

Scattering of Electrons in a Liquid due to Violation of Long Range Order

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Further development of the zone theory of liquids of the author is given by the investigation of the motion of electrons in a liquid in terms of cartesian coordinates. The assumed zero approximation wave functions are similar to the Bloch functions for crystals and satisfy equations which differ from the Schrödinger equation by small terms. Scattering of the electrons in a liquid due to violation of long range order in the atomic arrangement has been calculated and the dependence of the corresponding electron mean free path on wave number has been determined for small values of the wave number.

1. INTRODUCTION

IN earlier papers of the author^{1,2} it was shown theoretically that, for slight violation of local order in a crystal and disappearance of long range order, i.e., upon melting of the crystal, the energy spectrum of the electrons possesses a zone structure. The calculation was carried out in a distorted coordinate system ξ_1, ξ_2, ξ_3 such that in it the self-consistent potential of the electron in the liquid $V(\xi_1, \xi_2, \xi_3)$ is a periodic function of the cartesian coordinates x_1, x_2, x_3 . It was shown that, in the system of coordinates ξ the solution of the wave equation could be constructed from Bloch wave functions of the type

$$\psi_{\kappa} = G^{-3/2} u_{\kappa}(\xi_1, \xi_2, \xi_3) \exp \left\{ i \sum_{\alpha=1}^3 x_{\alpha} \xi_{\alpha} \right\}, \quad (1)$$

where $u_{\kappa}(\xi_1, \xi_2, \xi_3)$ is a function of the same periodicity as $V(\xi_1, \xi_2, \xi_3)$. The factor $G^{-3/2}$ appears because, for convenience in later calculations, the functions ψ_{κ} are normalized for the base region, which consists of G^3 elementary cells, and the function u_{κ} is normalized for a single elementary cell.

The stationary solution is a wave packet which consists of functions (1) and which moves progressively. Thus the disappearance of long range order has an unimportant effect on the energy spectrum of the electrons in the body and on the character of their motion. However, the disappearance of strict periodicity in the position of the atoms ought to lead to additional scattering of electrons, to a decrease in their mean free path, and to an increase in resistance. As was noted by Wilson³, the resistance of a liquid with electronic conductivity will be determined in part by the disorder of the regular positions of the atoms and in part from the thermal vibrations of the lattice.

We call the first component of resistance the "liquid" resistance, and the second component the "phonon" resistance.

Wilson³ obtained the ratio for the conductivity in the solid and liquid phases close to the melting point for a series of metals, and tried to explain the higher resistance upon liquefaction by a change in the Debye temperature θ which enters into the expression for the mean free path, assuming that the other quantities do not change appreciably during the melting process. For several metals, the agreement between the ratio of conductivities calculated by such a method and those obtained experimentally were satisfactory. However, for mercury the experimentally measured ratio was 4.1, the computed value, 2.23. Consequently, there is here an appreciable amount of an additional mechanism for the scattering of the electrons—the "liquid" resistance. It is not accidental that this resistance was specifically observed in mercury; actually, mercury liquefies at a low temperature, at which point the lattice vibrations are not very intense. One can assume that in other metals, which liquefy at much higher temperature, the "liquid" resistance is masked by the phonon resistance.

In the present work it is proposed to estimate the length of the mean free path of the electron in a liquid which is characterized by violations of long range order, i.e., by the "liquid" scattering of the electrons. The value of this length of mean free path allows us to compute, as is customary in a theory of electrical conductivity, the "liquid" resistance which ought to play a fundamental role at low temperatures in liquids with electronic conductivity. At high temperatures, this resistance is perhaps only a small correction to the ordinary phonon resistance; nevertheless, the existence of "liquid" resistance has a value in principle.

In carrying out the calculation, we do not take into account the thermal vibrations of the lattice and its local distortions, assuming that the length

of the free path is determined only by the violation of long range order.

Computation of the mean path length encounters the difficulty that in cartesian coordinates x the deviation from a periodic potential is large, and it is therefore not possible to use perturbation theory, employing the ordinary Bloch functions for the zeroth approximation. In the system of coordinates ξ where, as was shown in Refs. 1 and 2, the perturbation is small, it is difficult to describe the motion of the electron in the external field, since the homogeneous electrical field in the system ξ has varying components. Therefore, we solve the problem of the motion of the electron in the liquid, i.e., in a quasi-periodic potential, in rectangular coordinates, but as a zeroth approximation, we use, not the ordinary Bloch functions, but the quasi-Bloch functions of the form

$$\psi_k = G^{-3/2} u_k(\xi_1, \xi_2, \xi_3) e^{ikr}, \quad (2)$$

where u_k is a quasi-periodic function of the deformed coordinates ξ_1, ξ_2, ξ_3 . We note that the functions (2) are essentially different from (1) since

$$\sum_{\alpha=1}^3 x_{\alpha} \xi_{\alpha} \neq kr,$$

because the coordinates ξ_{α} are not cartesian.

2. CONSIDERATION OF THE MOTION OF AN ELECTRON IN A LIQUID IN CARTESIAN COORDINATES

We shall show that the quasi-Bloch functions (2) satisfy an equation which differs from the Schrödinger equation only in small terms of order ϵ - the degree of violation of local order in the melting of the crystal. For simplicity we first turn to the one-dimensional case, where the quasi-Bloch function has the form

$$\psi_k = G^{-1/2} u_k(\xi) e^{ikhx}, \quad (3)$$

where, in the one-dimensional case, the modulating function u_k is a strictly periodic function of ξ .

Substitution of the ordinary Bloch function $\psi_k = u_k(x) e^{ikx}$ in the Schrödinger equation for the crystal, i.e., for periodic $V(x)$, gives the following equation for the function $u_k(x)$ which is periodic in x :

$$\begin{aligned} d^2 u_k / dx^2 + 2ik du_k / dx \\ - (k^2 + \tilde{V} - \tilde{E}) u_k = 0, \end{aligned} \quad (4)$$

where, for brevity, we write

$$\tilde{V} = 2mV / \hbar^2; \quad \tilde{E} = 2mE / \hbar^2; \quad (5)$$

E is the total energy of the electron. It can be shown that for a periodic $V(\xi)$, the periodic function $u_k(\xi)$ satisfies the equation

$$\begin{aligned} d^2 u_k / d\xi^2 + 2ik du_k / d\xi \\ - (k^2 + \tilde{V} - \tilde{E}) u_k = 0. \end{aligned} \quad (6)$$

However, since ξ is not a cartesian coordinate, Eq. (6), in contrast to (4), is not an exact consequence of the Schrödinger equation.

We transform in Eq. (6) from ξ to x , setting, as in Ref. 1,

$$dx / d\xi = 1 + \epsilon\gamma, \quad (7)$$

where ϵ is a small quantity (the degree of violation of local order), and γ is an arbitrary function of the coordinates, of order of magnitude unity. As a result, we obtain

$$\begin{aligned} (1 + \epsilon\gamma)^2 \frac{d^2 u_k}{dx^2} + (1 + \epsilon\gamma) \left(2ik + \epsilon \frac{d\gamma}{dx} \right) \frac{du_k}{dx} \\ - (k^2 + \tilde{V} - \tilde{E}) u_k = 0. \end{aligned} \quad (8)$$

Multiplying Eqs. (4) and (8) by $(\hbar^2/2m)G^{-1/2}e^{ikx}$, we get the expressions $\hat{H}\psi_k = E_k\psi_k$ and $\hat{H}_0^k\psi_k = E_k\psi_k$, respectively. Here, comparing (4) and (8), one can be convinced that

$$\hat{H}\psi_k = \hat{H}_0^k\psi_k + \epsilon\hat{W}^k\psi_k + \epsilon^2\hat{\omega}^k\psi_k; \quad (9)$$

$$\hat{H}_0^k\psi_k = \frac{\hbar^2}{2mVG} \left[(1 + \epsilon\gamma)^2 \frac{d^2 u_k}{dx^2} \right. \quad (10)$$

$$\left. + (1 + \epsilon\gamma) \left(2ik + \epsilon \frac{d\gamma}{dx} \right) \frac{du_k}{dx} - (k^2 + \tilde{V}) u_k \right] e^{ikhx};$$

$$\hat{W}^k\psi_k \quad (11)$$

$$= - \frac{\hbar^2}{2mVG} \left[2\gamma \frac{d^2 u_k}{dx^2} + \left(2ik\gamma + \frac{d\gamma}{dx} \right) \frac{du_k}{dx} \right] e^{ikhx};$$

$$\hat{\omega}^k\psi_k = - \frac{\hbar^2}{2mVG} \left[\gamma^2 \frac{d^2 u_k}{dx^2} + \gamma \frac{d\gamma}{dx} \frac{du_k}{dx} \right] e^{ikhx}. \quad (12)$$

We see that the actual functions (3) satisfy equations which differ from the Schrödinger equation only by small terms. The equation $\hat{H}_0^k\psi_k = E_k\psi_k$ can be considered as the equation of

zeroth approximation, and the operators $\epsilon \hat{W}^k$ and $\epsilon^2 \hat{W}^k$ as the perturbation. Integrating by parts the products $(d^2 u_k / dx^2) e^{ikx}$ and $(du_k / dx) e^{ikx}$ in Eqs. (10)-(12), we can obtain expressions for the same operators; however, in what follows the expressions (10)-(12) are required directly.

The three-dimensional case can be similarly treated. The following equation for the periodic function $u_k(x_1, x_2, x_3)$ can be obtained from the Schrödinger equation:

$$\sum_{\alpha=1}^3 \frac{\partial^2 u_k}{\partial x_\alpha^2} + 2ik \cdot \sum_{\alpha=1}^3 i_\alpha \frac{\partial u_k}{\partial x_\alpha} - (k^2 + \tilde{V} - \tilde{E}) u_k = 0, \quad (13)$$

where i_α is the position of the coordinate axis x_α . Substituting x_α for ξ_α here, we get an equation which is entirely analogous to the one-dimensional case Eq. (6):

$$\sum_{\alpha=1}^3 \frac{\partial^2 u_k}{\partial \xi_\alpha^2} + 2ik \cdot \sum_{\alpha=1}^3 e_\alpha \frac{\partial u_k}{\partial \xi_\alpha} - (k^2 + \tilde{V} - E) u_k = 0, \quad (14)$$

where e_α is the site tangent to the coordinate line ξ_α . But, in contrast to the one-dimensional case, the solutions of Eq. (14) will not be strictly periodic functions of ξ_α . Actually, while the vector \mathbf{k} has a constant direction, the vectors \mathbf{e}_α have different directions in the various elementary cells. However, the direction of \mathbf{e}_α changes slowly from cell to cell; therefore, the u_k will be quasi-periodic functions of ξ_α in the sense that the values of u_k at corresponding points of neighboring cells will be equal to one another with accuracy to small order of ϵ . But even in cells that are distant from one another, the values of u_k will differ only slightly. It follows from Eq. (14) that they are as much different as the u_k in the ordinary Bloch functions, which correspond to identical absolute values, but to different directions of the vector \mathbf{k} . This difference is usually neglected in the theory of metals (see, for example, Bethe and Sommerfeld, Ref. 4, p. 188).

We transform in Eq. (14) from the coordinates ξ to the coordinates x ; after simple calculation, we obtain

$$\sum_{\beta=1}^3 \left\{ \sum_{\gamma=1}^3 \frac{\partial^2 u_k}{\partial x_\beta \partial x_\gamma} \sum_{\alpha=1}^3 \frac{\partial x_\beta}{\partial \xi_\alpha} \frac{\partial x_\gamma}{\partial \xi_\alpha} + \frac{\partial u_k}{\partial x_\beta} \left[\sum_{\alpha=1}^3 \frac{\partial^2 x_\beta}{\partial \xi_\alpha^2} + 2i \sum_{\gamma=1}^3 k_\gamma \sum_{\alpha=1}^3 \left[\sum_{x=1}^3 \left(\frac{\partial x_x}{\partial \xi_\alpha} \right)^2 \right]^{-1/2} \frac{\partial x_\beta}{\partial \xi_\alpha} \frac{\partial x_\gamma}{\partial \xi_\alpha} \right] \right\} \quad (15)$$

$$- (k^2 + \tilde{V} - E) u_k = 0.$$

If we neglect quantities of order ϵ , then in the limits of each elementary cell we can regard the system of coordinates ξ as a cartesian system, rotated relative to the system x . But then

$$\partial x_\beta / \partial \xi_\alpha = \cos(x_\beta, \xi_\alpha); \quad \partial^2 x_\beta / \partial \xi_\alpha^2 = 0;$$

$$\sum_{\alpha=1}^3 \frac{\partial x_\beta}{\partial \xi_\alpha} \frac{\partial x_\gamma}{\partial \xi_\alpha} = \cos(x_\beta, x_\gamma) = \delta_{\beta\gamma}; \quad \sum_{x=1}^3 \left(\frac{\partial x_x}{\partial \xi_\alpha} \right)^2 = 1.$$

Taking into account terms of order ϵ , we can set

$$\sum_{\alpha=1}^3 \frac{\partial x_\beta}{\partial \xi_\alpha} \frac{\partial x_\gamma}{\partial \xi_\alpha} = \delta_{\beta\gamma} + \epsilon \gamma_{\beta\gamma}; \quad \sum_{\alpha=1}^3 \frac{\partial^2 x_\beta}{\partial \xi_\alpha^2} = \frac{\epsilon \gamma_\beta}{a}; \quad (16)$$

$$\sum_{\alpha=1}^3 \left[\sum_{x=1}^3 \left(\frac{\partial x_x}{\partial \xi_\alpha} \right)^2 \right]^{-1/2} \frac{\partial x_\beta}{\partial \xi_\alpha} \frac{\partial x_\gamma}{\partial \xi_\alpha} = \delta_{\beta\gamma} + \epsilon \Gamma_{\beta\gamma}.$$

Here $\gamma_{\beta\gamma}$, γ_β and $\Gamma_{\beta\gamma}$ are arbitrary functions of the coordinates, which have order unity. They are determined somewhat differently than the functions $\gamma_{\beta\gamma}$ in Ref. 2, but possess the same properties, with the exception that here the mean values of $\gamma_{\beta\gamma}$ and $\Gamma_{\beta\gamma}$ cannot be simultaneously equated to zero; a is the lattice constant.

Substitution of Eq. (16) in Eq. (15) allows us to obtain our equation in the form

$$\hat{H}_0^k \psi_k = E_k \psi_k, \quad (17)$$

$$\hat{H}_0^k \psi_k \quad (18)$$

$$= \frac{\hbar^2}{2mG^{3/2}} \left[\sum_{\beta=1}^3 \left(\frac{\partial^2 u_k}{\partial x_\beta^2} + 2ik_\beta \frac{\partial u_k}{\partial x_\beta} \right) - (\tilde{V} + k^2) u_k + \epsilon \sum_{\beta=1}^3 \sum_{\gamma=1}^3 \left(\frac{\partial^2 u_k}{\partial x_\beta \partial x_\gamma} \gamma_{\beta\gamma} + 2ik_\gamma \frac{\partial u_k}{\partial x_\beta} \Gamma_{\beta\gamma} \right) + \frac{\epsilon}{a} \sum_{\beta=1}^3 \frac{\partial u_k}{\partial x_\beta} \gamma_\beta \right] e^{ikr}.$$

Comparing this with the actual expression for $\hat{H} \psi_k$, we conclude that

$$\hat{H} \psi_k = \hat{H}_0^k \psi_k + \epsilon \hat{W}^k \psi_k; \quad (19)$$

$$\hat{W}^k \psi_k = -\frac{\hbar^2}{2mG^{3/2}} \left[\sum_{\beta=1}^3 \sum_{\gamma=1}^3 \left(\frac{\partial^2 u_k}{\partial x_\beta \partial x_\gamma} \gamma_{\beta\gamma} + 2ik_\gamma \frac{\partial u_k}{\partial x_\beta} \Gamma_{\beta\gamma} \right) + \frac{1}{a} \sum_{\beta=1}^3 \frac{\partial u_k}{\partial x_\beta} \gamma_\beta \right] e^{ikr}. \quad (20)$$

In contrast to the one-dimensional case, the operator proportional to ϵ^2 is absent here. It is included as a factor in the operator $\epsilon \hat{W}^k$ and is obtained explicitly if we express $\Gamma_{\beta\gamma}$ by $\gamma_{\beta\gamma}$, which would appear to be an unnecessary complication. As in the one-dimensional case, we can, upon integrating by parts, obtain an expression for the operators \hat{H}_0^k and \hat{W}^k , but we shall not do this, inasmuch as the expressions $\hat{H}_0^k \psi_k$ and $\hat{W}^k \psi_k$ are used directly in what follows. We note only that the operators \hat{H}_0^k and \hat{W}^k depend on \mathbf{k} .

It is important to note that the functions (2) describe the motion of quasi-free electrons in a liquid in entirely the same way as the Bloch functions describe the quasi-free electrons in the crystal. The acceleration of the wave packet in an external field is computed in the same way, and one can use the method of the effective mass. Actually, the relation between the velocity and the energy of the electron, and also between the acceleration and the actual force, can be obtained without using the periodic function u_k , but only its property that they change slowly in their dependence on \mathbf{k} (Seitz⁵, pp. 332-336). But, by virtue of the identity of the Eqs. (13) and (14), the dependence on \mathbf{k} of the quasi-periodic functions u_k that we have introduced is the same as for ordinary periodic functions. Consequently, all the positions of the Bloch scheme are used in the case under consideration.

Since the operators \hat{H}_0^k are not self-adjoint and depend on \mathbf{k} , the problem of the orthogonality of their eigenfunctions ψ_k must be considered. For this purpose, as usual, we write down Eq. (17) for the functions ψ_k and ψ_k^* ; multiplying the first of these equations by ψ_k^* and the second by ψ_k , carry out integration over all space and subtract one from the other. As a result, we obtain

$$\int (\psi_k^* \hat{H}_0^k \psi_k - \psi_k \hat{H}_0^{k'} \psi_k^*) d\tau \quad (21)$$

$$= (E_k - E_{k'}) \int \psi_k^* \psi_k d\tau.$$

Substituting $\hat{H}_0^k = \hat{H} - \epsilon \hat{W}^k$ here, and making use of the self-adjoint property of the operator \hat{H} , we get

$$(E_k - E_{k'}) \int \psi_k^* \psi_k d\tau \quad (22)$$

$$= -\epsilon \int (\psi_k^* \hat{W}^k \psi_k - \psi_k \hat{W}^{k'} \psi_k^*) d\tau.$$

In view of the presence of the multipliers $\gamma_{\beta\gamma}$ and $\Gamma_{\beta\gamma}$ in \hat{W} and the factor $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}$, the expression under the integral sign on the right side of Eq. (22) is an arbitrary sign-varying function of the coordinates. Integrals of such a type were estimated in Refs. 1 and 2, their mean square values being proportional to $G^{-3/2}$, where G^3 is the number of elementary cells in the base region. In this way, the right side of Eq. (22) has the order $\epsilon G^{-3/2}$, i.e., it is practically equal to zero. This means that if $E_k \neq E_{k'}$, then

$$\int \psi_k^* \psi_k d\tau \sim \epsilon G^{-3/2} \approx 0, \quad (23)$$

i.e., the functions ψ_k are practically orthogonal.

3. SOLUTION OF THE KINETIC EQUATION FOR THE ELECTRON IN THE LIQUID

In view of the fact that the operators \hat{H}_0^k depend on \mathbf{k} , the derivation of the equation must be carried out anew from the theory of quantum processes. In particular, there remains an open question of the completeness of the set of functions ψ_k . Nevertheless, based on the analogy between ψ_k and the usual Bloch functions, and taking into account the large number G^3 of the functions ψ_k , we make the assumption that the solution of the time dependent Schrödinger equation

$$\hbar i \partial \psi / \partial t = \hat{H} \psi \quad (24)$$

can, with a sufficient degree of accuracy, be represented in the form of a series

$$\psi(\mathbf{r}, t) = \sum_{\mathbf{k}} c_{\mathbf{k}}(t) \psi_{\mathbf{k}}(\mathbf{r}) e^{iE_{\mathbf{k}}t/\hbar}. \quad (25)$$

Substituting Eq. (25) in (24), expanding each term of the sum on the right side of $\hat{H} \psi_k$ into $\hat{H}_0^k \psi_k$ and $\epsilon \hat{W}^k \psi_k$, integrating over the entire volume and taking into account (17) and (23), we arrive at the usual equation of the theory of quantum processes:

$$i\hbar \dot{c}(k') = \epsilon W_{k'k} \exp i\{(E_{k'} - E_k)t/\hbar\}, \quad (26)$$

where

$$W_{k'k} = \int \psi_k^* \hat{W}^k \psi_k d\tau = \frac{\hbar^2}{2mG^{3/2}a^2} I_{k'k}, \quad (27)$$

$$I_{k'k} = \frac{a^2}{G^{3/2}} \int u_{k'} \left[\sum_{\beta=1}^3 \sum_{\gamma=1}^3 \left(\frac{\partial^2 u_k}{\partial x_\beta \partial x_\gamma} \gamma_{\beta\gamma} + 2ik_\gamma \frac{\partial u_k}{\partial x_\beta} \Gamma_{\beta\gamma} \right) + \frac{1}{a} \sum_{\beta=1}^3 \frac{\partial u_k}{\partial x_\beta} \gamma_{\beta\beta} \right] e^{i(k-k')r} d\tau. \quad (28)$$

Subsequent calculation differs little from the usual theory of electrical conductivity (see, for example, Ref. 4, Sec. 34-35). Integration of Eq. (26) over the time gives

$$|c(k')|^2 = \varepsilon^2 |W_{k'k}|^2 \Omega(E_{k'} - E_k) \quad (29)$$

$$= \frac{\varepsilon^2 \hbar^4}{4m^2 G^3 a^4} |I_{k'k}|^2 \Omega(E_{k'} - E_k),$$

$$\Omega(\eta) = 2 \frac{1 - \cos(\eta t / \hbar)}{(\eta / \hbar)^2}. \quad (30)$$

In order to obtain the total change of the distribution function $f(k', t)$ as a result of liquid scattering, we must multiply Eq. (29) by the probability of the initial state $f(k)$, sum over all possible values of k , multiply (taking account of the Pauli principle) by the probability of nonoccupation of the state k' by $1 - f(k')$, and consider the inverse transitions from state k' to state k . As a result, we obtain

$$f(k', t) - f(k', 0) \quad (31)$$

$$= (\varepsilon^2 \hbar^4 / 4m^2 G^3 a^4) \sum_k \Omega(E_{k'} - E_k) \times \{ |I_{k'k}|^2 f(k) [1 - f(k')] - |I_{kk'}|^2 f(k') [1 - f(k)] \}.$$

We note that here the usual relations between the matrix elements of the forward and reverse processes of the transitions $W_{k'k} = W_{kk'}^*$ does not occur. However, if we limit ourselves to the isotropic approximation, employed in the classical theory of electrical conduction, then, as we shall see below, in Eq. (31)

$$|I_{k'k}|^2 \approx |I_{kk'}|^2. \quad (32)$$

Taking (32) into account, making appropriate reductions and differentiating (31) with respect to time, we get the change in the distribution function as a result of the "liquid" scattering:

$$\left(\frac{\partial f}{\partial t} \right)_k = \frac{\varepsilon^2 \hbar^4}{4m^2 G^3 a^4} \times \frac{\partial}{\partial t} \sum_k |I_{k'k}|^2 \Omega(E_{k'} - E_k) [f(k) - f(k')]. \quad (33)$$

We consider that the energy of the electron depends only on k , but not on the direction of k . We introduce in k -space the spherical system of coordinates k, θ, φ , the axis of which has the direction k' . In place of the sum over k we can write the integral

$$\sum_k F(k) = \Omega_0 \left(\frac{G}{2\pi} \right)^3 \int k^2 F(k) \sin \theta d\theta d\varphi dk; \quad (34)$$

Ω_0 is the volume of the elementary cell. The function $\Omega(\eta)$ has a sharp maximum for $\eta = 0$; therefore, upon integration over k on the right side of (33) over all factors except Ω , we can set $k = k'$ and carry out these multiplications under the integral sign over k . The remaining integral is equal to

$$\int_0^\infty \Omega(E_{k'} - E_k) dk \approx \frac{1}{dE/dk} \quad (35)$$

$$\times \int_{-\infty}^\infty \Omega(\eta) d\eta = \frac{2\pi \hbar t}{dE/dk}$$

and, consequently,

$$\left(\frac{\partial f}{\partial t} \right)_k = \frac{\varepsilon^2 \hbar^3 \Omega_0 k'^2}{16m^2 a^4 \pi^2 (dE/dk)} \times \int_0^\pi d\theta \int_0^{2\pi} d\varphi |I_{k'k}|^2 \sin \theta [f(k) - f(k')]. \quad (36)$$

The kinetic equation for the electrons in the liquid in the stationary case has the form

$$\partial f / \partial t = (\partial f / \partial t)_k + (\partial f / \partial t)_{\nabla\varphi, \nabla\mu, \nabla T} = 0; \quad (37)$$

where the last term describes the change in the distribution function because of the presence of a potential gradient of the concentration or temperature. For simplicity, we shall consider that the concentrations of electrons and the temperature in the liquid are constants and that a homogeneous field E_x is placed along the x -axis. In this case, as is well known [Ref. 4, Eq. (33.18)],

$$(\partial f / \partial t)_{\nabla\varphi} = - (eE_x / \hbar) \partial f / \partial x \quad (38)$$

and if the field is not too large, the distribution function is sought in the form

$$f = f_0(E) + f_1(E) k_x, \quad (39)$$

where the second term is a small correction.

We now substitute Eqs. (36) and (38) in (37); in Eq. (36) we put $f_1 k_x$ in place of f , since the terms with f_0 are eliminated, and we can replace f with f_0 in Eq. (38), neglecting the small correction. In

total, we get

$$\frac{\varepsilon^2 \hbar^3 \Omega_0 k'^2}{16m^2 a^4 \pi^2} \int_0^\pi d\theta \quad (40)$$

$$\int_0^{2\pi} d\varphi |I_{k'k}|^2 \sin \theta f_1(k_x - k'_x) = \frac{eE_x}{\hbar} \frac{\partial f_0}{\partial k'_x}$$

Let ϑ or ϑ' be, respectively, the angles between x and \mathbf{k} or \mathbf{k}' . Consequently, $k_x = k \cos \vartheta$; $k'_x = k' \cos \vartheta'$, whence $\cos \vartheta = \cos \vartheta' \cos \theta + \sin \vartheta' \sin \theta \sin \varphi$. Since (within the framework of the isotropic approximation) $I_{\mathbf{k}'\mathbf{k}}$ does not depend on φ , then, on integration over φ , the second term of this expression vanishes. For the remaining terms, integration over φ gives the factor 2π . On the other hand,

$$\frac{\partial f_0}{\partial k'_x} = \frac{df_0}{dE} \frac{dE}{dk'} \frac{k'_x}{k'}, \quad (41)$$

therefore, the factor $k'_x = k' \cos \vartheta'$ vanishes on the left and right sides of Eq. (40). Solving this equation with respect to f_1 , denoting by I

$$I = \int_0^\pi |I_{k'k}|^2 (1 - \cos \theta) \sin \theta d\theta \quad (42)$$

and dropping the prime from k , we obtain

$$f_1 = -\frac{8\pi m^2 a^4}{\varepsilon^2 \hbar^3 \Omega_0 k^3 I} \frac{eE_x}{\hbar} \frac{df_0}{dE} \left(\frac{dE}{dk}\right)^2. \quad (43)$$

Comparing this expression with the distribution function for free electrons:

$$f = f_0 - (df_0/dE) eE_x l v_x / v \quad (44)$$

and assuming

$$v_x / v = k_x / k, \quad \Omega_0 \approx a^3,$$

we get the free path length of the electron in the liquid:

$$l = \frac{8\pi m^2}{\hbar^4 I} \frac{1}{k^2} \left(\frac{dE}{dk}\right)^2 \frac{a}{\varepsilon^2}. \quad (45)$$

If we represent the energy of the electron in the form $E = \hbar^2 k^2 / 2m^*$, which can be done in each case for electrons in the conduction zones of a semiconductor, Eq. (45) is simplified and yields

$$l = (8\pi / I) (a / \varepsilon^2) (m / m^*)^2, \quad (46)$$

where m^* is the effective mass of the electron in the zone.

4. CALCULATION OF THE MATRIX ELEMENTS AND ESTIMATE OF THE ELECTRON MEAN FREE PATH

In order to estimate the mean free path l and to establish its dependence on k , i.e., on the energy of the electron, we must compute the coefficient $I_{\mathbf{k}'\mathbf{k}}$ in the expression for the matrix element of transition.

In analogy to what was done in the estimation of the matrix elements in Refs. 1 and 2, we decompose the integral in (28) into a set of integrals over the elementary cells. The factors $\gamma_{\beta\gamma}$, $\Gamma_{\beta\gamma}$ and γ_{β} remain nearly constant in the limits of each elementary cell and can be taken outside the integration over the cell. These quantities are arbitrary functions of the coordinates; therefore, summation of both the separated terms of Eq. (28) in the integral over a single elementary cell, as well as of the integrals over all G^3 elementary cells, are carried out according to the law of summation of random quantities, i.e., the squares are summed. Since the various cells are oriented in all possible ways with respect to the direction of \mathbf{k} , integrals over the individual cells, which are obtained after removing the factors $\gamma_{\beta\gamma}$, $\Gamma_{\beta\gamma}$ and γ_{β} from under the integral sign, are also random quantities, and therefore independent of the removed factors. But the average of the product of two independent random variables is equal to the product of the mean. Therefore, summation over G^3 elementary cells in the expression for the square modulus $I_{\mathbf{k}'\mathbf{k}}$ gives the product of the mean values of the squares of $\gamma_{\beta\gamma}$, $\Gamma_{\beta\gamma}$ and γ_{β} the mean square of the integral over one cell and by the factor G^3 [which reduces to the factor $(G^{-3/2})^2$ which follows from Eq. (28)]. As a result, we obtain

$$|I_{k'k}|^2 \approx \sum_{\beta=1}^3 \sum_{\gamma=1}^3 \overline{(\gamma_{\beta\gamma}^2 |\chi_{\beta\gamma}^{k'k}|^2)} \quad (47)$$

$$+ 4k^2_{\gamma} a^2 \overline{\Gamma_{\beta\gamma}^2 |\chi_{\beta}^{k'k}|^2} + \sum_{\beta=1}^3 \overline{\gamma_{\beta}^2 |\chi_{\beta}^{k'k}|^2}.$$

Here,

$$\chi_{\beta\gamma}^{k'k} = a^2 \int u_{\mathbf{k}'}^* \frac{\partial^2 u_{\mathbf{k}}}{\partial x_{\beta} \partial x_{\gamma}} e^{i\mathbf{q}\mathbf{r}} d\tau_0, \quad (48)$$

$$\chi_{\beta}^{k'k} = a \int u_{\mathbf{k}'}^* \frac{\partial u_{\mathbf{k}}}{\partial x_{\beta}} e^{i\mathbf{q}\mathbf{r}} d\tau_0, \quad \mathbf{q} = \mathbf{k} - \mathbf{k}'.$$

The bars over the symbols indicate averaging over all elementary cells, the integrals (48) extend over a single elementary cell.

In the isotropic approximation, and for cubic crystals,

$$\begin{aligned} \overline{\gamma_{11}^2} &= \overline{\gamma_{22}^2} = \overline{\gamma_{33}^2}; \\ \overline{\gamma_{12}^2} &= \overline{\gamma_{23}^2} = \overline{\gamma_{13}^2}; \quad \overline{\gamma_1^2} = \overline{\gamma_2^2} = \overline{\gamma_3^2}; \\ |\chi_{11}^{k'k}|^2 &= |\chi_{22}^{k'k}|^2 = |\chi_{33}^{k'k}|^2, \text{ etc.} \end{aligned} \quad (49)$$

Similar conditions exist for Γ . Consequently, Eq. (47) can be rewritten in the form

$$\begin{aligned} |I_{k'k}|^2 &\approx 3\overline{\gamma_{\beta\beta}^2} |\overline{\chi_{\beta\beta}^{k'k}}|^2 + 6\overline{\gamma_{\beta\gamma}^2} |\overline{\chi_{\beta\gamma}^{k'k}}|^2 \\ &+ 4k^2 a^2 (\overline{\gamma_{\beta\beta}^2} + 2\overline{\gamma_{\beta\gamma}^2}) |\overline{\chi_{\beta}^{k'k}}|^2 + 3\overline{\gamma_{\beta}^2} |\overline{\chi_{\beta}^{k'k}}|^2, \end{aligned} \quad (50)$$

where the indices β and γ are not equal. Since $k = k'$, then $u_{k'} = u_k$ in the isotropic approximation, and condition (32) follows from Eqs. (48) and (50).

To estimate the order of the quantities, we set

$$\overline{\gamma_{\beta\beta}^2} = \overline{\gamma_{\beta\gamma}^2} = \overline{\Gamma_{\beta\beta}^2} = \overline{\Gamma_{\beta\gamma}^2} = \overline{\gamma_{\gamma}^2} = 1 \quad (51)$$

and then

$$\begin{aligned} |I_{k'k}|^2 &\approx 3 |\overline{\chi_{\beta\beta}^{k'k}}|^2 + 6 |\overline{\chi_{\beta\gamma}^{k'k}}|^2 \\ &+ 3 |\overline{\chi_{\beta}^{k'k}}|^2 + 12k^2 a^2 |\overline{\chi_{\beta}^{k'k}}|^2. \end{aligned} \quad (52)$$

The integrals χ are of the order unity but depend on k and on the angle θ between \mathbf{k} and \mathbf{k}' . To explain this dependence, we expand the functions u_k in a triple Fourier series in the limits of one elementary cell:

$$u_k = \sum_{\nu_1=-\infty}^{\infty} \sum_{\nu_2=-\infty}^{\infty} \sum_{\nu_3=-\infty}^{\infty} A_{\nu_1\nu_2\nu_3}^k \exp\left\{\frac{2\pi i}{a} \sum_{\alpha=1}^3 \nu_{\alpha} \xi_{\alpha}\right\}. \quad (53)$$

It is assumed here that the elementary cell is a cube of edge a and the coordinates ξ , which are cartesian within the cell, are laid out along the edges of the cube. All this is valid, of course, to accuracy of a small order of ϵ . We neglect the difference in u_k in the various elementary cells.

Substituting (53) in (48) and carrying out the integration, we get

$$|\chi_{\beta\gamma}^{k'k}| = b_{\beta\gamma}^k \prod_{\alpha=1}^3 \frac{\sin(aq_{\alpha}/2)}{aq_{\alpha}/2} + B_{\beta\gamma}^k \prod_{\alpha=1}^3 \sin \frac{aq_{\alpha}}{2} \quad (54)$$

and similar expressions for $|\chi_{\beta}^{k'k}|$. Here

$$b_{\beta\gamma}^k = 4\pi^2 a^3 \sum_{\nu_1} \sum_{\nu_2} \sum_{\nu_3} |A_{\nu_1\nu_2\nu_3}^k|^2 \nu_{\beta} \nu_{\gamma}; \quad (55)$$

$$B_{\beta\gamma}^k = 4\pi^2 \sum_{\nu_1\nu_2\nu_3} \sum'_{\mu_1\mu_2\mu_3} \frac{A_{\nu_1\nu_2\nu_3}^{k*} A_{\mu_1\mu_2\mu_3}^k \mu_{\beta} \mu_{\gamma}}{\prod_{\alpha=1}^3 (\pi/a)(\mu_{\alpha} - \nu_{\alpha})}, \quad (56)$$

q_{α} is the component of the vector \mathbf{q} along the axis ξ_{α} . The prime on the summation sign signifies that the summation over μ_1, μ_2, μ_3 is carried out for $\mu_1 \neq \nu_1 \dots$. In the denominator of (56) we have neglected the term q_{α} in comparison with $(\pi/a)(\mu_{\alpha} - \nu_{\alpha})$. The coefficients b_{β}^k and B_{β}^k in the expressions for $|\chi_{\beta}^{k'k}|$ are obtained similarly. We note that, if (53) converges sufficiently rapidly, then the coefficients $B_{\beta\gamma}^k$ are small in comparison with $b_{\beta\gamma}^k$.

Investigation of Eq. (54) in the general form is difficult; we therefore assume that $aq_{\alpha}/2 \ll 1$. This is undoubtedly valid for electrons in the conduction band of a semiconductor, but can also be assumed for a metal, since there is little probability that all three numbers q_1, q_2 , and q_3 have values close to the maximum. But in this approximation, terms of second order can be neglected in Eq. (54). Expanding the sine terms in series and neglecting terms of second order with respect to aq_{α} , we get

$$\begin{aligned} |\chi_{\beta\gamma}^{k'k}| &\approx b_{\beta\gamma}^k \left(1 - \frac{a^2}{24} \sum_{\alpha=1}^3 q_{\alpha}^2\right) \\ &= b_{\beta\gamma}^k \left(1 - \frac{a^2 q^2}{24}\right) = b_{\beta\gamma}^k \left[1 - \frac{a^2 k^2}{12} (1 - \cos \theta)\right]. \end{aligned} \quad (57)$$

Similar expressions can be obtained for $\chi_{\beta}^{k'k}$.

Substitution of Eq. (57) in Eq. (50) gives, after we neglect fourth degree terms in ak ,

$$|I_{k'k}|^2 \approx b^k \left[1 - \frac{a^2 k^2}{6} (1 - \cos \theta)\right] + b_0^k k^2 a^2, \quad (58)$$

where

$$b^k = 3\overline{\gamma_{\beta\beta}^2} (b_{\beta\beta}^k)^2 + 6\overline{\gamma_{\beta\gamma}^2} (b_{\beta\gamma}^k)^2 + 3\overline{\gamma_{\beta}^2} (b_{\beta}^k)^2; \quad (59)$$

$$b_0^k = 4\overline{\Gamma_{\beta\beta}^2} (b_{\beta}^k)^2 + 8\overline{\Gamma_{\beta\gamma}^2} (b_{\beta}^k)^2. \quad (60)$$

The coefficients b^k and b_0^k depend very weakly on k (only through the dependence of u_k on k) and in the first approximation, we can neglect this dependence. Substituting (58) in (42), and carrying

out the integration, we get

$$I \approx c + c_1 a^2 k^2, \quad (61)$$

$$c = 2b^k, \quad c_1 = 2b_0^k - 4/9 b^k. \quad (62)$$

In accord with (46), the dependence of the length of the mean free path on the wave number has the form

$$l = \frac{8\pi}{c + c_1 a^2 k^2} \frac{a}{\varepsilon^2} \left(\frac{m}{m^*}\right)^2. \quad (63)$$

The coefficients c and c_1 are best obtained from experiment, since their calculation from theoretical formulas requires the knowledge of the coefficients of the expansion of the functions u_k in Fourier series and these theoretical formulas are very approximate.

It is evident that these calculations are applicable not only to liquids but also to amorphous solids, in particular, to amorphous semiconduc-

tors. In contrast to the liquids, solid amorphous bodies can exist at low temperatures, when "liquid" scattering exists; therefore, the theoretical laws obtained for the length of the mean free path of the electron are best compared with experimental data for amorphous semiconductors.

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