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LOCALIZED EXCITONS IN A LIQUID

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A hydrodynamic theory of the motion of a localized exciton in a liquid is developed. From the microscopic point of view, a localized exciton is a specifically ordered region in the neighborhood of an electron-excited molecule which moves along with the excitation. In the hydrodynamic theory, a localized exciton is regarded as a small dense region in the liquid. Expressions are obtained in the hydrodynamic approximation for the effective mass and the friction coefficient of a localized exciton in terms of the mean self-consistent force potential restraining the exciton. Estimates for the diffusion coefficient and the relaxation time of translational motion of the exciton are also obtained.

1. INTRODUCTION

THE participation of excitons in the processes of energy transfer in molecular crystals is today not subject to doubt. The situation should be similar in dielectric liquids. For example, there is every basis for supposing that excitons are responsible for the transfer of the energy of electron excitation in liquid scintillators.[1-3] As in crystals, we must assume here the existence of two forms of excitons—"localized" and "non-localized."[4] We shall be interested only in the former. If the lifetime of an electron-excited state of the individual molecule is sufficiently long, then a realignment of near order takes place in its vicinity, brought about by the inevitable interaction between excited and normal molecules. The transfer of the excitation to a neighboring molecule brings about a corresponding motion of the entire specifically oriented region as well. Then one must imagine a process of continuous transfer of the electron excitation, accompanied all the time by a moving region of specifically ordered molecules (although the molecules themselves in this case do not undergo any transfer). It then appears that just as the motion in a crystal of the localized exciton is a transfer of the electron excitation, adiabatically accompanied by wave deformation of the lattice, so the motion in the liquid of the localized exciton is a transfer of the electron excitation adiabatically accompanied by wave ordering.

The idea of localized excitons in liquids and their role in the process of energy transfer in liquid scintillators was first suggested by Protopopov.[2,3] He proposed a model of "orientons"—quasi-particles in the liquid corresponding to specifically oriented groups of molecules, which surround the excited molecule in the scintillation solution and which are moved along with the excitation. Here the motion of the "orienton" presumes only the motion of the mode of mean orientation of the molecules, and not of the molecules themselves.

A detailed theory of localized excitons in a liquid must be constructed on the microscopic level, which at the present time is extremely difficult, in view of the general state of liquid theory. However, if it is assumed that not too small a number of molecules take part in the process of formation of the exciton simultaneously (say several dozen molecules), then one can attempt to construct a hydrodynamic theory of motion of the exciton, without studying in detail the molecular mechanism of the corresponding complicated processes. The present research is devoted to the hydrodynamic theory of motion of the localized exciton as a quasi-particle in the liquid. It will be shown that under a very small number of initial assumptions, such a theory makes it possible to determine the effective mass, the diffusion coefficient, and other kinetic characteristics of the exciton that are related to them. Application of the theory to processes in liquid scintillators will be given in a separate work.

It is assumed below that all the necessary conditions that make possible formation of a localized exciton and a sufficiently long lifetime for it have been satisfied. The analysis of experimental data show that in many cases this actually occurs.[2,3] In this connection, the remark made in[2,3] that the localized exciton in a certain sense is self-sustaining is of great interest; that is, the comparatively highly ordered vicinity of the excited molecule in a certain measure protects it from rapid extinction as a result of molecular collisions.

2. THE QUIESCENT EXCITON

From the hydrodynamic point of view, a quiescent localized exciton must represent a small region inside the liquid, distinguished from the general background by its density. We assume

$$\rho(\mathbf{r}) = \rho_0 \exp\{-\bar{\Psi}(\mathbf{r})/kT\}, \qquad (1)$$

where ρ_0 is the normal density of the liquid and $\bar{\Psi}(\mathbf{r})$ is the mean self-consistent force potential preserving the existence of the exciton. The function $\bar{\Psi}(\mathbf{r})$ must vanish rapidly upon increase in distance from the center of the exciton, and, moreover, one must assume $|\bar{\Psi}(\mathbf{r})/kT| \ll 1$ because of the small compressibility of real liquids, which makes large differences of $\rho(\mathbf{r}) - \rho_0$ impossible.

One must assume the function $\bar{\Psi}(\mathbf{r})$ to be given in the hydrodynamic theory. For simplicity, we assume that $\bar{\Psi}(\mathbf{r}) = \bar{\Psi}(|\mathbf{r}|)$. However, in principle, this function could be computed by methods of statistical physics from the (assumed) known forces of interaction of the excited molecule with the normal one and between the normal molecules themselves. Then $\bar{\Psi}(|\mathbf{r}|)$ is the smoothed (average) value of the true self-consistent potential (or local free energy) $\Psi(\mathbf{r})$ of the excess forces acting on the normal molecule in the neighborhood of the excited one, and which includes both the direct effect of the excited molecule on the normal one, and also the indirect effect which is transferred through the neighboring molecules. We shall not pause to consider this in further detail. We only note that the inequality $|\bar{\Psi}/kT| \ll 1$ refers only to the function $\bar{\Psi}$, but not to Ψ. The latter may exceed kT at isolated points, which is necessary for stability of the exciton relative to thermal fluctuations.

It follows from Eq. (1) that the force acting per unit mass on the liquid in the vicinity of the center of the exciton is equal to

$$\mathbf{K}(\mathbf{r}) = \frac{1}{\rho}\nabla p = -\frac{c^2}{kT}\nabla\bar{\Psi}(|\mathbf{r}|), \qquad (2)$$

where p is the pressure and c^2 is the value of the derivative $(\partial p/\partial\rho)_T$ (the square of the isothermal sound velocity in the liquid).

3. EFFECTIVE MASS OF THE LOCALIZED EXCITON

We consider the motion of the localized exciton in an ideal liquid. As a result of the motion the shape and structure of the exciton can change, and one must bring in corrections for the motion to Eqs. (1) and (2). We shall now write

$$\rho(\mathbf{r}) = \rho_0 \exp\left\{-\frac{\bar{\Psi}(|\mathbf{r}|)}{kT} + \sigma(\mathbf{r})\right\} \qquad (3)$$

and, correspondingly,

$$\mathbf{K}(\mathbf{r}) = -\frac{c^2}{kT}\nabla\bar{\Psi}(|\mathbf{r}|) + c^2\nabla\sigma(\mathbf{r}). \qquad (4)$$

Furthermore, as always, we shall consider motion in the system of coordinates in which the center of the exciton is at rest, so that the flow of liquid is stationary and at infinity it is uniform with velocity **U**. The equation of continuity can then be written, with the aid of (3), in the form

$$\operatorname{div}\mathbf{v} = \frac{1}{kT}\mathbf{v}\nabla\bar{\Psi}(|\mathbf{r}|) - \mathbf{v}\nabla\sigma(\mathbf{r}), \qquad (5)$$

while Euler's equation can be written in the form

$$(\mathbf{v}\nabla)\mathbf{v} = -c^2\nabla\sigma(\mathbf{r}). \qquad (6)$$

with the aid of (3) and (4). As boundary conditions, we shall require the absence of singularities in $\mathbf{v}(\mathbf{r})$ and $\sigma(\mathbf{r})$ everywhere and a rapid approach $\mathbf{v} \to \mathbf{U}$ and $\sigma \to 0$ as $|\mathbf{r}| \to \infty$.

In the case $\bar{\Psi}(|\mathbf{r}|) = 0$, we would have identically $\mathbf{v} = \mathbf{U}$ and $\sigma = 0$ everywhere. Inasmuch as $|\bar{\Psi}/kT|$ is considered as a small quantity, then **v** and σ will deviate little from their limiting values **U** and 0. If we set $\mathbf{v} = \mathbf{U} + \mathbf{v}'$ and linearize Eqs. (5) and (6) in $\mathbf{v}'$ and σ, then it is clear from Eq. (6) that the field of $\mathbf{v}'$ will be potential. We therefore write

$$\mathbf{v} = \mathbf{U} + U\nabla\varphi(\mathbf{r}). \qquad (7)$$

Furthermore, if we direct the Oz axis along the vector **U**, then the linearized equations of motion and continuity take the form

$$\frac{U^2}{c^2}\frac{\partial\varphi}{\partial z} + \sigma = 0, \qquad (8)$$

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \left(1 - \frac{U^2}{c^2}\right)\frac{\partial^2\varphi}{\partial z^2} = \frac{1}{kT}\frac{\partial\bar{\Psi}}{\partial z}. \qquad (9)$$

For very rapid motions of the exciton, when $U \sim c$, Eqs. (8) and (9) contain "relativistic" effects of distortion of the field of velocities and of the structure of the exciton as a result of the motion. In the normal case, the ratio U/c is small. For example, if we take as U the mean thermal velocity of the molecules of the liquid, then this ratio is approximately equal to the ratio of the velocity of sound in the corresponding gas to the velocity of sound in the liquid. For ordinary liquids, this ratio is of the order of 0.1, and one can neglect effects of the order of $(U^2/c^2) \sim 0.01$ in the effects occurring in our equations. Then, for slow motions of the exciton, it follows from Eq. (8) that $\sigma \approx 0$, i.e., the shape of the exciton is not changed in the motion, and for the single remaining unknown function $\varphi(\mathbf{r})$ we get the equation

$$\Delta\varphi = \frac{1}{kT}\overline{\Psi}'(r)\cos\theta, \tag{10}$$

where we have switched to spherical coordinates. As a boundary condition, we require the absence of singularities of φ over all states and the rapid vanishing of φ as $r \to \infty$.

It is easy to prove that the solution satisfying these conditions is

$$\varphi(r, \theta) = \frac{\cos\theta}{kTr^2}\int_0^r \overline{\Psi}(r)\, r^2 dr. \tag{11}$$

The field of velocities of the flow of the liquid outside and inside the exciton is then determined by Eqs. (7) and (11).

We now return to the initial set of coordinates (in which the liquid is at rest at infinity) and compute the kinetic energy of the liquid flow. We have

$$E_\mathrm{k} = {}^1\!/_2\int \rho\,(\mathbf{v} - \mathbf{U})^2\, dV \approx {}^1\!/_2\, \rho_0 U^2 \int (\nabla\varphi)^2\, dV, \tag{12}$$

where we have neglected small corrections associated with the difference of ρ and ρ_0 in the last term. The coefficient for $1/2\ U^2$ in this expression is obviously the effective mass of the localized exciton:

$$E_\mathrm{k} = {}^1\!/_2 M_\mathrm{eff} U^2, \tag{13}$$

$$M_\mathrm{eff} = \rho_0\int\left\{\left(\frac{\partial\varphi}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial\varphi}{\partial\theta}\right)^2\right\} dV, \tag{14}$$

where the function $\varphi(\mathbf{r}, \theta)$ must be taken from (11).

To estimate the effective mass, in accord with Eq. (14), we consider the very simple potential of the form

$$\overline{\Psi}(r) = \begin{cases} \varepsilon\,(r/R - 1), & r < R, \\ 0, & r > R, \end{cases} \tag{15}$$

where R and ϵ are constants with the dimensions of length and energy, respectively. We find from Eq. (11) that in this case

$$\varphi(r, \theta) = \frac{\varepsilon}{12RkT}(3r^2 - 4Rr)\cos\theta, \qquad r \leqslant R, \tag{16}$$

$$\varphi(r, \theta) = -\frac{\varepsilon R^3}{12kTr}\cos\theta, \qquad r \geqslant R, \tag{16$'$}$$

and further calculations from Eq. (14) leads to the effective mass equal to

$$M_\mathrm{eff} = \frac{2\pi}{15}\left(\frac{\varepsilon}{kT}\right)^2 \rho_0 R^3. \tag{17}$$

Since the total mass of all particles in a sphere of radius R is $M = 4\pi\rho_0 R^3/3$, we then obtain

$$M_\mathrm{eff} = {}^1\!/_{30}\,(\varepsilon/kT)^2\, M \ll M, \tag{18}$$

in connection with the assumed smallness of the ratio ϵ/kT.

It can be shown that in the real case the value of the effective mass of the localized exciton is of the order of a single molecule.

4. MOTION OF THE EXCITON IN A VISCOUS LIQUID

We now take into account the viscosity of the liquid in which our localized exciton is moving. If we start out from the Navier-Stokes equation instead of the Euler equation, then, after simple substitutions, we get the following linearized equation for the slow motions, in place of Eqs. (8) and (9):

$$\sigma = L\Delta\varphi, \tag{19}$$

$$\Delta\left(\varphi + L\frac{\partial\varphi}{\partial z}\right) = \frac{1}{kT}\frac{\partial\overline{\Psi}}{\partial z}, \tag{20}$$

where we discard terms of the order of $(U/c)^2$ and introduce a characteristic length L associated with viscosity and equal to

$$L = \frac{U}{\rho_0 c^2}\left(\frac{4}{3}\eta + \zeta\right). \tag{21}$$

Here, η and ζ are the coefficients of shear and bulk viscosity. It is evident from (19) that now, because of the viscosity, deformation of the excitons will take place even at small velocities.

Equation (20) can be solved exactly. It is not difficult to prove that the correct exact solution will be

$$\varphi(x, y, z) = \frac{1}{L}\int_{-\infty}^{z} e^{(u-z)/L}\varphi_0(x, y, u)\, du, \tag{22}$$

where φ_0 is the velocity potential of ideal flow, determined by Eq. (11). After a simple substitution of the variable of integration, we can also write

$$\varphi(x, y, z) = \int_0^\infty e^{-\tau}\varphi_0(x, y, z - L\tau)\, d\tau. \tag{23}$$

This form of writing the expression makes it easy to obtain the asymptotic series for φ in powers of L:

$$\varphi(x, y, z) = \sum_{n=0}^{\infty}(-L)^n\frac{\partial^n\varphi_0}{\partial z^n}. \tag{24}$$

Thus for vanishingly small viscosity, the resultant solution goes over continuously into the solution for the ideal liquid. For small but finite L, we get from (23) or (24)

$$\varphi(x, y, z) \approx \varphi_0(x, y, z - L). \tag{25}$$

Let us now compute the dissipation of energy of fluid flow as a result of the viscosity. From the general theory (see [5]) we have

$$-\frac{\partial E_\mathrm{k}}{\partial t} = U^2\int\left[2\eta\left(\frac{\partial^2\varphi}{\partial x_i\,\partial x_k}\right)^2 + \left(\zeta - \frac{2}{3}\eta\right)(\Delta\varphi)^2\right] dV. \tag{26}$$

Returning to the initial picture of motion of the exciton through a liquid that is motionless as a whole, we must interpret the result of (26) as the work per unit time of the friction force experienced by the exciton, equal to $\mathbf{F}_{\mathrm{fr}} = -h(-\mathbf{U})$, where $(-\mathbf{U})$ is the velocity of motion of the exciton itself, with a friction coefficient

$$h = \int \left[2\eta \left(\frac{\partial^2 \varphi}{\partial x_i \partial x_k} \right)^2 + \left(\zeta - \frac{2}{3}\eta \right) (\Delta\varphi)^2 \right] dV. \qquad (27)$$

For slow motions and small viscosity, we can, in accord with (24), replace φ by φ_0 in (27); then

$$h \cong \int \left[2\eta \left(\frac{\partial^2 \varphi_0}{\partial x_i \partial x_k} \right)^2 + \left(\zeta - \frac{2}{3}\eta \right) (\Delta\varphi_0)^2 \right] dV. \qquad (28)$$

If as an illustration we return again to the simple model of the exciton described by the potential (15), we find from (16) and (28) that

$$h = \frac{4\pi}{9} \left(\frac{59}{60}\eta + \zeta \right) \left(\frac{\varepsilon}{kT} \right)^2 R. \qquad (29)$$

It is interesting to compare the resultant equations with the Stokes formula

$$h = 6\pi\eta R^*, \qquad (30)$$

where R^* is the effective dimension of the exciton, regarded as a solid sphere. We see that in our case the friction is a result not only of the shear but also of the bulk viscosity, and that the effective collision radius of the exciton is very small. For our simple model,

$$R^* \approx \frac{2}{27} \left(\frac{\varepsilon}{kT} \right)^{'} \left(1 + \frac{\zeta}{\eta} \right) R \ll R. \qquad (31)$$

In the general case, when the ratio (L/R), where R is a linear dimension of the region occupied by the exciton, is negligibly small, replacing Eq. (27) by (28) is invalid, and the friction coefficient depends on the velocity: $h = h(U)$. For example, in this same simple model (15)—(16) using the first three terms of the asymptotic series (24), we get from the general equation (27)

$$h(U) = h_0 \left\{ 1 + 1.54 \frac{\eta - 3{,}50\zeta}{\eta + \zeta} \left(\frac{L}{R} \right)^2 + \ldots \right\}, \qquad (32)$$

where h_0 is determined from Eq. (29).

Actually, this dependence is clearly not very significant. For example, for benzene, using the tabular data for ρ_0, c, η and ζ and setting $R = 10^{-7}$ cm, for the case in which U is equal to the mean velocity for normal temperatures, we obtain from (21) that $(L/R)^2 \sim 0.1$.

5. CONCLUSION

The possibility of setting up a direct experiment for discovering localized excitons in liquids in the sense used in this paper would be of great interest. In principle, the simplest such experiments would be those having as an aim the observation of the following three effects upon irradiation of the liquid: 1) increase in density of the liquid, 2) change in the dielectric constant or of the index of refraction of the liquid, and 3) the appearance of additional light scattering. All three effects are easily calculated on the basis of the theory set forth above, but are shown to be very small for those real concentrations of excitons which can be obtained by experiment.

More realistic is the indirect way of investigation of those conseqeuences which follow from the theory relative to the kinetics and concentration dependence of processes taking place in liquid scintillators. The further development of the theory of localized excitons along the line of radioluminescence, needed for this purpose, can be based entirely on the material given above. Thus a knowledge of the effective mass and friction coefficient suffice for an estimate of the two most important kinetic characteristics of the excitons:[6] the relaxation time of the translational motion

$$\tau = M_{\mathrm{eff}}/h \qquad (33)$$

and the diffusion coefficient

$$D = kT/h = kT\tau/M_{\mathrm{eff}}. \qquad (34)$$

The experimental investigation of these same characteristics can give us some indications relative to the dimensions of the localized excitons, the depth and shape of the potential well described by the potential $\overline{\Psi}$ and so forth.

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