On a Theory of the Electrical Conductivity of Metals

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The fluctuations of potential of the internal electric field in the electron-ion plasma of a metal are calculated, also, the electrical resistivity dependent on the scattering of electrons by these fluctuations.

1. INTRODUCTION

At present, mathematical methods have been developed for calculating the collective Coulomb interactions in a system of many particles (a plasma)[1-4]. Up to now, however, these methods have not found wide use in the theory of metals. This is apparently no accident and is explained by the circumstance that in the approximation of a metal by an isotropic plasma, the periodic distribution of the ions of the metal (crystalline lattice) and the presence of "non-collectivized" electrons in the atomic cores (ions) are not taken into consideration.

The consideration of periodicity in a three-dimensional distribution of ions[5] is linked with mathematical difficulties. Non-collectivized electrons of the atomic cores generally were not allowed for in the foundations of plasma theory. Disregarding these difficulties, it makes sense to attempt to apply the theory of an isotropic plasma to the study of certain physical properties of the alkali metals with the aim of clarifying the results which come out of the plasma model of a metal. In the alkali metals, the periodicity in distribution of ions and the non-collectivized electrons of the atomic cores apparently play a lesser role than in non-alkali metals, and in the former, the "valence" electrons can be considered completely collectivized.

In the theory of a plasma, essentially the dynamics of the electrons were studied and only in a few works[1,6] was the motion of the ions also taken into account. In the investigation of the physical properties of a metallic plasma which depend on temperature (for example, the electrical and thermal conductivity, scattering of light, specific heat, surface tension and others), along with the dynamics of the electrons it is also necessary to take into account the motion of the ions. Precisely in these cases the motion of the ions plays a basic role; it determines the temperature of the metal and thus also the character of the behavior of the "free" electrons. The thermal motion of the ions leads to fluctuations of physical quantities such as the density of the number of particles, the energy, the internal electric field and others. Fluctuations of physical quantities play a significant role in applications. Thus, for example, the scattering of light is computed through fluctuations of the density of the number of particles. Through fluctuations of the density of electric charge the internal electric field is calculated which determines the temperature dependent electrical resistance of metals.

The aims of the present paper were (1) the computation of the fluctuations associated with thermal motion, taking into account the collective Coulomb interactions between the electrons and the ions, and (2), the computation of the electrical resistivity of a metal plasma which depends on the scattering of conduction electrons by fluctuations of the internal electric field.

II. THE FLUCTUATIONS OF PHYSICAL QUANTITIES IN THE ELECTRON-ION PLASMA

In the study of fluctuations in a plasma, it is convenient to express all physical quantities through the fluctuation of density of the number of particles. Fluctuations of large absolute value have slight probability and do not play a substantial role. The study of small fluctuations, however, is equivalent to the study of small oscillations of the plasma about a fundamental state characterized by an absence of fluctuations.

We take the state of the plasma at the absolute zero of temperature as its fundamental state.

[1] A. A. Vlasov, *Theory of Many Particles* GITTL, 1950.

[2] Iu. L. Klimontovich and V. P. Silin, J. Exper. Theoret. Phys. USSR 23, 151 (1952)

[3] D. N. Zubarev, J. Exper. Theoret. Phys. USSR 25, 548 (1953)

[4] D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951); 85, 338 (1952)

[5] P. S. Zyrianov, J. Exper. Theoret. Phys. USSR 25, 441 (1953)

[6] V. P. Silin, J. Exper. Theoret. Phys. USSR 23, 649 (1952)

Moreover, the distribution of electrons in energy or wave number conforms to a Fermi function f_{01}, and of ions to a δ-like function f_{02} (for example, a Bose function), but the spatial distribution of each is of the same kind. At temperatures of the metal plasma different from absolute zero, thermal motion begins, and leads to fluctuations.

The character of the behavior of fluctuations of density in ensembles of "ideal" and "non-ideal" particles is essentially different. In ensembles of "ideal" particles, fluctuations of density are resolved by diffusion in the course of time, whereas in ensembles of "non-ideal" particles the behavior of the fluctuations with time suggests the propagation of a disturbance in an elastic string. On consideration of the details of the fluctuations of density in "non-ideal" ensembles it is necessary to take into account collective interactions. For the calculation of these interactions, one can employ a kinetic equation with a self-consistent field[1] or the methods of references 3 and 4, having generalized them to two kinds of particles (electrons and ions).

The equations which allow for collective interactions have the form[1]

$$\frac{\partial f_i}{\partial t} + (\mathbf{v}\nabla_r) f_i + \frac{e_i}{m_i}(\mathbf{E}\nabla_v) f_i = 0, \qquad (1)$$

$$\mathbf{E} = -\nabla\Phi,$$

$$\Delta\Phi = -4\pi \sum_{i=1}^{2} e_i \int f_i \, d\mathbf{v} \qquad (i = 1, 2),$$

where the f_i are the distribution functions of the electrons and of the ions. The symbol $i = 1$ refers to the electrons and $i = 2$ to the ions. In equations (1) only the Coulomb interactions are treated.

For the study of fluctuations (small variations) the non-linear system of equations (1) can be linearized, assuming in Eq. (1)

$$f_i = f_{0i} + \varphi_i(\mathbf{r}, \mathbf{v}, t) \qquad \varphi_i \ll f_{0i} \qquad (2)$$

and retaining terms linear in φ_i. A solution of the linearized equations can be sought in the form of a superposition of plane waves

$$\varphi_i = \sum_q g_i(\mathbf{q}, \mathbf{v})\, e^{i\omega t - i\mathbf{qr}}. \qquad (3)$$

Substituting Eq (3) in the linearized equations, we find

$$\varphi_i = \sum_q \alpha_i^{-1} F_i(\mathbf{q}, \mathbf{v}) \frac{1}{2}(R_i e^{-i\mathbf{qr}} + R_i^* e^{i\mathbf{qr}}), \qquad (4)$$

where

$$R_i(\mathbf{q}, t) = e^{i\omega t} \int g_i(\mathbf{q}, \mathbf{v})\, d\mathbf{v}, \quad R_i(\mathbf{q}) = R_i^*(-\mathbf{q}),$$

$$F_i(\mathbf{q}, \mathbf{v}) = (\mathbf{q}\nabla_v) f_{0i} [m_i(\omega - \mathbf{qv})]^{-1};$$

f_{01} and f_{02} are degenerate functions, Fermi and Bose, respectively:

$$\alpha_i = \int F_i(\mathbf{v}, \mathbf{q})\, d\mathbf{v}.$$

The condition for existence of non-zero solutions gives the dispersion equation

$$1 - V^{(11)}(q)\alpha_1 - V^{(22)}(q)\alpha_2 = 0, \qquad (5)$$

where $V^{(ii)}(q) = 4\pi e_i^2 / q^2$ is the Fourier component of the Coulomb potential.

In reference 6 it was shown that the dispersion equation (5) gives two branches of oscillations: acoustical and electronic. Thermal motion excites only the acoustical branch of vibrations. For excitation of electronic oscillations an energy $\hbar\omega_{01}$ (ω_{01} is the Langmuir frequency of electronic oscillations) of the order of 10^{-11} erg is needed. This corresponds to temperatures of the order of 10^4 °K, at which metals no longer exist. For the acoustical vibrations, $\omega^2/q^2 \ll p_0^2/m_1$ (p_0 is the limiting Fermi momentum), and the damping is negligibly small[6].

For these conditions, we get from Eq (5)

$$\omega^2 = \frac{\omega_{02}^2 u_0^2}{\omega_{02}^2 + u_0^2 q^2} q^2, \qquad (6)$$

where

$$\omega_{02}^2 = 4\pi\rho_{02}\frac{e_2^2}{m_2}, \qquad u_0^2 = \frac{z}{3}\frac{p_0^2}{m_1 m_2}, \qquad z = \left|\frac{e_2}{e_1}\right|,$$

ρ_{02} is the mean density of the number of ions.

In case $q^2 \ll \omega_{02}^2/u_0^2 = q_D^2$ the dispersion vanishes and Eq. (6) goes over to $\omega = u_0 q$; u_0 plays the role of the velocity of sound in the metal plasma, q_D ---the role of Debye wave number.

By means of Poisson's equation and Eqs. (4) and (5), we find

$$\Phi = 4\pi e_2 \sum_q \left[\frac{\omega_{02}^2}{\omega^2} q^2 V^{(22)}(q)\right]^{-1} \frac{1}{2}(R_2 e^{-i\mathbf{qr}} - R_2^* e^{i\mathbf{qr}}) \qquad (7)$$

The distribution functions of electrons and ions (4) describe in the linear approximation the possible states of the system of electrons and ions, wherein one state differs from another only in the set of superposition coefficients $R_i(q)$ (the Fourier component of density). Therefore, it is very convenient to accept the quantities $R_i(q)$ as

dynamical variables which describe the state of the system. The advantages of such a choice of variables are evident if one goes over to the Hamiltonian method of description of small oscillations. The density of the Hamiltonian function of the system of electrons and ions, considering only the Coulomb forces, has the form

$$H = \frac{1}{2}\int m_1 v^2 f_1\, d\mathbf{v} + \frac{1}{2}\int m_2 v^2 f_2\, d\mathbf{v} + \frac{1}{8\pi}(\nabla\Phi)^2 + \Phi\sum_{i=1}^{2} e_i \int f_i\, d\mathbf{v}. \tag{8}$$

The first two terms represent the density of the kinetic energy of the electrons and of the ions, the third, the energy of the electric field, and the fourth, the energy of interaction of the electrons and ions with this field.

Differentiating Eq. (8) with respect to time and substituting for $\partial f/\partial t$ From Eq. (1), we obtain from

$$\frac{\partial H}{\partial t} = -\sum_{i=1}^{2} \operatorname{div} \mathbf{T}_i - {}^1/_2\, e_i \mathbf{E}\int v^2 (\nabla_{\mathbf{v}} f_i)\, d\mathbf{v} + \frac{1}{8\pi}\frac{\partial}{\partial t}(\nabla\Phi)^2 + \frac{\partial}{\partial t}\Big[\Phi\sum_{i=1}^{2} e_i \int f_i d\mathbf{v}\Big], \tag{9}$$

where

$$\mathbf{T}_i = {}^1/_2 \int m_i v^2 (\mathbf{v} f_i)\, d\mathbf{v}$$

is the vector of current density of the kinetic energy.

Transforming the second term in Eq. (9) by integration by parts, assuming minuteness of the deviation of the distribution functions f_i from their equilibrium values f_{0i} and using the solutions (4), we get, in place of Eq. (9),

$$\frac{\partial H}{\partial t} = \sum_{i=1}^{2}\Big\{-\operatorname{div}\mathbf{T}_i + e_i \mathbf{E}\int \mathbf{v}\Big[f_{0i} + \sum_q \frac{F_i}{2\alpha_i}(R_i e^{-i\mathbf{qr}} + R_i^* e^{-i\mathbf{qr}})\Big] d\mathbf{v}\Big\} + \frac{1}{8\pi}\frac{\partial}{\partial t}\Big[\sum_q \frac{2\pi e_2 \omega^2}{\omega_{02}^2 q^2} i\mathbf{q}\,(R_2 e^{-i\mathbf{qr}} + R_2^* e^{i\mathbf{qr}})\Big]^2 + \frac{\partial}{\partial t}\Big\{\sum_{i=1}^{2}\frac{2\pi e_2\omega^2}{\omega_{02}^2 q^2}(R_i e^{-i\mathbf{qr}} - R_i^* e^{i\mathbf{qr}})\, e_i \int\Big[f_{0i} + \sum_q \frac{F_i}{2\alpha_i}(R_i e^{-i\mathbf{qr}} + R_i^* e^{i\mathbf{qr}})\Big] d\mathbf{v}\Big\}. \tag{10}$$

In the case of acoustical vibrations, it is possible to disregard the kinetic energy of the well-regulated movement of the electrons. Thereupon, integrating Eq. (10) first over the volume of the system, with the hypothesis that the current T_i through the boundary of the system reduces to zero, and then over time, we get for the complete Hamiltonian function $\mathcal{H}$ the expression

$$\mathcal{H} = \sum_q \frac{m_2\omega^2}{4\rho_{02}q^2}\Big(1 + \frac{\omega^2}{\omega_{02}^2}\Big)(R_2 R_2^* + R_2^* R_2) + \text{const}. \tag{11}$$

We introduce new variables with the aid of the equation

$$R_2(q) = i\sqrt{2}\,\frac{\rho_{02} q}{(1 + \omega^2/\omega_{02}^2)^{1/2}} X_q. \tag{12}$$

Considering that $X_q \sim R_2(q) = \rho_2(q)\, e^{i\omega t}$, and assuming $im_2\,\omega\rho_{02} X_q = i\mu\omega X_q = P_q$, we transform $\mathcal{H}$ to the form

$$\mathcal{H} = \sum_q \Big\{\frac{P_q P_{-q}}{2\mu} + \frac{\mu\omega^2 X_q X_{-q}}{2}\Big\} + \text{const}, \tag{13}$$

where

$$\text{const} = \int\sum_{i=1}^{2}\frac{m v_i^2}{2} f_{0i}\, d\mathbf{v}\, d\mathbf{r} + \int\Big(\sum_{i=1}^{2} e_i f_{0i}\, d\mathbf{v}\,\Phi\Big) d\mathbf{r}.$$

The Fourier components of the potential of the internal electric field are expressed in terms of X_q by the formula

$$\Phi_q = \frac{i}{\sqrt{2}}\frac{m_2}{e_2}\Big[1 + \frac{\omega^2}{\omega_{02}^2}\Big]^{-1}\frac{\omega^2}{q} X q. \tag{14}$$

The transition to the quantum description of small oscillations (fluctuations) is achieved by the replacement of P_q by the operator $-i\hbar\,\partial/\partial X_q$. For the characteristic values of the energy of the vibrations, we get the formula

$$\mathcal{E} = \text{const} + \sum_q (N_q + {}^1/_2)\,\hbar\omega(q). \tag{15}$$

In the case of thermodynamic equilibrium, N_q is a Bose-Planck function, and the mean-square values can be found by means of the probability distribution of the coordinate of an oscillator[7] Thus, using the kinetic equations (1) and quantization of small oscillations (fluctuations), we have found formulas for the fluctuations of the density of the number of particles, the Fourier component

[7] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Clarendon, 1938

of the potential of the internal electric field and the energy density.

In the following we shall take up a case which is not without interest. If we carry out calculations, analogous to those done above, for a system consisting of one sort of particle with mass m_2 and charge e_2, but with the interaction potential

$$V(r) = \left(\frac{e}{r}\right)\exp(-q_D r), \qquad (16)$$

which satisfies the equation

$$\Delta V - q_D^2 V = 0, \qquad (17)$$

where $q_D = \omega_{02}/u_0$, then we get formulas in exact agreement with Eq. (6) and Eqs. (12)-(14).

From this observation it follows that in the calculation of fluctuations of physical quantities in an electron-ion plasma (accounting for collective Coulomb interactions) the role of the electrons boils down to a Debye screening of the electric charge of the ion-points. For this reason and, of course, since the mean speed of the chaotic motions of the ions is significantly less than the mean speed of the electrons, the Debye cloud of polarization is nearly indistinguishable from a sphere.

III. ON THE ELECTRICAL CONDUCTIVITY OF METALS

The motion of conduction electrons through an ideal periodic metal lattice takes place entirely without hindrance, i.e., the electrical resistivity is zero. In order to explain the incidence of the finite electrical resistivity of a metal, it is necessary to consider the thermal motion of the atomic residues (lattice vibrations). Owing to this motion, the periodicity of the potential of the lattice is disturbed and electrons are no longer able to travel unimpeded through the metal. This circumstance, in the final analysis, also leads to the emergence of electrical resistivity.

In other words, the thermal motion of the ions sets up fluctuations in the potential of the internal electric field in the metal, and the scattering of electrons by these fluctuations is the cause of the finite value of the electrical resitivity. Thus, for computing the electrical resistivity of a metal, it is necessary to know the fluctuations of potential in the internal electric field. The phenomenological introduction of these fluctuations (of the perturbing potential) in Bloch's theory[8] was combined with additional hypotheses. Thus, for instance, in references 8-10 the hypothesis of "deformed" ions was proposed, but in reference 11 a hypothesis of "rigid" ions. For such an introduction of fluctuations of potential, the "constant" of the interaction between electrons and thermal vibrations of the lattice remains unknown and this makes a comparison of theory with experiment difficult.

The thermal motion of ions of a metal in the solid phase bears the character of oscillations about equilibrium positions which are considered stationary (held fast). If we disregard thermal expansion, then a change in temperature causes only a change in the amplitude of vibrations of the ions. Such a (oscillatory) motion of the ions of a metal can be described by an equivalent system of non-interacting oscillators. For this, quantities proportional to the Fourier components of the density of the number of ions serves as dynamical variables (the coordinates of the oscillators or the independent variables). These variables we shall call collective variables. They describe the collective oscillations of the density of ions. Experiment shows that in a solid metal the ions possess also, so to speak, individual degrees of freedom, which lead to the chaotic progressive transfer of ions or to self-diffusion (intermixing). This will be gone into in more detail in another place, in connection with the discussion of the question of the electrical resistivity of liquid metals.

For the calculation of the electrical resistivity of metals in the solid phase, one can apparently disregard the individual degrees of freedom of ions (inasmuch as the number of such ions is comparatively small) and compute the scattering of the conduction electrons by the fluctuations of potential of the internal electric field, determined only by the collective oscillations. The calculations are especially simple in the case of high temperatures $T > \Theta_D$, where Θ_D is the Debye characteristic temperature. In this case, as is known, it is possible to introduce the free-path length of a conduction electron l_x. This length is expressed by the square of a matrix element of the interaction energy of an electron with the internal electric field: $B(\mathbf{k}, \mathbf{k}')$. According to reference 12, this

[8] F. Bloch, Z. Phys. 59, 208 (1930)

[9] H. A. Bethe and A. Sommerfeld, *Electron Theory of Metals*, 1938

[10] L. Brillouin, *Les Statistiques Quantiques*, Paris, 1930

[11] L. Nordheim, Ann. Physik 9, 607 (1931)

[12] F. Seitz, *Modern Theory of Solids*, McGraw-Hill, New York, 1940, p. 526

relation has the form

$$\frac{1}{l_x} = 16\pi^3 \left(\frac{dk}{dE}\right)_0^2 \times Vk_0^2 \int_0^\pi B(\mathbf{k}, \mathbf{k}')(1 - \cos\vartheta)\sin\vartheta\, d\vartheta, \quad (18)$$

where V is the volume of the metal (we assume in the following $V = 1$ cm^3), $\hbar k_0^2 / 2m_1 = E_0$ is the limiting energy of the Fermi distribution, the quantity $B(\mathbf{k}, \mathbf{k}')$ depends on $\mathbf{k}$ and on the angle ϑ between $\mathbf{k}$ and $\mathbf{k}'$,

$$|\mathbf{k}| = |\mathbf{k}'|; \quad (19)$$

in accordance with Eq. (14) and with the definition of the matrix element.

$$B|\mathbf{k}, \mathbf{k}'| = |(\psi_\mathbf{k}|e_1\Phi|\psi_{\mathbf{k}'})|^2. \quad (20)$$

Substituting normalized free-electron wave functions here in place of the $\psi_\mathbf{k}$, we find

$$B(\mathbf{k}, \mathbf{k}') = \left[\frac{m_2^2\omega_{02}^4 u_0^4 q^2 X_q^2}{2(\omega_{02}^2 + 2u_0^2q^2)(\omega_{02}^2 + u_0^2q^2)}\right]_{\mathbf{q}=\mathbf{k}'-\mathbf{k}} \quad (21)$$

For $T > \Theta$ the mean square value of the coordinate of an oscillator with mass μ and frequency ω is

$$\overline{X_q^2} = \frac{\varkappa T}{\mu\omega^2} = \frac{\varkappa T}{m_2\rho_{02}\omega^2} \quad (22)$$

($\varkappa$ is Boltzmann's constant).

Substituting the expressions (20) and (22) in Eq. (18) and carrying out the integration over ϑ, taking Eq. (19) into account, we find

$$l_x = \frac{16\pi z\rho_{02}E_0^2}{\varkappa T m_2 u_0^2 I(q_D)}, \quad (23)$$

where

$$I(q_D) = \int_0^{q_D} q^3[1 + 2u_0^2q^2/\omega_{02}^2]^{-1}\,dq \approx {}^1/_8\, q_D^4.$$

Substituting l_x in the well-known formula for the electrical conductivity σ

$$\sigma = \rho^{-1} = \frac{e_1^2\rho_{01}}{m_1 v(k_0)} l_x$$

[m_1 is the mass of an electron, e_1 its charge, ρ_{01} is the mean density of electrons, $v(k_0)$ is the limiting velocity of the Fermi distribution], we get after the simplifications

$$\sigma = \rho^{-1} = \frac{10\pi\hbar^3}{(m_1e_1z)^2}\frac{p}{\varkappa T}, \quad (24)$$

where p is the pressure of the degenerate electron gas, equal to

$${}^1/_5(3\pi^2)^{2/3}(\hbar^2/m)(\rho_{01})^{5/3}.$$

For the alkali metals one can assume the number of collectivized electrons per atom $z = 1$. For $T = 273°\,\mathrm{K} > \Theta_D$ formula (24) gives the following values (in units of 10^{16} cps):

$$\sigma_{Na} = 26, \quad \sigma_K = 10, \quad \sigma_{Rb} = 6, \quad \sigma_{Cs} = 4.$$

These values do no differ appreciably from those measured experimentally in the same units:

$$\sigma_{Na} = 21, \quad \sigma_K = 13, \quad \sigma_{Rb} = 7, \quad \sigma_{Cs} = 5.$$

It is not difficult to compute $\Theta = \hbar\omega_{max}/\varkappa$ as well. The maximum frequency of the acoustical vibrations ω_{max} which enters in here is determined by Eq. (6) if the q in it is set equal to q_D, the maximum wave number. Finally, we get

$$\Theta = \hbar\omega_{02}/\sqrt{2}\varkappa.$$

The values of Θ calculated by this formula:

$$\Theta_{Na} = 230°, \quad \Theta_K = 130°,$$

$$\Theta_{Rb} = 78°, \quad \Theta_{Cs} = 58°,$$

are close to the Debye characteristic temperatures, found from measurements of specific heats:

$$(\Theta_D)_{Na} = 150° - 202°\,\mathrm{K},$$

$$(\Theta_D)_K = 100° - 126°\mathrm{K},$$

$$(\Theta_D)_{Rb} = 62° - 85°\mathrm{K},$$

$$(\Theta_D)_{Cs} = 55° - 68°\mathrm{K}.$$

Other authors[6, 13] have compared the experimentally measured velocity of propagation of sound in the alkali metals with that calculated from the plasma model. The discrepancy between theory and experiment in this case did not exceed 15%.

The quantitative comparison of theory with experiment shows us to what extent the properties of alkali metals can be approximated by the properties of an electron-ion plasma.

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[13] D. Bohm and T. Staver, Phys. Rev. 84, 836 (1951)

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