

Chapter 6. Elements of Kinetics

This chapter gives a brief introduction to physical kinetics, with the main focus on the Boltzmann equation, especially in the relaxation-time approximation, which allows, in particular, a very reasonable description of major electron transport (such as the electric current and thermoelectric phenomena) in metals and semiconductors.

6.1. The Liouville theorem

Physical kinetics is the branch of statistical physics which deals with systems out of thermodynamic equilibrium. Major tasks of kinetics include:

- (i) for autonomous systems (those out of external fields): transient processes (“relaxation”) leading from an arbitrary initial state of a system to its thermodynamic equilibrium;
- (ii) for systems in variable external fields (say, in a sinusoidal “ac” field): the nonstationary, periodic oscillations of system’s parameters; and
- (iii) for systems in a constant (“dc”) external field: dc transport effects.

In the last case, we are dealing with stationary ($\partial/\partial t = 0$ everywhere), but non-equilibrium situations, in which the effect of an external field, continuously driving the system out of equilibrium, is balanced by simultaneous “relaxation” – trend toward equilibrium. Perhaps the most important effect of this class is the dc current in conductors, which alone justifies the inclusion of the basic notions of kinetics into this course.

Actually, the reader who has reached this point of the notes, already has a good taste of physical kinetics, because the subject of the last part of Chapter 5 *was* the kinetics of a “Brownian particle”, i.e. of any “heavy” system with one or a few degrees of freedom, interacting with environment consisting of many “lighter” components. Indeed, equations discussed in that part - whether the Langevin equation (5.65) or the Fokker-Plank equation (5.155) - are valid if the environment is in thermodynamic equilibrium, but the system of our interest is not necessarily so. As a result, we could use those equations to discuss such nonequilibrium phenomena as the Kramers problem.

This chapter is devoted to a more traditional subject of kinetics: a system of very many *similar* particles – generally, interacting with each other, but not much, so that the energy of the system still may be partitioned into a sum of the components, with particle interactions considered as a perturbation. Actually, we have already started the job of describing such a system in Sec. 5.8, in the course of deriving the Fokker-Planck equation for a single classical particle. Indeed, in the absence of particle interactions, i.e. with the probability current densities given by Eqs. (5.125) and (5.148), the continuity equation (5.146) takes the form

$$\frac{\partial w}{\partial t} + \nabla_q (w\dot{\mathbf{q}}) + \nabla_p (w\dot{\mathbf{p}}) = 0. \quad (6.1)$$

If particles are similar and do not interact, the probability density $w(\mathbf{q}, \mathbf{p}, t)$ which obeys this equation, describes each particle, and their ensemble as a whole.

Let us rewrite this equation in the Cartesian component form,

$$\frac{\partial w}{\partial t} + \sum_j \left[\frac{\partial}{\partial q_j} (w \dot{q}_j) + \frac{\partial}{\partial p_j} (w \dot{p}_j) \right] = 0, \quad (6.2)$$

where index j lists all degrees of freedom of the particle, and assume that its motion in the external field may be described by a Hamiltonian function $H(q_j, p_j, t)$. Plugging into Eq. (2) the Hamiltonian equations of motion:¹

$$\dot{q}_j = \frac{\partial H}{\partial p_j}, \quad \dot{p}_j = -\frac{\partial H}{\partial q_j}, \quad (6.3)$$

we get

$$\frac{\partial w}{\partial t} + \sum_j \left[\frac{\partial}{\partial q_j} \left(w \frac{\partial H}{\partial p_j} \right) - \frac{\partial}{\partial p_j} \left(w \frac{\partial H}{\partial q_j} \right) \right] = 0. \quad (6.4)$$

At parentheses differentiation, mixed terms $w \partial^2 H / \partial q_j \partial p_j = w \partial^2 H / \partial p_j \partial q_j$ cancel, and, using Eq. (3) again, we get the so-called *Liouville theorem*²

$$\frac{\partial w}{\partial t} + \sum_j \left(\frac{\partial w}{\partial q_j} \dot{q}_j + \frac{\partial w}{\partial p_j} \dot{p}_j \right) = 0. \quad (6.5)$$

Since the left-hand part of this equation is just the full derivative of the probability density considered as a function of the generalized coordinates $q_j(t)$ of a particle, its generalized momenta components $p_j(t)$, and (possibly) time t , the Liouville theorem (5) may be presented in a surprisingly simple form:

$$\frac{dw(\mathbf{q}, \mathbf{p}, t)}{dt} = 0. \quad (6.6)$$

Physically this means that the probability $dW = w d\mathbf{q} d\mathbf{p}$ to find a Hamiltonian particle in a small volume of the coordinate-momentum space $[\mathbf{q}, \mathbf{p}]$, with the center moving in accordance to the deterministic law (3), does not change with time. This is not quite surprising, because according to the fundamental Einstein relation (5.82), one needs non-Hamiltonian forces (such as viscosity) to have diffusion.

For an ideal gas of 3D particles, we may select the usual Cartesian coordinates r_j (with $j = 1, 2, 3$) for the generalized coordinates q_j , so that p_j become the Cartesian components mv_j of the usual (linear) momentum, and this elementary volume is just $d^3 r d^3 p$ – see Fig. 1. In this case Eqs.(3) are just

$$\dot{r}_j = \frac{p_j}{m} \equiv v_j, \quad \dot{p}_j = \mathfrak{F}_j, \quad (6.7)$$

so that the Liouville equation becomes

$$\frac{\partial w}{\partial t} + \sum_{j=1}^3 \left(v_j \frac{\partial w}{\partial r_j} + \mathfrak{F}_j \frac{\partial w}{\partial p_j} \right) = 0, \quad (6.8)$$

¹ See, e.g., CM Sec. 10.1.

² Actually, this is just one of theorems bearing the name of J. Liouville (1809-1882).

and may be conveniently presented in the vector form³

$$\frac{\partial w}{\partial t} + \mathbf{v} \cdot \nabla w + \mathcal{F} \cdot \nabla_p w = 0. \quad (6.9)$$

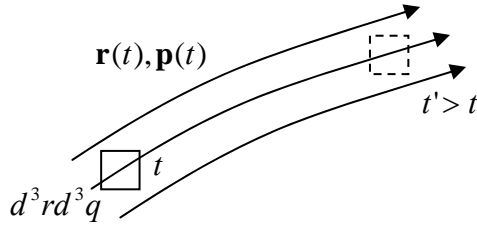


Fig. 6.1. Cartoon presentation of the Liouville theorem in the 6D space $[\mathbf{r}, \mathbf{p}]$.

6.2. The Boltzmann equation and relaxation-time approximation

The situation becomes more complex if particles interact. Generally, a system of N particles in 3D space has to be described by probability density w being a function of $6N + 1$ arguments ($3N$ Cartesian coordinates, plus $3N$ momentum components, plus time). The solution of any equation describing time evolution of such a function is evidently hopeless for a typical ensemble of $N \sim 10^{23}$ particles. Hence, kinetics of realistic ensembles hinges on making reasonable approximations.

One of the most useful approximations (sometimes called *Stosszahlansatz*, German for the “collision number assumption”) was suggested by L. Boltzmann for a gas of particles which move freely most of the time, but interact during short time intervals, when a particle comes close to either an immobile scattering center (say, an impurity in a conductor) or to another particle of the gas. Such a brief “scattering” event changes particle’s momentum, and may be approximately described by the addition of a special term (called the “scattering integral”) to the right-hand part of Eq. (9):

$$\frac{\partial w}{\partial t} + \mathbf{v} \cdot \nabla w + \mathcal{F} \cdot \nabla_p w = \left. \frac{\partial w}{\partial t} \right|_{\text{scattering}}, \quad (6.10)$$

while still keeping w a function of only 7 arguments: 3 Cartesian coordinates and 3 momentum components of just one particle, plus time. The concrete form of the scattering integral depends on the scattering object. If the scattering center does not belong to the ensemble under consideration (again, for example, an impurity atom in a conductor – see Fig. 2), then the scattering integral may be obtained by an evident generalization of the master equation (4.100):

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' [-\Gamma(\mathbf{p}; \mathbf{p}') w(\mathbf{r}, \mathbf{p}, t) + \Gamma(\mathbf{p}'; \mathbf{p}) w(\mathbf{r}, \mathbf{p}', t)], \quad (6.11)$$

where the physical sense of $\Gamma(\mathbf{p}; \mathbf{p}')$ is the rate (i.e. the probability per unit time) for the particle to be scattered from the state with momentum \mathbf{p} into the state with momentum \mathbf{p}' . Most elastic interactions are *reciprocal*, i.e. obey the following relation (closely related to the reversibility of time in Hamiltonian systems): $\Gamma(\mathbf{p}; \mathbf{p}') = \Gamma(\mathbf{p}'; \mathbf{p})$, so that Eq. (11) may be rewritten as⁴

³ Here and below, I use index-free symbol ∇ as defined in MA Eq. (8.1), i.e. for the vector differentiation in the usual (“direct”) space.

⁴ One may wonder whether this approximation may work for Fermi particles, for whom the Pauli principle forbids scattering into the already occupied state, so that for scattering $\mathbf{p} \rightarrow \mathbf{p}'$, factor $w(\mathbf{r}, \mathbf{p}, t)$ in Eq. (12) has to be

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \Gamma(\mathbf{p}; \mathbf{p}') [w(\mathbf{r}, \mathbf{p}', t) - w(\mathbf{r}, \mathbf{p}, t)]. \quad (6.12)$$

With such scattering integral, Eq. (10), called the *Boltzmann transport equation*, stays linear in w , but becomes integro-differential, harder to solve than the differential equations.

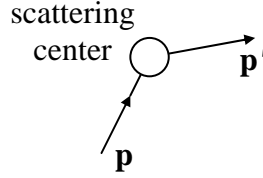


Fig. 6.2. Particle scattering event.

The equation becomes even more complex if the scattering is due to mutual interaction of the particles (Fig. 3). In this case, the probability of the scattering event scales as a product of two single-particle probabilities (considered independent of each other), and the simplest form of the scattering integral is⁵

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \int d^3 p \cdot [-\Gamma(\mathbf{p}, \mathbf{p}; \mathbf{p}', \mathbf{p}') w(\mathbf{r}, \mathbf{p}, t) w(\mathbf{r}, \mathbf{p}', t) + \Gamma(\mathbf{p}', \mathbf{p}'; \mathbf{p}, \mathbf{p}) w(\mathbf{r}, \mathbf{p}', t) w(\mathbf{r}, \mathbf{p}, t)]. \quad (6.13)$$

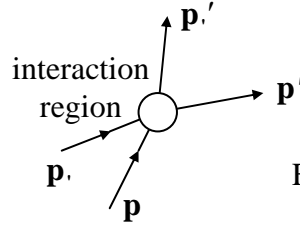


Fig. 6.3. Particle-particle scattering

Here I took into account that due to the conservation of the total momentum at scattering,

$$\mathbf{p} + \mathbf{p} = \mathbf{p}' + \mathbf{p}', \quad (6.14)$$

one of the momenta is not an independent argument, so that the integration in Eq. (13) may be restricted to a 6D p -space rather than the 9D one. For a reciprocal interaction, Eq. (13) may be a bit simplified,

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \int d^3 p \Gamma(\mathbf{p}, \mathbf{p}; \mathbf{p}', \mathbf{p}') [w(\mathbf{r}, \mathbf{p}', t) w(\mathbf{r}, \mathbf{p}', t) - w(\mathbf{r}, \mathbf{p}, t) w(\mathbf{r}, \mathbf{p}, t)], \quad (6.14)$$

multiplied by the probability $[1 - w(\mathbf{r}, \mathbf{p}', t)]$ that the final state is available. Generally, this is a valid argument, but one should notice that if this modification has been done with both terms of Eq. (12), it yields

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \Gamma(\mathbf{p}; \mathbf{p}') \{w(\mathbf{r}, \mathbf{p}', t) [1 - w(\mathbf{r}, \mathbf{p}, t)] - w(\mathbf{r}, \mathbf{p}, t) [1 - w(\mathbf{r}, \mathbf{p}', t)]\}.$$

Opening both square brackets, we see that the probability density products cancel, bringing us back to Eq. (12).

⁵ This was the approximation used by L. Boltzmann to prove the famous *H-theorem*, stating that entropy of the gas described by it can only grow (or stay constant), $dS/dt \geq 0$. As was stated in Chapter 1, since the model is very approximate, that result does not seem too fundamental nowadays, despite all its historic significance.

but it still makes Eq. (10) a *nonlinear* integro-differential transport equation, excluding such powerful solution methods of solution as the Fourier expansion (which hinges on the linear superposition principle).

This is why most results based on the Boltzmann transport equation have been based on its further simplifications, most notably the *relaxation-time approximation*, frequently dubbed *RTA*. This approximation uses the fact that in the absence of spatial gradients ($\nabla = 0$), and external forces ($\mathcal{F} = 0$), Eq. (10) yields

$$\frac{\partial w}{\partial t} = \frac{\partial w}{\partial t} \Big|_{\text{scattering}}, \quad (6.15)$$

so that the thermal equilibrium probability distribution $w_0(\mathbf{r}, \mathbf{p}, t)$ has to turn any scattering integral into zero. Hence at *small* deviations at equilibrium,

$$\tilde{w}(\mathbf{r}, \mathbf{p}, t) \equiv w(\mathbf{r}, \mathbf{p}, t) - w_0(\mathbf{r}, \mathbf{p}, t) \rightarrow 0, \quad (6.16)$$

the scattering integral should be proportional to the deviation \tilde{w} , and the simplest reasonable model of the integral is

$$\frac{\partial w}{\partial t} \Big|_{\text{scattering}} = -\frac{\tilde{w}}{\tau}, \quad (6.17)$$

where τ is a constant (which, according to Eq. (15), has to be positive for system' stability) which is called the *relaxation time*.

The relaxation-time approximation is quite reasonable if the angular distribution of the scattering rate is dominated by small angles between vectors \mathbf{p} and \mathbf{p}' – as it is, for example, for the Rutherford scattering by a Coulomb center.⁶ Indeed, in this case the two functions w , participating in Eq. (12) are close to each other, so that the loss of the second momentum argument is not too essential. However, while using the RTA equation, which results from Eqs. (10) and (17),

$$\frac{\partial w}{\partial t} + \mathbf{v} \cdot \nabla w + \mathcal{F} \cdot \nabla_p w = -\frac{\tilde{w}}{\tau}, \quad (6.18)$$

the reader should always remember this is just an approximation, sometimes giving completely wrong results. For example, it prescribes the same time scale, τ , to the relaxation of the net *momentum* distribution of the system, and to its *energy* relaxation, while in real systems the latter process (which requires inelastic interactions) may be substantially longer. Naturally, in the following sections, I will describe only those applications of this approximation which give a reasonable description of reality.

6.3. The Ohm law and Drude formula

Despite its shortcomings, Eq. (18) is adequate for quite a few important applications. The most important of them is deriving the Ohm law for dc current in a gas whose only deviation of ideality is the scattering term in the form of Eq. (17),⁷ and hence described, in equilibrium, by the equilibrium probability w_0 of an ideal gas (see Sec. 3.1):

⁶ See, e.g., CM Sec. 3.7.

⁷ As was mentioned in Sec. 3.3, conduction electrons in metals and degenerate semiconductors may be reasonably well described as a degenerate, ideal Fermi gas, but typically with a non-spherical Fermi surface, due to crystal

$$w_0(\mathbf{r}, \mathbf{p}, t) = \frac{g}{(2\pi\hbar)^3} \langle n_k \rangle, \quad (6.19)$$

where g is the spin degeneracy factor (equal to 2 for electrons), and $\langle n_k \rangle$ is average occupancy of each quantum state, which obeys either the Fermi-Dirac distribution or the Bose-Einstein distribution

$$\langle n_k \rangle = \frac{1}{e^{(\varepsilon - \mu)/T} \pm 1}, \quad \varepsilon = \varepsilon(p) = \frac{p^2}{2m}, \quad (6.20)$$

(Up to a point, our calculations will be valid for both statistics, and hence for a classical gas as well.)

Now let a uniform, dc electric field \mathbf{E} be applied to the gas, exerting force $\mathcal{F} = q\mathbf{E}$ on each particle with electric charge q . Then the stationary solution to Eq. (18), with $\partial/\partial t = 0$, should also be stationary and spatially-uniform ($\nabla = 0$), so that this equation is reduced to

$$q\mathbf{E} \cdot \nabla_p w = -\frac{\tilde{w}}{\tau}. \quad (6.21)$$

Let us assume the electric field to be relatively low as well, so that the perturbation \tilde{w} of the probability that it produces, is relatively small. (I will quantify this condition *a posteriori*.) Then in the left-hand side of Eq. (21) we can neglect that perturbation, by replacing w for w_0 , because that side already has a small factor \mathbf{E} . As a result, this equation yields

$$\tilde{w} = -\tau q \mathbf{E} \cdot \nabla_p w_0 = -\tau q \mathbf{E} \cdot (\nabla_p \varepsilon) \frac{\partial w_0}{\partial \varepsilon}. \quad (6.22)$$

But $\nabla_p \varepsilon$ is the gradient of the kinetic energy,

$$\varepsilon = \frac{p_1^2 + p_2^2 + p_3^2}{2m}, \quad (6.23)$$

in the momentum space, i.e. a vector with Cartesian components

$$(\nabla_p \varepsilon)_j = \frac{\partial \varepsilon}{\partial p_j} = \frac{p_j}{m} = v_j, \quad (6.24)$$

so that Eq. (22) may be rewritten as

$$\tilde{w} = -\tau q \mathbf{E} \cdot \mathbf{v} \frac{\partial w_0}{\partial \varepsilon}. \quad (6.25)$$

Let us use this result to calculate density \mathbf{j} of the resulting dc electric current. The contribution of each quantum state to the current is $q\mathbf{v}w$, so that the total density is

$$\mathbf{j} = \int q\mathbf{v}w d^3 p = q \int \mathbf{v}(w_0 + \tilde{w}) d^3 p. \quad (6.26)$$

anisotropy. For the sake of simplicity, I will focus on an isotropic gas; the generalization to the anisotropic case is rather straightforward.- see, e.g., Chapter 13 in N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Saunders College, 1976.

Since in the equilibrium state (with $w = w_0$), the current has to be zero, integral of the first term in the parentheses has to vanish. For the integral of the second term, plugging in Eq. (25), and also using Eq. (19), we get

$$\mathbf{j} = q^2 \tau \int \mathbf{v}(\mathbf{E} \cdot \mathbf{v}) \left(-\frac{\partial w_0}{\partial \varepsilon} \right) d^3 p = \frac{gq^2 \tau}{(2\pi\hbar)^3} \int \mathbf{v}(\mathbf{E} \cdot \mathbf{v}) \left(-\frac{\partial \langle n_k \rangle}{\partial \varepsilon} \right) d^2 p_{\perp} dp, \quad (6.27)$$

where dp is the differential's component along vector \mathbf{p} , while $d^2 p_{\perp} = p^2 \sin\theta d\theta d\varphi$ is the elementary area of a sphere of radius p in the momentum space. In spherical coordinates, with the polar axis direction along vector \mathbf{E} , we have $(\mathbf{E} \cdot \mathbf{v}) = Ev \cos\theta$. Now separating vector \mathbf{v} outside the parentheses into a component $(\mathbf{E}/E)v \cos\theta$ (of length $v \cos\theta$), directed along vector \mathbf{E} , and a perpendicular component, of length $v \sin\theta$, we see that the integral of the latter component over angle φ gives zero, because it is directed, in each point, perpendicular to the polar axis. Hence, as we could expect, the net current is directed along the electric field and obeys the *Ohm law*,

$$\mathbf{j} = \sigma \mathbf{E}, \quad (6.28)$$

with a field-independent *electric conductivity*⁸

$$\sigma = \frac{gq^2 \tau}{(2\pi\hbar)^3} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \cos^2\theta \int_0^{\infty} p^2 dp v^2 \left(-\frac{\partial \langle n_k \rangle}{\partial \varepsilon} \right). \quad (6.29)$$

Using the fact that $\sin\theta d\theta$ is just $-d(\cos\theta)$, we see that the integral over θ equals $(2/3)$, that over $d\varphi$ is of course just 2π , and the integral over p may be readily transformed to that over energy $\varepsilon = p^2/2m$ (so that $vd p = p dp/m = d\varepsilon$, and $p^2 dp v^2 = p^2 v d\varepsilon = (2m\varepsilon)(2\varepsilon/m)^{1/2} d\varepsilon$). As a result, the conductivity equals

$$\sigma = \frac{gq^2 \tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^{\infty} (8m\varepsilon^3)^{1/2} \left(-\frac{\partial \langle n_k \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (6.30)$$

So far, the calculation (first carried out by A. Sommerfeld in 1927) is valid for any gas (Bose, Fermi, or classical), an arbitrary temperature. Let us work out the remaining integral for the most important case of a degenerate Fermi gas, with $T \ll \varepsilon_F$.⁹ As was discussed in Sec. 3.3, in this limit, factor $(-\partial \langle n_k \rangle / \partial \varepsilon)$ approaches delta-function $\delta(\varepsilon - \varepsilon_F)$, and the conductivity does not depend on temperature – at least explicitly:

$$\sigma = \frac{gq^2 \tau}{(2\pi\hbar)^3} \frac{4\pi}{3} (8m\varepsilon_F^3)^{1/2} = \frac{q^2 \tau}{m} \frac{g}{(2\pi\hbar)^3} \frac{4\pi}{3} (2m\varepsilon_F)^{3/2} = \frac{q^2 \tau}{m} \frac{g}{(2\pi\hbar)^3} \frac{4\pi p_F^3}{3}. \quad (6.31)$$

But the last fraction of this product is just the volume of the Fermi sphere in the momentum space, so that the product of the last two fractions is the total density of quantum states filled at $T = 0$, i.e. the total density $n \equiv N/V$ of electrons in the gas. Hence, the Sommerfeld's result is reduced to the *Drude formula*,

⁸ Notice that the conductivity does not depend on the particle charge sign; this is why the Hall effect of magnetic field, which lacks this ambivalence, is typically used to determine the charge of current carriers (electrons or holes) in semiconductors.

⁹ Calculations for the classical gas (which are important, in particular, for non-degenerate semiconductors) are left for the reader – see Problem 2.

$$\sigma = \frac{q^2 \tau}{m} n, \quad (6.32)$$

which should be well familiar to the reader from an undergraduate physics course.

This leaves us with an important conceptual question. The very structure of Eq. (30) implies that the only quantum states contributing to electric conductance are those where the derivative $(-\partial \langle n_k \rangle / d\varepsilon)$ is significant. At $T \ll \varepsilon_F$, these are the states at the very surface of the Fermi sphere (the so-called *Fermi surface*). On the other hand, the classical derivation of Eq. (32) (carried out by P. Drude in 1900), involves *all* electrons.¹⁰ So, what exactly electrons are responsible for conductance: all of them, or only those on the Fermi surface?

For the resolution of this paradox, let us return to Eq. (22) and analyze the physical meaning of that result. In particular, let us compare it with the following model distribution

$$w_{\text{model}} \equiv w_0(\mathbf{r}, \mathbf{p} - \tilde{\mathbf{p}}, t), \quad (6.33)$$

where $\tilde{\mathbf{p}}$ is some constant, small vector, which describes a small shift of the unperturbed distribution w_0 in the momentum space as a whole. Performing the Taylor expansion of Eq. (33) in this small parameter, and keeping only two leading terms, we get

$$w_{\text{model}} \approx w_0(\mathbf{r}, \mathbf{p}, t) + \tilde{w}_{\text{model}}, \quad \tilde{w}_{\text{model}} = \mathbf{p} \cdot \nabla_{\mathbf{p}} w_0(\mathbf{r}, \mathbf{p}, t). \quad (6.34)$$

Comparing the model perturbation with the first form of Eq. (22), we see that they exactly coincide if

$$\tilde{\mathbf{p}} = q\mathbf{E}\tau. \quad (6.35)$$

This means that Eq. (22) describes a small shift of the equilibrium distribution of electrons by $qE\tau$ (in p -space) along the direction of electric field,¹¹ and gives the following picture of the electron transport in a degenerate gas (Fig. 4).

¹⁰ As a reminder, in the elementary derivation of Eq. (32), τ is the average time of scattering of an electron, at which it loses all the deterministic component of its velocity, \mathbf{v}_E , provided by electric field \mathbf{E} , on the top of electron's random thermal motion (which does not contribute to the net current). Using the 2nd Newton law to describe the electron acceleration by the field, $d\mathbf{v}_E/dt = q\mathbf{E}/m$, we get $\langle \mathbf{v}_E \rangle = \tau q\mathbf{E}/m$. Multiplying this result by the particle charge q and density $n = N/V$, we get the Ohm law $\mathbf{j} = \sigma\mathbf{E}$, with σ given by Eq. (32). Note that P. Drude also used the same arguments to derive a very simple (and very reasonable) approximation for the complex conductivity in the ac field of frequency ω : $\sigma(\omega) = \sigma(0)/(1 - i\omega\tau)$, with $\sigma(0)$ given by Eq. (32); sometimes the name “Drude formula” is used for this expression rather than for Eq. (32) – see Problem 1.

¹¹ By the way, since the scale of the fastest change of w_0 in the momentum space is of the order of $\partial w_0 / \partial p = (\partial w_0 / \partial \varepsilon)(d\varepsilon/dp) \sim (1/T)v_F$, linear approximation (34) is valid if $eE\tau \ll T/v_F$, i.e. if $eEl \ll T$, where $l \equiv v_F\tau$ is called the *mean free path*. This is the promised quantitative condition of the electric field smallness; since its left-hand part of this relation is just the average energy given to the particle by the electric field between two scattering events, the condition may be interpreted as the smallness of electron gas “overheating” by the field. However, another condition is also necessary – see below.

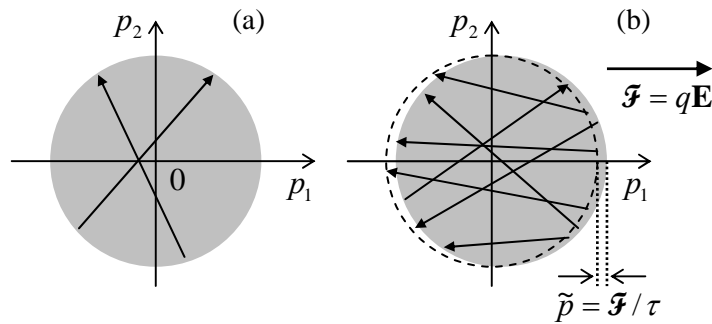


Fig. 6.4. Filling of momentum states in a degenerate electron gas: (a) in the presence and (b) in the absence of external electric field \mathbf{E} . Arrows show representative scattering events.

At $\mathbf{E} = 0$, the system is in equilibrium, so that the quantum states inside the Fermi sphere ($\mathbf{p} < \mathbf{p}_F$), are occupied and those outside of it are empty (Fig. 4a). Electron scattering events happen only between states within a very thin layer ($|p^2/2m - \varepsilon_F| \sim T$) at the Fermi surface, because only in this layer the states are partially occupied, so that both components of the product $w(\mathbf{r}, \mathbf{p}, t)[1 - w(\mathbf{r}, \mathbf{p}', t)]$, mentioned in Sec. 1, are finite. These scattering events, on the average, do not change the equilibrium probability distribution, because they are uniformly spread over the Fermi surface.

In the instant it has been turned on, the electric field starts to accelerate all electrons in its direction, i.e. the whole Fermi sphere starts moving along the field. For elastic scattering events (with $p'^2 = p^2$), this creates additional occupied states at the leading front of the sphere, and additional free empty states on its trailing edge (Fig. 4b). As a result, now there are more scattering events bringing electrons from the leading edge to the trailing edge, than in the opposite direction. This creates the average backflow of states occupancy in the momentum space. These two trends cancel each other, and the Fermi sphere finally approaches the stationary (though not thermally-equilibrium!) state, with the shift (35) relatively to its thermal-equilibrium position.

Figure 4b presents an answer to the question which of the two different interpretations of the Drude formula is correct, and its final verdict is: *either*. On one hand, we can look at the shifted Fermi sphere as a result of shift (25) of all electrons in the momentum space. On the other hand, each state deep inside the sphere gives exactly the same contribution into the net current density as it did without the field. All these internal contributions to the net current cancel each other, so that the applied field changes the situation only at the Fermi surface. Thus it is equally legitimate to say that only the surface states are responsible for the finite net current. As usual in physics, formulas (or drawings, such as Fig. 4), give a more clear and unambiguous description of the reality than words – the privilege many other scientific (and “scientific”) disciplines lack, resulting in unending and empty debates.

Let me also mention the second paradox related to the Drude formula, which is often misunderstood (not only by students :-). As was emphasized above, τ is the average time of *elastic* scattering which by itself does not change the total energy of the electron gas. The question is how can such scattering may be responsible for Ohmic resistivity $\rho \equiv 1/\sigma$, and hence for the Joule heat production, with power density $\mathcal{P}/V = \mathbf{j} \cdot \mathbf{E} = \rho j^2$? The answer is that the Drude and Sommerfeld formulas describe just the “bottleneck” of the resistivity formation. In the scattering picture (Fig. 4b) the elastically scattered electron states are predominantly located above the (shifted) Fermi surface, and need to relax onto it via some inelastic process which releases their additional energy in the form of heat (in solid state materials, described by phonons – see Sec. 2.6). The rate and other features of these inelastic phenomena do not participate in the Drude formula, but for that, their intensity should be sufficient to avoid gas overheating by the applied field. This gives an additional restriction on the simple

theory described above. In some semiconductors, the overheating effects, resulting in deviations from the Ohm law, i.e. from a linear relation between \mathbf{j} and \mathbf{E} , may be readily observed already at modest applied voltages.

6.4. Electrochemical potential and drift-diffusion equation

Now let us generalize our calculation to the case when transport is caused (or affected) by a time-independent spatial gradient of the probability distribution, $\nabla w \neq 0$, caused either by that of the particle concentration $n = N/V$ (and hence of the chemical potential μ , see Eq. (3.34)), while still considering temperature constant. If the gradient of w is sufficiently small, we can repeat arguments of the last section and replace w for w_0 in the second term of Eq. (18). With electric field \mathbf{E} presented as $(-\nabla\phi)$, where ϕ is the electrostatic potential, Eq. (22) now becomes

$$\tilde{w} = -\tau \mathbf{v} \cdot \left(\frac{\partial w_0}{\partial \varepsilon} q \nabla \phi + \nabla w_0 \right). \quad (6.36)$$

Since in any of quantum distributions (20), $\langle n_k \rangle$ is a function of ε and μ only in combination $(\varepsilon - \mu)$, it obeys the following relation,

$$\frac{\partial \langle n_k \rangle}{\partial \mu} = -\frac{\partial \langle n_k \rangle}{\partial \varepsilon}. \quad (6.37)$$

Using it, the gradient of $w_0 \propto n$ may be presented as¹²

$$\nabla w_0 = -\frac{\partial w_0}{\partial \varepsilon} \nabla \mu, \quad (6.38)$$

so that Eq. (29) becomes

$$\tilde{w} = -\tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot (q \nabla \phi + \nabla \mu) = -\tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot q \nabla \Phi, \quad (6.39)$$

where the sum

$$\Phi \equiv \phi + \frac{\mu}{q} \quad (6.40)$$

is called the *electrochemical potential*.¹³ Now repeating the calculation of the electric current made in the last section, we get the following generalization of the Ohm law (28):

$$\mathbf{j} = \sigma (-\nabla \Phi) = \sigma \mathcal{E}, \quad (6.41)$$

where the effective electric field \mathcal{E} is the (minus) gradient of the electrochemical potential, rather of the electrostatic potential:

¹² Since we consider w_0 as a function of two *independent* arguments \mathbf{r} and \mathbf{p} , taking its gradient, i.e. differentiation over \mathbf{r} does not involve differentiation over the kinetic energy ε (which is a function of \mathbf{p} only), and the right-hand part of Eq. (38) is expressed via derivative $\partial w_0 / \partial \varepsilon$ only for the convenience of what follows.

¹³ In electronic engineering literature, variable $q\Phi = \mu + q\phi$ it is frequently called the “local Fermi level”.

$$\boldsymbol{\mathcal{E}} \equiv -\nabla\Phi = \mathbf{E} - \frac{\nabla\mu}{q}. \quad (6.42)$$

The physics of this very important result may be explained in two ways. First of all, let us have a look at the energy spectrum of a uniform Fermi gas confined in a volume of finite size. In order to ensure such confinement, we need a piecewise-constant potential $U(\mathbf{r})$ (a “potential well”) with a flat bottom – see Fig. 5a. (In a conductor, such profile is provided by the crystal lattice of positively charged ions of the crystal lattice.) The well should be of a sufficient depth $U_0 > \varepsilon_F \equiv \mu|_{T=0}$ in order to provide the confinement of the overwhelming majority of the particles, with energies below or slightly above the Fermi level ε_F . This means that there should be a substantial distance,

$$\psi \equiv U_0 - \mu \gg T, \quad (6.43)$$

between the Fermi energy of a particle inside the well, and its potential energy outside the well. (The latter is usually called the “vacuum level”). The difference defined by Eq. (43) is called the *workfunction*;¹⁴ for most conducting materials, its is between 4 and 5 eV, so that relation $\psi \gg T$ is well fulfilled for the room temperature ($T \approx 0.026$ eV), and actually for all temperatures up to the material evaporation point.

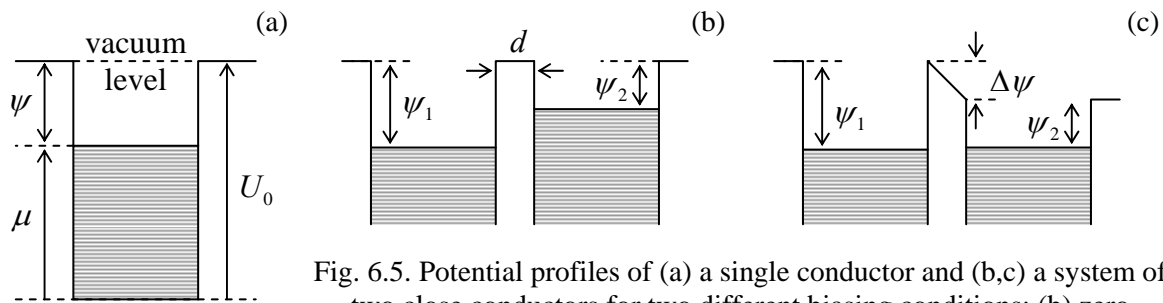


Fig. 6.5. Potential profiles of (a) a single conductor and (b,c) a system of two close conductors for two different biasing conditions: (b) zero electrostatic field, (c) zero voltage $V \equiv \Delta\Phi$.

Now let us consider two conductors, with different values of ψ , located at small distance d – see Fig. 5b,c. Panel (b) shows the case when the electric field $\mathbf{E} = -\nabla\phi$ in the free-space gap between the conductors equals zero, i.e. their electrostatic potentials ϕ are equal) – Fig. 5b.¹⁵ If there is an opportunity for particles to cross the gap (e.g., by tunneling through the potential barrier), there will be an average flux of particles from the gas with higher Fermi level to that with the lower Fermi level (as measured from the same reference energy, e.g., from the vacuum level), because the chemical equilibrium requires their equality – see Secs. 1.5 and 2.7. If the particles have an electric charge (as electrons do), the equilibrium will be automatically achieved by the transferred particles recharging the

¹⁴ Sometimes called the “electron affinity”, though the latter term is mostly used for atoms and molecules.

¹⁵ In electronic engineering, the situation shown in Fig. 5b is called the *flat-band condition*, because in semiconductors, any electric field at the surface, i.e. any finite surface charge leads to “band bending” – a gradual change of the background potential U_0 and hence all energy band and gap edges. For an introduction to these issues, which are crucial for semiconductor device operation, see, e.g., Chapter 6 of J. R. Hook and H. E. Hall, *Solid State Physics*, 2nd ed. Wiley, 1991, or Chapter 3 of S. M. Sze, *Semiconductor Devices*, 2nd ed., Wiley, 2001.

effective capacitor formed by the conductors, until the electrostatic potential difference reaches the value¹⁶ reproducing that of the workfunctions (Fig. 5c):

$$q\Delta\phi = \Delta\psi = -\Delta\mu. \quad (6.44)$$

This equilibrium value creates the electric field,¹⁷

$$E \equiv -\frac{\Delta\phi}{qd} = \frac{\Delta\mu}{qd} = \frac{\nabla\mu}{q}, \quad (6.45)$$

which is clearly visible in Fig. 5c as the potential profile tilt. Comparing this expression with definition (42) of the effective field \mathcal{E} , we see that the equilibrium, i.e. the absence of current, is achieved exactly when $\mathcal{E} = 0$, in accordance with relation (41).

For another interpretation of Eq. (41), let us modify Eq. (38) for the particular case of a classical gas whose local density $n \equiv dN/dV$ obeys Eq. (3.34), which may be presented as

$$n(\mathbf{r}) = \text{const} \times \exp\left\{\frac{\mu(\mathbf{r})}{T}\right\}. \quad (6.46)$$

Taking gradient of the both parts of this relation, we get

$$\nabla n = \frac{\partial n}{\partial \mu} \left(\nabla\mu - \frac{\mu}{T} \nabla T \right) = \text{const} \times \frac{1}{T} \exp\left\{\frac{\mu}{T}\right\} \left(\nabla\mu - \frac{\mu}{T} \nabla T \right) = \frac{n}{T} \left(\nabla\mu - \frac{\mu}{T} \nabla T \right), \quad (6.47)$$

so that at $T = \text{const}$, current density (41) may be presented as

$$\mathbf{j} = \sigma(-\nabla\Phi) = \frac{q^2\tau}{m} n \left(-\nabla\phi - \frac{1}{q} \nabla\mu \right) = q \frac{\tau}{m} (nq\mathbf{E} - T\nabla n). \quad (6.48)$$

Hence the current may be viewed as consisting of two independent parts: one due to the “usual” electric field $\mathbf{E} = -\nabla\phi$, and another due to the particle concentration gradient. This is exactly the physics of the “mysterious” term $\nabla\mu$ in Eq. (42), though only in the classical limit its result may be presented in the simple form (48).

Besides being very useful for practice,¹⁸ Eq. (48) gives us a very pleasant surprise. Plugging it into the continuity equation for electric charge,

$$\frac{\partial(qn)}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (6.49)$$

we get (after the division of all terms by $q\tau/m$) the so-called *drift-diffusion equation*:¹⁹

¹⁶ In most physics literature, this difference is called the *contact potential difference*, while in electrochemistry (for which it is one of key notions) the term “Volta potential” is more common.

¹⁷ Most voltmeters belong to the “electrodynamic” variety, are based on measurement of small current flowing through them, and hence measure the difference of electrochemical potentials Φ , defined by Eq. (40). However, there exist special “electrostatic” voltmeters which measure the difference of electrostatic potentials ϕ between two surfaces. (They are based on an initial measurement of such difference $\Delta\Phi = \Delta\psi/q$ which implements the flat-band condition shown in Fig. 5b, and provides zero surface charges)

¹⁸ In particular, in physics of semiconductor devices, where electrons in the conduction band, and holes in the valence band, may be frequently treated as classical gases – see, e.g., textbooks cited in Footnote 15.

$$\frac{m}{\tau} \frac{\partial n}{\partial t} = \nabla(n \nabla U) + T \nabla^2 n, \quad U \equiv q\phi. \quad (6.50)$$

Comparing it with Eq. (5.128), we see that the drift-diffusion equation is identical to the Smoluchowski equation, if we parallel ratio τ/m with mobility $\mu_m = 1/\eta$ of a Brownian “particle”²⁰

$$\frac{\tau}{m} \leftrightarrow \mu_m \equiv \frac{1}{\eta}, \quad (6.51)$$

and hence the following combination, $\tau T/m$, with the diffusion constant D (5.82). As a result, Eq. (48) is frequently rewritten as an expression for the particle flow density $\mathbf{j}_N \equiv N \mathbf{j}_w = \mathbf{j}/q$:

$$\mathbf{j}_N = \mu_m n q \mathbf{E} - D \nabla n. \quad (6.52)$$

Intellectually, this similarity is deeply satisfying. Indeed, in our (or rather Einstein’s :-) treatment of the Brownian motion in Chapter 5, we have assumed a strong hierarchy of the total system, consisting of a large “Brownian particle” in an environment of many smaller particles. On the other hand, in this chapter we are considering a gas of similar particles. Nevertheless, the equations describing the dynamics of their probability distribution, are the same – at least within the relaxation-time approximation (17).

6.5. Thermoelectric effects

Now let us generalize our analysis even further, to the effects of a finite (thought relatively small) temperature gradient. Again, since for any of statistics (20), the average occupancy $\langle n_k \rangle$ is a function of just one combination of all its arguments, $\xi = (\varepsilon - \mu)/T$, its partial derivatives obey not only Eq. (30), but also the following property,

$$\frac{\partial \langle n_k \rangle}{\partial T} = -\frac{1}{T^2} \frac{\partial \langle n_k \rangle}{\partial \xi} = -\frac{\varepsilon - \mu}{T} \frac{\partial \langle n_k \rangle}{\partial \varepsilon}. \quad (6.53)$$

As a result, Eq. (38) becomes

$$\nabla w_0 = -\frac{\partial w_0}{\partial \varepsilon} \left(\nabla \mu + \frac{\varepsilon - \mu}{T} \nabla T \right), \quad (6.54)$$

giving the following generalization of Eq. (39):

$$\tilde{w} = -\tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot \left[q \nabla \Phi + \frac{\varepsilon - \mu}{T} \nabla T \right]. \quad (6.55)$$

Now, repeating the calculation of current density, we get a result which is traditionally presented as

$$\mathbf{j} = \sigma(-\nabla \Phi) + \sigma \mathcal{S}(-\nabla T), \quad (6.56)$$

with

¹⁹ Sometimes this term is associated with Eq. (48).

²⁰ As a reminder, results of the Brownian motion analysis Sec. 5.5-5.9 are also applicable to many systems with completely different physics.

$$\sigma \mathcal{S} = \frac{gq\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} \frac{(\varepsilon - \mu)}{T} \left(-\frac{\partial \langle n_k \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (6.57)$$

For a degenerate Fermi gas, with $T \ll \varepsilon_F$, this integral may be calculated using the Sommerfeld expansion formula (3.59). Indeed, combining it with Eqs. (3.60) and (3.61), for any function $f(\varepsilon)$, with $f(0) = 0$, we may rewrite that approximation as

$$\int_0^\infty f(\varepsilon) \left(-\frac{\partial \langle n_k \rangle}{\partial \varepsilon} \right) d\varepsilon = f(\mu) + \frac{\pi^2}{6} T^2 \frac{d^2 f}{d\varepsilon^2} \Big|_{\varepsilon=\mu}. \quad (6.58)$$

In particular, for integral (57), we may take $f(\varepsilon) \equiv (8m\varepsilon^3)^{1/2}(\varepsilon - \mu)/T$, so that $f(\mu) = 0$ and $d^2 f/d\varepsilon^2|_{\varepsilon=\mu} = 3(8m\mu)^{1/2}/T \approx 3(8m\varepsilon_F)^{1/2}/T$, and Eq. (58) yields

$$\sigma \mathcal{S} = \frac{gq\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \frac{\pi^2}{6} T^2 \frac{3(8m\varepsilon_F)^{1/2}}{T}. \quad (6.59)$$

Comparing the result with Eq. (31), for constant \mathcal{S} we get a simple expression independent of τ ²¹

$$\mathcal{S} = \frac{\pi^2}{2q} \frac{T}{\varepsilon_F} = \frac{c_V}{q}, \quad (6.60)$$

where $c_v \equiv C_V/N$ is the heat capacity of the gas per unit particle – cf. Eq. (3.70).

Constant \mathcal{S} is called either the *Seebeck coefficient*,²² or the “thermoelectric power”, or just “thermopower”. In order to understand its physical sense, it is sufficient to consider a conductor carrying no current, then Eq. (56) yields

$$\nabla(\Phi + \mathcal{S}T) = 0. \quad (6.61)$$

Thus, the temperature gradient creates the gradient of the effective electric potential Φ , i.e. the effective field \mathcal{E} – see Eq. (42). This is the *Seebeck effect* (see Footnote 23). Figure 6 shows the standard way of its measurement, using a usual (electrodynamic) voltmeter and a “*thermocouple*” of two different materials, with different coefficients S .

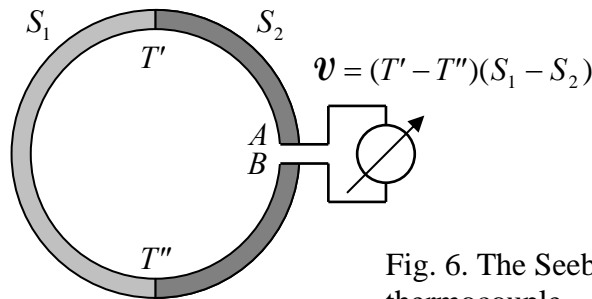


Fig. 6. The Seebeck effect in a thermocouple.

²¹ Such independence infers that Eq. (53) should have a broader validity than in our simple model of an isotropic gas. This is indeed the case – at $T \ll \varepsilon_F$, this result turns out to be valid for any form of the Fermi surface, and for any dispersion law $\varepsilon(\mathbf{p})$.

²² Named after T. J. Seebeck who experimentally discovered, in 1821 (independently of J. C. A. Peltier), the effect, as expressed by Eq. (62).

Integrating Eq. (61) around the loop from point A to point B , and neglecting the temperature drop across the voltmeter, we get the following simple expression for the thermally-induced difference of the electrochemical potential, frequently also called the *thermoelectric power*:

$$\mathcal{V}_{AB} \equiv \Phi_A - \Phi_B = (\mathcal{S}_1 - \mathcal{S}_2)(T' - T''). \quad (6.62)$$

(Notice that according to Eq. (62), an attempt to measure voltage across any two points of a uniform conductor, using voltmeter's wires made of the same material ($\mathcal{S}_1 = \mathcal{S}_2$), would fail, due to the unintentional gradient of potential in the wires.)

The thermocouple is a popular, inexpensive method of temperature measurement – especially in the few-hundred °C range (where gas- and fluid-base thermometers are not too practicable) and if 1°C-scale accuracy is sufficient. The “responsivity” ($\mathcal{S}_1 - \mathcal{S}_2$) of a typical popular thermocouple, chromel-constantan,²³ is about 68 $\mu\text{V}/^\circ\text{C}$. In order to understand why typical values of \mathcal{S} are so small, let us discuss physics of the Seebeck effect. Superficially, it is very simple: particles, heated by an external source, diffuse from it toward the colder parts of the conductor, carrying electrical current with them if they are charged. However, this naïve argument neglects the fact that at $\mathbf{j} = 0$, there should be no total flow of particles. For a more subtle understanding, notice that the Seebeck effect is described by the factor $(\varepsilon - \mu)/T$ in integral (57), which changes sign at the Fermi surface, i.e. at the same energy where the term $(-\partial\langle n_k \rangle / \partial\varepsilon)$, describing the state availability for transport (due to their intermediate occupancy $0 < n_k < 1$), reaches its peak. The only reason why that integral does not vanish completely, and hence $\mathcal{S} \neq 0$, is the growth of first factor under the integral (which describes the number of available quantum states and their energy) with ε , so the hotter particles (with $\varepsilon > \varepsilon_F$) carry more heat than the colder ones.

The Seebeck effect is not the only result of temperature gradient; the same diffusion of hotter particles also causes a flow of *heat* from the region of higher T to those with lower T – the familiar effect of *thermal conductance*. The heat (i.e. thermal energy) flow density may be calculated similarly to that of the electric current – see Eq. (26), with the natural replacement of the electric charge q of each particle for the thermal energy $(\varepsilon - \mu)$ of its state:²⁴

$$\mathbf{j}_H = \int (\varepsilon - \mu) \mathbf{v} w d^3 p. \quad (6.63)$$

Again, at equilibrium ($w = w_0$) the heat flow vanishes, so that w may be replaced by its perturbation \tilde{w} , which already has been calculated – see Eq. (55). The substitution of that expression into Eq. (63), and its transformation exactly similar to that done above for the electric current \mathbf{j} , yields

$$\mathbf{j}_H = \sigma \Pi (-\nabla \Phi) + \kappa (-\nabla T), \quad (6.64)$$

with

$$\sigma \Pi = \frac{g q \tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} (\varepsilon - \mu) \left(-\frac{\partial\langle n_k \rangle}{\partial\varepsilon} \right) d\varepsilon, \quad (6.65)$$

²³ Both these materials are *alloys*, i.e. solid solutions: chromel is 10% chromium in 90% nickel, while constantan is 45% nickel and 55% copper.

²⁴ One more way to look at Eq. (63) is as at the difference between the total energy flow density, $\mathbf{j}_E = \int \varepsilon \mathbf{v} w d^3 p$, and the product of a constant (μ) by the particle flow density, $\mathbf{j}_N = \int \mathbf{v} w d^3 p = \mathbf{j}/q$ – cf. Eq. (52).

and

$$\kappa = \frac{g\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} \frac{(\varepsilon - \mu)^2}{T} \left(-\frac{\partial \langle n_k \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (6.66)$$

Besides an extra factor T , integral (60) is the same as in Eq. (57), so that constant Π (called the *Peltier coefficient*), is simply and fundamentally related to the Seebeck coefficient:²⁵

$$\Pi = ST. \quad (6.67)$$

On the other hand, integral (65) may be readily calculated, for the most important case of degenerate Fermi gas, using the Sommerfeld expansion (58) with $f(\varepsilon) \equiv (8m\varepsilon^3)^{1/2}(\varepsilon - \mu)^2/T$, for which $f(\mu) = 0$ and $d^2f/d\varepsilon^2|_{\varepsilon=\mu} = 2(8m\mu^3)^{1/2}/T \approx 2(8m\varepsilon_F^3)^{1/2}/T$:

$$\kappa = \frac{g\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \frac{\pi^2}{6} T^2 \frac{2(8m\varepsilon_F^3)^{1/2}}{T}. \quad (6.68)$$

Comparing the result with Eq. (31), get the so called *Wiedemann-Franz law*²⁶

$$\kappa = \frac{\pi^2}{3} \frac{T}{q^2} \sigma. \quad (6.69)$$

From the very definition of this relation between the electric conductivity σ and *thermal conductivity* κ , it is clear that it is more general than our formal derivation might imply. Indeed, it is straightforward to show that the Wiedemann-Franz law is also valid for an arbitrary shape of the Fermi surface and, moreover, well beyond the relaxation-time approximation. (For example, it is also valid for scattering integral (12) with arbitrary angular dependence of rate Γ , provided that scattering is elastic.) Experiments show that the law is well obeyed by most metals, but only at relatively low temperatures $T \ll T_D$, when thermal conductance due to electrons is well above one due to lattice vibrations, i.e. phonons – see Sec. 2.6.

Now let us discuss the less evident, first term of Eq. (64). It describes the so-called *Peltier effect*, which may be measured in the geometry similar to that shown in Fig. 6, but driven by a dc voltage source – see Fig. 7.

²⁵ The simplicity of this relation (first discovered experimentally in 1854 by W. Thompson, a.k.a. Lord Kelvin) is not occasional. This is one of fundamental *Onsager reciprocal relations* between kinetic coefficients (L. Onsager, 1931), which are model-independent, i.e. valid within very general assumptions. These coefficients also describe mutual correlation between simultaneous fluctuations of thermodynamic variables. Unfortunately, I have no time left for a discussion of this interesting topic. The interested reader may be referred, for example, to Secs. 119 and 120 in L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed., Pergamon, 1980.

²⁶ It was named after G. Wiedemann and R. Franz who noticed the constancy of ratio κ/σ for various materials, at the same temperature, as early as in 1853. The direct proportionality of the ratio to the absolute temperature was noticed by L. Lorenz in 1872. Due to his contribution, the Wiedemann-Franz law is frequently presented as $\kappa/\sigma = LT$, where constant L , called the *Lorenz number*, in SI units is close to $2.45 \times 10^{-8} \text{ W}\cdot\Omega/\text{K}^2$. Theoretically, Eq. (63) was derived in 1928 by A. Sommerfeld.

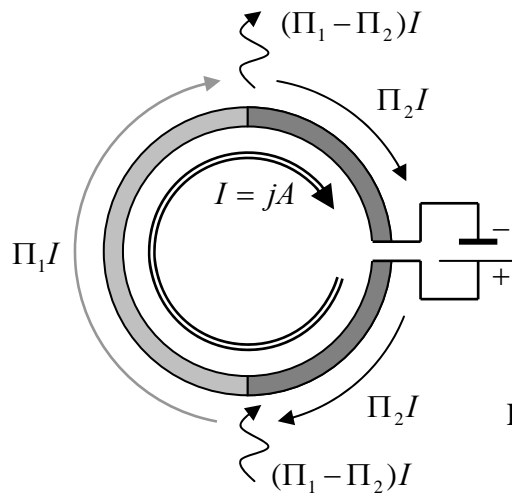


Fig. 7. The Peltier effect.

The voltage induces a certain dc current $I = jA$, necessarily the same in all cross-sections of the loop. However, according to Eq. (64), if the materials 1 and 2 are different, power $\mathcal{P} = j_H A$ of the heat flow is different in two parts of the loop. Indeed, if the whole system is kept at the same temperature ($\nabla T = 0$), integration of the equation over the cross-section yields

$$\frac{(P)_{1,2}}{I} = \frac{(j_H)_{1,2}}{j} = \Pi_{1,2}. \quad (6.70)$$

This means that in order to sustain constant temperature, power

$$P = (\Pi_1 - \Pi_2)I \quad (6.71)$$

has to be extracted from one junction of the two materials, and inserted into another junction. If a constant temperature is not maintained, the former junction is heated, while the latter one is cooled (on the top of the bulk, Joule heating), thus implementing a thermoelectric heat pump.

Such pumps, with no moving parts, are very convenient for modest (by a few tens °C) cooling of relatively small components of various systems (from sensitive radiation detectors in spacecraft, all the way to cold drinks). It is straightforward to use above formulas to show that the efficiency of active materials used in such thermoelectric refrigerators may be characterized by the following dimensionless figure-of-merit, $ZT \equiv (\sigma S^2 / \kappa) T$. For the best materials found so far, ZT is in the range from 2 to 3, providing the coefficient of performance, defined by Eq. (1.71), of the order of 0.5 - a few times lower than that of traditional, mechanical refrigerators. The search for composite materials (including those with nanoparticles) with higher values of Z is one of active parts of applied solid state physics.²⁷

Let me finish the course by saying that due to time restrictions I was able to barely scratch the surface of physical kinetics. A much more detailed coverage of this important part of physics may be found, for example, in the textbook by L. P. Pitaevskii and E. Lifshitz, *Physical Kinetics*, Butterworth-Heinemann, 1981.

²⁷ See, e.g., D. M. Rowe (ed.), *Thermoelectrics Handbook: Macro to Nano*, CRC Press, 2005.

6.6. Problems

6.1. Use the relaxation-time approximation of the Boltzmann equation to prove the Drude formula for complex conductivity at frequency ω ,

$$\sigma(\omega) = \frac{\sigma(0)}{1 - i\omega\tau},$$

where $\sigma(0)$ is the dc conductivity given by Eq. (6.30) of the lecture notes, and give a physical interpretation of the formula.

6.2. Calculate the electric conductivity σ , thermal conductivity κ , as well as thermoelectric coefficients S and Π , for a classical, ideal gas of charged particles. Discuss the results.