On the Theory of Electric Conductivity of Liquid Metals

YU. P. KRASNYĬ AND N. P. KOVALENKO

Odessa State University

Submitted September 14, 1971

Zh. Eksp. Teor. Fiz. **62**, 828–832 (February, 1972)

We construct a theory of electric conductivity of liquid metals with allowance for the influence of the dynamics of the ion subsystem on the electron scattering. It is shown that the resistance is determined by the scattering of the electrons by all types of collective ion motions connected with changes of the density. A connection is found between the coefficient of the electric conductivity and the dynamic structure factor of the ion subsystem. Ziman's well known result for the electric conductivity is obtained in the particular case when only elastic scattering is taken into account.

1. Modern theories of the electric conductivity of liquid metals are based on the notion of almost-free electrons scattered by a disordered system of ions[1-3], the interaction with the latter being described within the framework of the pseudopotential theory[4-6]. Such an approach leads to Ziman's well known formula[1] which connects the coefficient of electric conductivity σ with the static structure factor S(**k**) of the ion subsystem. Numerical calculations based on Ziman's formula have revealed satisfactory qualitative agreement between the theoretical and experimental values of σ, but no quantitative agreement was observed for many metals[7-9]. This has stimulated a number of papers in which attempts were made to refine Ziman's theory. This refinement involved either the use of different types of pseudopotentials, or more accurate (theoretical or experimental) values of the structure factor, or finally a change in the very structure of Ziman's formula (for example, by taking into account the next higher terms in the perturbation-theory series for the electric conductivity). Springer[10] and Neal[11] used Kubo's formula for the electric conductivity, and used its expansion in terms of the energy of the electron-ion interaction to obtain and estimate the first correction to Ziman's formula. It turned out that this correction is quite large and its inclusion makes the results of Ziman's formula worse rather than better. Therefore Ashcroft and Schaich[12] estimated numerically about 10 turns of the series that refines Ziman's formula. The terms of this series decrease quite slowly, but the series itself is an alternating one, and the total correction to the Ziman result turns out to be small. More recently, the thought has arisen that the electric resistance of metals, as the result of scattering of electrons by the ion system, should depend not only on the statistical arrangement of the ions (which causes the appearance of the structure factor S(**k**) in the expression for σ), but also on the dynamics of the ion subsystem[13-15]. In such a case it is natural to expect the electric conductivity to be expressed in terms of a dynamic structure factor S(**k**; ω), which contains information on all the types of the collective motions in the ion subsystem. In the present paper we demonstrate, in second order in the pseudopotential, that the electric conductivity is indeed expressed in terms of the dynamic structure factor S(**k**, ω). Ziman's formula is in this case a particular of our result. It can be regarded as the simplest approximation that takes into account only elastic collisions between the electrons and the ion. In the general case the resistance is determined by the scattering of the electrons from all types of collective ion motions connected with the change of density.

2. We consider a system of N ions with charge z and N_e = zN electrons occupying a volume V. Using the diffraction model of a metal[4], we write down the Hamiltonian $\mathscr{H}$ of the system in the form

$$\hat{\mathscr{H}} = \hat{H}_e - \mu_e\hat{N}_e + \hat{H}_i - \mu_i\hat{N}_i; \tag{1}$$

$$\hat{H}_i - \mu_i\hat{N}_i = \sum_{n=1}^{N}\left\{\frac{\mathbf{p}_n{}^2}{2M} - \mu_i\right\} + \frac{1}{2}\sum_{\substack{nn'\\(n\neq n')}} V(|\mathbf{R}_n - \mathbf{R}_{n'}|), \tag{2}$$

$$\hat{H}_e - \mu_e\hat{N}_e = \sum_{\mathbf{k}\mathbf{k}'\sigma}\left\{\left(\frac{\hbar^2\mathbf{k}^2}{2m} - \mu_e\right)\delta_{\mathbf{k}\mathbf{k}'} + \rho(\mathbf{k}-\mathbf{k}')\,w(\mathbf{k}-\mathbf{k}')\right\}a_{\mathbf{k}\sigma}{}^+ a_{\mathbf{k}\sigma}; \tag{3}$$

$$w(\mathbf{k}) = \begin{cases} 0, & \mathbf{k} = 0; \\ \dfrac{N}{V}\displaystyle\int w(\mathbf{r})e^{-i\mathbf{k}\mathbf{r}}\,d\mathbf{r}, & \mathbf{k}\neq 0; \quad \rho(\mathbf{k}) = \dfrac{1}{N}\displaystyle\sum_{n=1}^{N} e^{-i\mathbf{k}\mathbf{R}_n}. \end{cases} \tag{4}$$

The indices e and i denote here the electron and ion subsystems; w(**r**) is the local screened pseudopotential of the electron-ion interaction; V(R) is the potential of the direct ion-ion interaction; μ_e and μ_i, mnM are the chemical potentials and masses of the electrons and ions, respectively; $a_{\mathbf{k}\sigma}^+$ and $a_{\mathbf{k}\sigma}$ are the operators of creation and annihilation of electrons in a state with momentum ħ**k** and spin σ; $\delta_{\mathbf{k}\mathbf{k}'}$ is the Kronecker symbol. In the temperature interval characteristic of liquid metal, the ion subsystem can be regarded as obeying the laws of classical statistical mechanics, whereas the electrons obey Fermi statistics. Therefore only the electronic part of (1) actually takes an operator form.

To find the electric conductivity of the system we use Kubo's linear reaction theory

$$\sigma = \frac{1}{V}\sum_{\mathbf{k}\sigma}\frac{e\hbar k_\nu}{m}f_\nu(\mathbf{k}), \tag{5}$$

$$f_\nu(\mathbf{k}) = \frac{i}{\hbar}\int_0^\infty \langle[\hat{a}_{\mathbf{k}\sigma}{}^+(t)\hat{a}_{\mathbf{k}\sigma}(t);\ \hat{d}_\nu(0)]\rangle\,dt. \tag{6}$$

In these formulas, the Greek indices denote the Cartesian coordinates x, y, and z; $\hat{d}_\nu$ is the operator of the dipole moment of the electron gas; the angle brackets represent quantum-mechanical and statistical averaging over the ensemble with Hamiltonian $\mathscr{H}$. It can be shown that, accurate to terms quadratic in the pseudopotential w, the function $f_\nu(\mathbf{k})$ satisfies the usual kinetic equation[17]:

$$-e\frac{\partial n}{\partial k_\nu}=\frac{v_0}{(2\pi)^2\hbar}\int d\mathbf{k}_1|w(\mathbf{k}-\mathbf{k}_1)|^2S\left(\mathbf{k}-\mathbf{k}_1;\ \frac{E-E_1}{\hbar}\right)[f_\nu(\mathbf{k})-f_\nu(\mathbf{k}_1)],$$

$$E=\frac{\hbar^2\mathbf{k}^2}{2m},\quad n=\left[1+\exp\left(\frac{E-\mu_e}{k_B T}\right)\right]^{-1},\quad v_0=\frac{V}{N},\tag{7}$$

$S(\mathbf{k}, \omega)$ is the Fourier transform of the Van Hove correlation function or the dynamic structure factor:

$$S(\mathbf{k},\omega)=\frac{1}{2\pi N}\int\limits_{-\infty}^{+\infty}\left\langle\sum_{n_1,n_2}\exp[-i\mathbf{k}\mathbf{R}_{n_1}(t)]\exp[i\mathbf{k}\mathbf{R}_{n_2}(0)]\right\rangle e^{i\omega t}\,dt.\tag{8}$$

The integral equation (7) is solved by expanding the product $|w|^2S$ in Legendre polynomials and the function $f_\nu(\mathbf{k})$ in spherical functions:

$$|w(\mathbf{k}-\mathbf{k}_1)|^2S\left(\mathbf{k}-\mathbf{k}_1;\ \frac{E-E_1}{\hbar}\right)=\sum_l a_lP_l(\cos\gamma).$$

$$f_\nu(\mathbf{k})=\sum_{lm}f_{lm}(E)Y_{lm}(\theta,\varphi).\tag{9}$$

Here θ and φ are the polar angles defining the direction of the vector $\mathbf{k}$; γ is the angle between the directions of $\mathbf{k}$ and $\mathbf{k}_1$. Substituting these expansions in (7) and using the theorem for the addition of Legendre polynomials, we obtain the following equation for $f_{10}(E) \equiv f(E)$:

$$\left(\frac{4\pi}{3}\right)^{1/2}\left(-\frac{\partial n}{\partial E}\right)\frac{e\hbar k}{m}=\frac{v_0}{2\pi\hbar^2}\int\limits_0^\infty dk_1k_1^2\int\limits_0^\pi d\gamma\sin\gamma|w(\mathbf{k}-\mathbf{k}_1)|^2$$

$$\times S\left(\mathbf{k}-\mathbf{k}_1;\ \frac{E-E_1}{\hbar}\right)[f(E)-f(E_1)\cos\gamma].\tag{10}$$

Since the electron gas is strongly degenerate at the temperatures in question, it follows that $E \sim E_F$, where E_F is the Fermi energy. The energy lost by the electron in interactions with ions is $E - E_1$. In liquid metals, this energy is of the order of k_BT. Since $E \sim E_F \gg k_BT$ up to the critical point, it can be assumed that $f(E_1) \approx f(E)$. Introduction of such an approximation in (10) leads to an error at least of order w^3 for f, and is therefore admissible in an approximation that is quadratic in the pseudopotential. Equation (10) can now easily be solved:

$$f(E)=\left(\frac{4\pi}{3}\right)^{1/2}\left(-\frac{\partial n}{\partial E}\right)\frac{e\hbar k}{m}\tau(k),\tag{11}$$

$$\tau^{-1}(k)=\frac{v_0}{2\pi\hbar^2}\int\limits_0^\infty dk_1k_1^2\int\limits_0^\pi d\gamma\sin\gamma|w(\mathbf{k}-\mathbf{k}_1)|^2S\left(\mathbf{k}-\mathbf{k}_1;\ \frac{E-E_1}{\hbar}\right)(1-\cos\gamma).\tag{12}$$

Substituting (9) in (5) and summing over the spin variable, we obtain a final expression for the electric-conductivity coefficient:

$$\sigma=\frac{1}{3}\left(\frac{e\hbar}{\pi m}\right)^2\int\limits_0^\infty dk\,k^4\tau(k)\left(-\frac{\partial n}{\partial E}\right)\approx\frac{ze^2\tau(k_F)}{v_0m},\tag{13}$$

where $\hbar k_F$ is the electron momentum corresponding to the Fermi energy and z/v_0 is the electron density.

3. Ziman's theory of the electric conductivity of liquid metals also leads to formula (13), but in his theory the expression for $\tau(k_F)$, the relaxation time, is different. To determine the connection between our and Ziman's equations, we transform (12), reversing the order of integration:

$$\tau^{-1}(k_F)=\frac{v_0}{4\pi\hbar^2k_F}\int\limits_0^\infty dx|w(x)|^2x\int\limits_{|x-k_F|}^{x+k_F}dk_1S\left(x;\ \frac{\hbar k_F^2}{2m}-\frac{\hbar k_1^2}{2m}\right)$$

$$\times[x^2-(k_F-k_1)^2].\tag{14}$$

From this we can easily verify that (14) goes over into the Ziman expression if $S(\mathbf{k}, \omega)$ has a δ-like character with respect to ω for any $\mathbf{k}$. Then the second integral in (14) differs from zero only when $0 \le x \le 2k_F$. Therefore the upper limit of the first integral can be limited to the value $2k_F$, and the limits of the second integral can be shifted by $\pm\infty$. Finally, making in the second integral the change of variable

$$\hbar(k_F^2-k_1^2)/2m\approx\hbar k_F(k_F-k_1)/m=-\omega,$$

we arrive at the Ziman formula

$$\tau^{-1}(k_F)=\frac{v_0m}{4\pi\hbar^3k_F^3}\int\limits_0^{2k_F}dx|w(x)|^2x^3\int\limits_{-\infty}^{\infty}S(x;\omega)\,d\omega$$

$$=\frac{v_0m}{4\pi\hbar^3k_F^3}\int\limits_0^{2k_F}dx|w(x)|^2S(x)x^3.\tag{15}$$

This is precisely the conclusion arrived at by Mannari[14] and Rice[15] in an investigation of the influence of inelastic scattering on the electric conductivity. Obviously, however, such an approximation is crude and corresponds to allowance for only the elastic scattering of the ion-subsystem electrons. As shown by experiment[18-20], the dependence of $S(\mathbf{k}, \omega)$ on ω is much more complicated. In addition to the elastic maximum at $\omega = 0$, there are a few side maxima corresponding to the presence of collective nodes of motion of the ion subsystem. In addition, these maxima have by far not a δ-like character, and the half-width of the peaks is as a rule very large.

For liquids, unfortunately, there is no known exact expression for $S(\mathbf{k}, \omega)$, with the exception of the limiting case $\omega \to 0$ and $k \to 0$ (hydrodynamic limit). However, even in the hydrodynamic limit there exists, besides the elastic maximum, two side maxima corresponding to collective motions of the type of acoustic waves, from which the electrons are scattered.

In conclusion, the authors are grateful to Professor I. Z. Fisher for interest in the work and for stimulating discussions.

---

[1] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

[2] C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. **7**, 865 (1962).

[3] J. M. Ziman, Adv. Phys. **16**, 551 (1967).

[4] W. A. Harrison, Pseudopotentials in the Theory of Metals, Benjamin, 1966.

[5] E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. **52**, 557 (1967) [Sov. Phys. JETP **25**, 365 (1967)].

[6] E. G. Brovman and Yu. Kagan, Neutron Inelastic Scattering (Proc. Sympos. Copenhagen) Vienna, Vol. 3, p. 1, 1968.

[7] L. Sundström, Phil. Mag. **11**, 657 (1965).

[8] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[9] A. O. Animalu, Phil. Mag. **11**, 379 (1965).

[10] B. Springer, Phys. Rev. A (1964–1965) **136**, 115 (1964); Phys. Rev.

154, 621 (1967).

[11]T. Neal, Phys. Fluids **13**, 249 (1970).

[12]N. W. Ashcroft and W. Schaich, Phys. Rev. **1**, 1371 (1970).

[13]S. Fischer and S. A. Rice, J. Chem. Phys. **51**, 3352 (1969).

[14]J. Mannari, Progr. Theor. Phys. **26**, 51 (1961).

[15]M. J. Rice, Phys. Rev. B **2**, 4800 (1970).

[16]R. Kubo, J. Phys. Soc. Jap. **12**, 570 (1957).

[17]G. Baym, Phys. Rev. A (1964–1965) **135**, 1691 (1964).

[18]V. V. Golikov and Zh. A. Kozlov, Ukr. Fiz. Zh. (Russ. Ed.) **15**, 1773 (1970).

[19]S. J. Cocking and P. A. Egelstaff, Proc. Phys. Soc. Lond. **1**, 507 (1968).

[20]P. D. Randolph and K. S. Singwi, Phys. Rev. **152**, 99 (1966).

Translated by J. G. Adashko
98