omega > 0. \tag{16}$$

Although within the framework of the phenomenological theory we now cannot find $F_\nu(k)$, $\Phi_\nu(k)$, and $A_{k\nu}$ for a known function $\chi_{\parallel}(\mathbf{k}, \omega)$, we can nevertheless use Eq. (17) to determine most of the parameters of interest in kinetic problems. As an example, we show below the way in which, from a knowledge of $\chi_{\parallel}(\mathbf{k}, \omega)$, it is possible to calculate the energy of reorganization E_s — the chief parameter in the theory of charge transfer in polar media [8, 9]. First of all, we make one observation. Because of the strong interaction of the charge with the polarization, all studies at present use the adiabatic theory of perturbations, and $\mathbf{P}(\mathbf{r}, t)$ is adopted for the slow subsystem. If this treatment is to be correct, it is necessary to separate from the total polarization the so-called inertia-less part [8], which is characterized by frequencies $\omega > \omega_c$, where the order of magnitude of ω_c coincides with that of the frequency of motion of the charge undergoing redistribution during the reaction. For example, if we are dealing with processes of electron transfer, $\omega_c \sim 10^{15-16}$ sec^{-1}. This calculation procedure can be carried out formally by the replacement

$$\chi_{\parallel}(\mathbf{k}, \omega) \to \chi(\mathbf{k}, \omega) = \begin{cases} \dfrac{1}{4\pi}\left(\dfrac{1}{\varepsilon(\mathbf{k}, \omega_c)} - \dfrac{1}{\varepsilon(\mathbf{k}, \omega)}\right) \equiv \dfrac{c(k, \omega)}{4\pi}, & \omega < \omega_c. \\ 0 & \omega > \omega_c \end{cases} \tag{17}$$

Let us now proceed to the calculation of E_s. As shown in [3], E_s can be written in the form:

$$E_s = \frac{1}{2} \sum_{\mathbf{k}\nu} (\mathbf{D}^{(i)}_{\mathbf{k}} - \mathbf{D}^{(f)}_{\mathbf{k}})^2 \frac{|A_{\mathbf{k}\nu}|^2 F_\nu(k)}{\omega^2_{\mathbf{k}\nu}}, \tag{18}$$

where $D^{(i)}$ and $D^{(f)}$ represent the inductions of the charge taking part in the transition, at the start and at the end of the reaction. According to Eqs. (14) and (16), Eq. (18) can be written in the form

$$E_s = \frac{1}{\pi} \sum_{\mathbf{k}} (\mathbf{D}_{\mathbf{k}}^{(i)} - \mathbf{D}_{\mathbf{k}}^{(f)})^2 \int_0^{\omega_c} \operatorname{Im} \chi(\mathbf{k}, \omega) \frac{d\omega}{\omega}. \tag{19}$$

If it is assumed that there is almost no absorption of light at frequencies $\omega > \omega_c$, Eq. (19) can be simplified

$$E_s \simeq \frac{1}{2} \sum_{\mathbf{k}} (\mathbf{D}_{\mathbf{k}}^{(i)} - \mathbf{D}_{\mathbf{k}}^{(f)})^2 \operatorname{Re} \chi(\mathbf{k}, 0). \tag{20}$$

Finally, if we completely neglect spatial dispersion ($k \to 0$) we obtain

$$E_s \simeq \frac{c_0}{8\pi} \int (\mathbf{D}^{(i)}(\mathbf{r}) - \mathbf{D}^{(f)}(\mathbf{r}))^2 \, d\mathbf{r}, \tag{21}$$

which coincides with the result obtained by Pekar [8, 9].

In conclusion it should be noted that, strictly speaking, all the results obtained in the present work are applicable only for $k \ll 1/a$, where a represents the interatomic distances in the liquid. If, however, the function $\chi(\mathbf{k}, \omega)$ for $k \sim 1/a$ is known experimentally, the above equations can be used as interpolation equations for qualitative estimations, by analogy with the phenomenological theory of liquid helium, where the roton branch is produced at $k \sim 1/a$.

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