CONTRIBUTION TO THE THEORY OF COLLECTIVE OSCILLATIONS IN POLAR LIQUIDS

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It is shown that in polar liquids longitudinal electrostatic waves are possible; they are accompanied by oscillations of the molecule dipole moments and are not related to displacements of the molecules themselves. Together with the sound vibrations, these waves form two different branches of the collective oscillations that can propagate in polar liquids.

1. We consider in this paper collective oscillations in a liquid consisting of polar molecules. As is well known [1], in a number of cases such a liquid is distinguished by a definite order: some of the molecules of the liquid form the so called frame of the structure, corresponding to a somewhat distorted structure of the solid phase, and the remaining molecules fill the voids of the frame. In particular, such a structure is possessed by water.[1)]

The dipole moments of the molecules forming the frame of the structure are oriented (in the equilibrium state) in a strictly defined manner. In the case of water, in particular, only six equilibrium orientations are possible, and only one of these orientations is allowed for any specified aggregate of orientations of the neighboring molecules of the frame. This makes it possible to represent the frame of the polar-liquid structure by the model of a liquid polycrystal consisting of spontaneously polarized crystallites, assuming that small (but macroscopic) values of the liquid have nonzero multiple moments, and that the multipole moments of such crystallites (and not the moments of individual molecules of the frame) are randomly oriented in the absence of an external field. We shall show now that such a model of the frame of the polar-liquid structure leads to the possibility of propagation of longitudinal electric oscillations with linear dispersion law in the liquid.

2. We shall assume first that small macroscopic volumes of liquid are characterized by nonzero dipole moment, and construct the Lagrange function describing small oscillations of the dipole moments of the frame molecules. If we disturb the equilibrium distribution of the dipoles, then obviously the potential energy per unit volume increases by an amount $(\frac{1}{2})\alpha_1(\partial P_i/\partial x_j)^2$, where **P** is the polarization vector (the dipole-moment density vector) and α_1 is a constant (we shall disregard for simplicity the possibility that α_1 may have a tensor character). Noting that the energy of interaction of two dipoles $\mathbf{q}_1$ and $\mathbf{q}_2$ located at points $\mathbf{r}_1$ and $\mathbf{r}_2$ is proportional to $q_1q_2|\mathbf{r}_1-\mathbf{r}_2|^{-3}$, we can readily see that, in order of magnitude, $\alpha_1 \sim \alpha^2$, where are the dimensions of the molecules[2)]. Further, the kinetic energy of rotation of each individual dipole is $(\frac{1}{2})Jq^{-2}\dot{q}^2$, where J is its moment of inertia. Therefore the kinetic energy per unit volume should be of the form $(\frac{1}{2})\mu_1\dot{\mathbf{P}}_2$, where μ_1 is a constant equal in order of magnitude to $\sim Jn^{-1}q^{-2} \sim ma^2n^{-1}q^{-2}$ (m = mass and q = dipole moment of the molecule, n = number of molecules per unit volume). Recognizing that the energy of the dipole in an extraneous electric field $\mathbf{E}^e$ is $-\mathbf{q}\cdot\mathbf{E}^e$, we get the Lagrangian

$$L = \int d\mathbf{r}\left\{\frac{\mu_1}{2}\dot{P}^2 - \frac{\alpha_1}{2}\left(\frac{\partial \mathbf{P}}{\partial x_i}\right)^2 + \mathbf{P}\mathbf{E}^e\right\}. \qquad (1)$$

Having the Lagrangian, we can obtain the equations of motion of the vector **P** in the extraneous electric field:

$$\mu_1\ddot{\mathbf{P}} - \alpha_1\Delta\mathbf{P} = \mathbf{E}^e. \qquad (2)$$

[1)] The fraction of the molecules making up the frame of the structure increases with decreasing temperature [2] and depends essentially on the presence of dissolved substances. For water at T = 25°C the number of molecules of the frame is equal to half the total number of molecules [3].

[2)] In fact, owing to the presence of hydrogen bonds, the energy of interaction of two molecules of a polar liquid, is not equal to the energy of interaction of two dipoles (and exceeds the latter somewhat); this does not affect, however, the order-of-magnitude estimates.

Solving this equation, we get for the Fourier components of the function $\mathbf{P}$

$$\mathbf{P} = (\alpha_1 k^2 - \mu_1\omega^2)^{-1}\mathbf{E}^e. \tag{3}$$

Comparing this relation with the expression for the polarization vector in an external electric field, $\mathbf{P} = \kappa\epsilon^{-1}\mathbf{E}^e$, where κ and $\epsilon = 1 + 4\pi\kappa$ are the electric susceptibility and the dielectric constant of the system, and recognizing that $ak \ll 1$, we get

$$\varepsilon(k,\omega) = (4\pi)^{-1}\mu_1(\omega^2 - V^2k^2), \tag{4}$$

where $V^2 = \alpha_1/\mu_1$ (the field E^e is assumed longitudinal). Equating the function ϵ to zero, we see that longitudinal electric oscillations can propagate in the system, with a linear dispersion, $\omega = Vk$, and with a phase velocity on the order of $V \sim qn^{1/2}m^{-1/2}$.

3. Let us consider now a liquid in which small macroscopic volumes have nonzero quadrupole moment (but zero dipole moment). The Lagrangian has in this case the form

$$L = \int d\mathbf{r}\left\{\frac{\mu_2}{2}(\dot{D}_{ij}^2) - \frac{\alpha_2}{2}\left(\frac{\partial D_{ij}}{\partial x_l}\right)^2 + \frac{1}{6}D_{ij}\frac{1}{\partial x_i}E_j^e\right\} \tag{5}$$

where D_{ij} is the tensor of quadrupole-moment density, and α_2 and μ_2 are constants whose order of magnitude is $\alpha_2 \sim 1$ and $\mu_2 \sim Jn^{-1}Q^{-2}$ (Q^2 is the square of the quadrupole moment of the molecule). The Lagrangian (5) leads to an equation of motion for the tensor D in the form

$$\mu_2\ddot{D}_{ij} - \alpha_2\Delta D_{ij} = \frac{1}{6}\frac{\partial}{\partial x_i}E_j^e. \tag{6}$$

Solving this equation and noting that the density of the quadrupole moment D_{ij} is equivalent, from the point of view of the equations of electrostatics, to the polarization vector $P_i = (-1/6)\,\partial D_{ij}/\partial x_j$ we can readily determine the dielectric constant of the system of quadrupoles. Introducing the notation $V^2 = \alpha_2/\mu_2$ and $\nu = 1 + \pi(9\alpha_2)^{-1}$, we get

$$\varepsilon(k,\omega) = (\omega^2 - V^2k^2)(\omega^2 - \nu V^2k^2)^{-1}. \tag{7}$$

Equating the function ϵ to zero, we obtain the dispersion of the longitudinal electric oscillations, $\omega = Vk$; the phase velocity of these oscillations is of the order $V \sim Qa^{-1}n^{1/2}m^{-1/2}$.

4. Of course, in order for the oscillations in question to be weakly damped it is necessary to satisfy the condition $\omega\tau \gg 1$, where ω is the frequency of the wave and τ is the relaxation time of the dipole moments of the molecules making up the frame of the structure of the liquid. The time τ must, generally speaking, differ from the relaxation time that determines the viscosity of the liquid. We can expect τ to be close to the relaxation time τ_0 of the dipole moments of the molecules of the solid phase[3].

We emphasize that the oscillations in question represent oscillations of the dipole moments of a fraction of the molecules of the liquid, and unlike sound wave, they are not connected with the displacements of the molecules itself. Thus, these oscillations differ in principle from sound waves and form a different possible oscillation mode of a polar liquid. In some sense, these oscillations are analogous to spin waves in magnetically-ordered crystals.

We note that collective oscillations of this type can in principle take place in substances consisting of polar molecules in the solid phase, too, although in this case the oscillations of the dipole moments of the molecules are hindered by the more rigid coupling (compared with the frame of the structure of the liquid) between the molecules in the crystal lattice[4].

Longitudinal electrostatic oscillations of a polar liquid can be excited with the aid of a post antenna placed in the liquid and fed with high-frequency current. The excited longitudinal oscillations should in this case propagate along the antenna direction. We emphasize that these oscillations were different from radio waves both in polarization and in propagation velocity.

In conclusion I am grateful to A. I. Akhiezer for useful discussions.

[1] L. Pauling, The Nature of Chemical Bond, 3rd ed., Ithaca, N. Y. (1960) p. 472.

[2] H. S. Frank and A. S. Quist, J. Chem. Phys. 34, 604 (1961).

[3] M. D. Danford and H. A. Levy, J. Amer. Chem. Soc. 84, 3965 (1962).

[4] P. Debye, Polar Molecules, Dover, 1929.

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40

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[3] For ice at melting temperature, the value of τ_0 (determined from the dispersion of the transverse dielectric constant) is $\tau_0 \sim 2 \times 10^{-6}$ sec [4].

[4] In a gas consisting of polar molecules, longitudinal electric oscillations are also possible. These oscillations take place in the high frequency region, $\omega \gg \omega_R$, $\omega \gg k\bar{v}$, where $\omega_R \sim T^{1/2}J^{-1/2}$ is the average rotation frequency of the molecules and $\bar{v} \sim T^{1/2}m^{-1/2}$ is the average velocity of their thermal motion (T = temperature, m = mass, and J = moment of inertia of the molecule); they are perfectly analogous to Langmuir oscillations of a plasma, and, in particular, have an essentially nonlinear dispersion law.