SOME PROBLEMS CONCERNING THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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An approximate solution is obtained to the linearized Boltzmann equation, on the basis of which the transmission laws are then generalized. The hyperbolic equation of heat conduction is also derived.

A fundamental problem in nonequilibrium thermodynamics is to establish a relation between the distribution of the generalized potential and the flux of the generalized charge. A body elastically deformable under small shearing stresses is called a solid. Most solids have a crystalline structure. A crystal is a substance with a regular periodic structure containing one or more atoms of elements. "Electron gas" and ion oscillations in the crystal lattice are transmitters of generalized charge. Among the most important processes interfering with the motion of electrons in metals and semiconductors is the scatter of charge carriers by lattice oscillations. The electron–lattice interaction is responsible for the fact that both the electrical and the thermal conductivity of metals as well as the mobility of electrons and holes in semiconductors at higher temperatures are functions of the temperature, and it plays a decisive role in thermoelectric effects such as superconductivity.

The aggregate of conduction electrons can be characterized by the distribution function. The electron velocity in a crystal is defined as

$$\mathbf{v}_{\mathrm{K}} = \frac{1}{h^*} \nabla_{\mathrm{K}} \varepsilon (\mathbf{k}), \tag{1}$$

where $h^* = h/2\Pi$ with h denoting the Planck constant, **k** denoting the wave vector, and ε denoting the energy of an electron; the wave vector **k** varies according to

$$h^* \dot{\mathbf{k}} = \mathbf{F}, \tag{2}$$

where $\dot{\mathbf{k}} = d\mathbf{k}/dt$, t denotes time, and F denotes the force acting on an electron. The distribution function $f(\mathbf{k}, \mathbf{r}, t)$ is defined so that the number of electrons in a six-dimensional volume element dkdV at time t will be

$$\frac{1}{4\Pi^3} f(\mathbf{k}, \mathbf{r}, t)\, d\mathbf{k}\, dV. \tag{3}$$

During equilibrium the distribution $f(\mathbf{k}, \mathbf{r}, t)$ depends on ε only and becomes the Fermi distribution

$$f_0(\varepsilon) = \frac{1}{1 + e^{(\varepsilon - \eta)/k_0 T}}, \tag{4}$$

with η denoting the chemical potential, k_0 denoting the Boltzmann constant, and T denoting the temperature. According to Liouville's theorem, the total increment of the distribution function within the time dt is

$$\frac{df}{dt} = -\dot{\mathbf{k}} \nabla_{\mathrm{K}} f - \mathbf{v} \nabla_{\mathrm{r}} f + \frac{\partial f}{\partial t} + \left[\frac{\partial f}{\partial t}\right]_{\text{collision}} = 0. \tag{5}$$

Here $[\partial f/\partial t]$ collision denotes the increase in the number of electrons in the volume dkdV due to scatter. Equation (5) is the Boltzmann kinetic equation. We linearize the collision integral by introducing a relaxation time τ^* based on the equality

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$$\left[\frac{\partial f}{\partial t}\right]_{\text{collision}} = -\frac{f-f_0}{\tau^*}. \tag{6}$$

This relaxation time, being a time constant, characterizes the exponential law according to which the perturbed distribution f(**k**, r, t) tends toward the equilibrium distribution f_0. The approximation (6) is not valid for pure metals at temperatures about half as high as the Debye temperature. The relaxation time introduced here will be meaningful, if it does not depend on the kind of perturbation. It can be shown that the relaxation time has a physical significance whenever the change in the energy of an electron during one collision is much smaller than k_0T. At very low temperatures the electron–lattice scatter becomes very weak and the relaxation process associated with the elastic scatter of electrons at impurities becomes predominant. In this case equality (6) is entirely valid. The solution to (5) under condition (6) will now be sought in the following form:

$$f(\mathrm{k},\ \mathbf{r},\ t) = f_0(\varepsilon) + f_1(\mathrm{k},\ \mathbf{r},\ t), \tag{7}$$

with the assumption that

$$f_1(\mathrm{k},\ \mathbf{r},\ t) = -\Phi(\mathrm{k},\ \mathbf{r},\ t)\frac{\partial f_0}{\partial \varepsilon} \tag{8}$$

and f_1(**k**, r, t) assumed much smaller than $f_0(\varepsilon)$. Inserting (7) into (5) yields

$$\mathbf{Pv}\frac{\partial f_0}{\partial \varepsilon} + \frac{e}{ch^*}(\mathbf{v}\times\mathbf{H})\cdot\nabla_{K}f_1 = \frac{\Phi}{\tau^*}\frac{\partial f_0}{\partial \varepsilon} + \frac{\partial \Phi}{\partial t}\frac{\partial f_0}{\partial \varepsilon}, \tag{9}$$

where

$$\mathbf{P} = e\mathbf{E} - (\varepsilon - \eta)\nabla \ln T; \quad \nabla_r f \approx \Delta_r f_0 = \frac{\partial f_0}{\partial T}\nabla T + \frac{\partial f_0}{\partial \eta}\nabla\eta. \tag{10}$$

Here H is the magnetic field intensity and E is the electric field intensity. On the basis of (4), we can write

$$\nabla_{\mathbf{r}} f \approx -\frac{\partial f_0}{\partial \varepsilon}\left[\nabla\eta + (\varepsilon - \eta)\nabla \ln T\right]. \tag{11}$$

The second term on the left-hand side of Eq. (9) can be expressed as

$$\frac{e}{ch^*}(\mathbf{v}\times\mathbf{H})\nabla_{K}f_1 = \frac{e}{ch^2}(\mathbf{H}\cdot\vec{\Omega}\Phi)\frac{\partial f_0}{\partial \varepsilon}, \tag{12}$$

where

$$\Omega = \nabla_k\varepsilon \times \nabla_k.$$

Then (9) can also be written as

$$\frac{\partial \Phi}{\partial t} + \frac{\Phi}{\tau^*} = \mathbf{Pv} + \frac{e}{ch^{*^2}}(\mathbf{H}\cdot\vec{\Omega}\Phi). \tag{13}$$

This equation is the fundamental one in the relaxation approximation.

Let us find the solution to Eq. (13).

Case I. H = 0, i. e., there is no magnetic field present. Now (13) becomes

$$\Phi = \int_0^t \mathbf{Pv}\tau^*\frac{e^{\frac{\zeta - t}{\tau^*}}}{\tau^*}\,d\zeta. \tag{14}$$

When E ≠ 0 and ∇T = 0, then we have P = eE and

$$f(\mathrm{k},\ \mathbf{r},\ t) = f_0(\varepsilon) - \frac{\partial f_0}{\partial \varepsilon}\int_0^t \tau^* e\mathbf{Ev}\frac{e^{\frac{\zeta - t}{\tau^*}}}{\tau^*}\,d\zeta. \tag{15}$$

When E = 0 and ∇T ≠ 0, then

$$f(\mathrm{k},\ \mathbf{r},\ t) = \frac{\tau^*(\varepsilon - \eta)}{h^*}\frac{\partial \varepsilon}{\partial \mathbf{k}}\frac{\partial f_0}{\partial \varepsilon}\int_0^t \frac{\nabla T}{T}\frac{e^{\frac{\zeta - t}{\tau^*}}}{\tau^*}\,d\zeta. \tag{16}$$

Case II. H $\neq 0$ and the energy surfaces are of arbitrary form. Equation (13) can be solved by the iteration method, with

$$\Phi^{(0)} = \int_0^t \mathbf{P}\mathbf{v}\tau^* \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta, \tag{17}$$

taken as the zeroth approximation. Then the first approximation is

$$\Phi^{(1)} = \Phi^{(0)} + \frac{e\tau^*}{ch^{*2}} \int_0^t \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} (\mathbf{H}\cdot\vec{\Omega}\Phi_0)\, d\zeta. \tag{18}$$

In analogous manner it is possible to find also the subsequent approximations. The iterative approximation process converges when $(e\tau^*H/m^*c) \ll 1$, where m* denotes the effective electron mass.

Using this method, the author has determined the distribution function under certain assumptions. With the distribution function known, one can then find the characteristics of the transmission process.

The flux of generalized charge is determined according to the formula

$$\mathbf{I}(\mathbf{r}, t) = \frac{e}{4\Pi^3} \int \mathbf{v}_k f(\mathbf{k}, \mathbf{r}, t)\, d\mathbf{k}. \tag{19}$$

The electrical current at H = 0 and ∇T = 0 is calculated as

$$\mathbf{I} = e^2 k_1 \int_0^t \mathbf{E} \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta, \tag{20}$$

where

$$k_n = \frac{1}{12\Pi^3} \int \tau^* (\mathbf{v}\cdot\mathbf{v})\, \varepsilon^{n-1} \frac{\partial f_0}{\partial \varepsilon} dk, \quad \int dk = \int\int_s \frac{ds d\varepsilon}{|\nabla_k \varepsilon|}. \tag{20a}$$

In the derivation of (20) it has been assumed that τ^* is isotropic, i. e., independent of the wave vector k. The electrical conductivity is

$$\sigma = \frac{\mathbf{I}}{\mathbf{E}} = k_1 e^2. \tag{21}$$

On the basis of (20), we obtain the relation

$$\mathbf{I} + \tau^* \frac{\partial \mathbf{I}}{\partial t} = k_1 e^2 \mathbf{E} \quad \text{or} \quad \mathbf{I} + \tau^* \frac{\partial \mathbf{I}}{\partial t} = \sigma \mathbf{E}. \tag{22}$$

Equation (22) represents the generalized Ohm's Law.

Let us calculate the current and the energy when H = 0 and ∇T $\neq 0$. The formal expressions for these quantities are

$$\mathbf{I} = k_1 \left\{ e^2 \int_0^t \mathbf{E} \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta - e \int_0^t T\nabla \left(\frac{\eta}{T}\right) \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta \right\} - k_2 e \int_0^t \frac{\nabla T}{T} \frac{c^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta, \tag{23}$$

$$\mathbf{q} = k_2 \left\{ e \int_0^t \mathbf{E} \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta - \int_0^t T\nabla \left(\frac{\eta}{T}\right) \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta \right\} - k_3 e \int_0^t \frac{\nabla T}{T} \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta, \tag{24}$$

where k_n is found from (20a).

In Eq. (23) we let I = 0, then system (23)-(24) yields the value of q:

$$\mathbf{q} = \frac{k_2^2 - k_1 k_3}{k_1} \int_0^t \frac{\nabla T}{T} \frac{e^{\frac{\zeta-t}{\tau^*}}}{\tau^*} d\zeta. \tag{25}$$

Let us assume that $(k_2^2 - k_1 k_3)/k_1 = -\varkappa^*$, with $\varkappa^*/T = \varkappa$ denoting the thermal conductivity. Now (25) yields the generalized equation of heat conduction

$$\mathbf{q} + \tau^* \frac{\partial \mathbf{q}}{\partial t} = -\varkappa \nabla T, \tag{26}$$

first derived by A. V. Lykov.

On the basis of these results, we will examine the thermoelectric effects. From (23) follows a relation between the electric field intensity and the temperature gradient. When $\mathbf{I} = 0$ and $\nabla\eta = 0$, then (23) yields

$$E_{\text{abs}} = \frac{k_2 - \eta k_1}{e k_1 T}. \tag{27}$$

Expression (27) represents the absolute value of the thermoelectromotive force which governs the Seebeck effect.

Let us calculate the rate of heat generation per unit volume of solid

$$W = \mathbf{IE} - \operatorname{div} \mathbf{q}, \tag{28}$$

where IE is the work of the electric field and div q is the divergence of the thermal flux. We now insert E into (28), according to (23), and

$$\operatorname{div} \mathbf{q} = -\varkappa^* \int_0^t \operatorname{div}\left(\frac{\nabla T}{T}\right) \frac{e^{\frac{\zeta - t}{\tau^*}}}{\tau^*} d\zeta,$$

then

$$W = \mathbf{I}\left[\frac{\left(1 + \tau^* \frac{\partial}{\partial t}\right)\mathbf{I}}{\sigma} - \mathbf{E}_{\text{abs}}\right] - \operatorname{div} \mathbf{q} \tag{29}$$

or

$$W = \frac{\mathbf{I}^2}{\sigma} + \frac{\tau^*}{2\sigma} \frac{\partial \mathbf{I}^2}{\partial t} - \mathbf{I} T \nabla E_{\text{abs}} - \operatorname{div} \mathbf{q}. \tag{30}$$

The first term and the fourth term in (30) characterize the Joule heat and the dissipation of thermal flux, i. e., processes of heat generation associated with electrical and thermal condictivity. The third term describes the reversible heat generation, namely the Thompson heat W_T. The second term characterizes the additional heat generation $W_D = (\tau^*/2\sigma)(\partial I^2/\partial t)$, indicating that a nonsteady electric current produces an additional heat source.

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