

so that they can be treated as an ideal gas. But the numerical values of the significant parameters are then quite different. First, the mass of the electron is very small, about 10^{-27} g or 7000 times less than that of the He atom. This makes the de Broglie wavelength of the electron much longer,

$$\bar{\lambda} \approx (0.6 \times 10^{-8}) \sqrt{7000} \approx 50 \times 10^{-8} \text{ cm}$$

In addition, there is about one conduction electron per atom in the metal. Since there is roughly one atom in a cube 2×10^{-8} cm on a side,

$$\bar{N} \approx 2 \times 10^{-8} \text{ cm}$$

This is much smaller than for the He gas case; i.e., the electrons in a metal form a very dense gas. Hence the criterion (7.4.3) is certainly not satisfied. Thus there exists no justification for discussing electrons in a metal by classical statistical mechanics; indeed, a completely quantum-mechanical treatment is essential.

THE EQUIPARTITION THEOREM

7.5 Proof of the theorem

In classical statistical mechanics there exists a very useful general result which we shall now establish. As usual, the energy of a system is a function of some f generalized coordinates q_i and corresponding f generalized momenta p_i ; i.e.,

$$E = E(q_1, \dots, q_f, p_1, \dots, p_f) \quad (7.5.1)$$

The following is a situation of frequent occurrence:

a. The total energy splits additively into the form

$$E = \epsilon_i(p_i) + E'(q_1, \dots, p_f) \quad (7.5.2)$$

where ϵ_i involves only the one variable p_i and the remaining part E' does not depend on p_i .

b. The function ϵ_i is quadratic in p_i ; i.e., it is of the form

$$\epsilon_i(p_i) = b p_i^2 \quad (7.5.3)$$

where b is some constant.

The most common situation is one where p_i is a momentum. The reason is that the kinetic energy is usually a quadratic function of each momentum component, while the potential energy does not involve the momenta.

If in assumptions (a) and (b) the variable were not a momentum p_i but a coordinate q_i satisfying the same two conditions, the theorem we want to establish would be exactly the same.

We ask the question: What is the mean value of ϵ_i in thermal equilibrium if conditions (a) and (b) are satisfied?

If the system is in equilibrium at the absolute temperature $T = (k\beta)^{-1}$, it is distributed in accordance with the canonical distribution; the mean value

$\bar{\epsilon}_i$ is then, by definition, expressible in terms of integrals over all phase space

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \dots, p_f)} \epsilon_i dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \dots, p_f)} dq_1 \dots dp_f} \quad (7.5.4)$$

By condition (a) this becomes

$$\begin{aligned} \bar{\epsilon}_i &= \frac{\int e^{-\beta(\epsilon_i + E')} \epsilon_i dq_1 \dots dp_f}{\int e^{-\beta(\epsilon_i + E')} dq_1 \dots dp_f} \\ &= \frac{\int e^{-\beta \epsilon_i} \epsilon_i dp_i \int e^{-\beta E'} dq_1 \dots dp_f}{\int e^{-\beta \epsilon_i} dp_i \int e^{-\beta E'} dq_1 \dots dp_f} \end{aligned}$$

where we have used the multiplicative property of the exponential function and where the last integrals in both numerator and denominator extend over all terms q and p except p_i . These integrals are equal and thus cancel; hence only the one-dimensional integrals survive:

$$\bar{\epsilon}_i = \frac{\int e^{-\beta \epsilon_i} \epsilon_i dp_i}{\int e^{-\beta \epsilon_i} dp_i} \quad (7.5.5)$$

This can be simplified further by reducing the integral in the numerator to that in the denominator. Thus

$$\begin{aligned} \bar{\epsilon}_i &= \frac{-\frac{\partial}{\partial \beta} \left(\int e^{-\beta \epsilon_i} dp_i \right)}{\int e^{-\beta \epsilon_i} dp_i} \\ \bar{\epsilon}_i &= -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right) \end{aligned} \quad (7.5.6)$$

Up to now we have made use only of the assumption (7.5.2). Let us now use the second assumption (7.5.3). Then the integral in (7.5.6) becomes

$$\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i = \int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i = \beta^{-\frac{1}{2}} \int_{-\infty}^{\infty} e^{-b y^2} dy$$

where we have introduced the variable $y \equiv \beta^{\frac{1}{2}} p_i$. Thus

$$\ln \int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i = -\frac{1}{2} \ln \beta + \ln \int_{-\infty}^{\infty} e^{-b y^2} dy$$

But here the integral on the right does not involve β at all. Hence (7.5.6) becomes simply

$$\bar{\epsilon}_i = -\frac{\partial}{\partial \beta} \left(-\frac{1}{2} \ln \beta \right) = \frac{1}{2\beta}$$

or

$$\bar{\epsilon}_i = \frac{1}{2} kT \quad (7.5.7)$$

Note the great generality of this result and that we obtained it *without* needing to evaluate a single integral.

Equation (7.5.7) is the so-called "equipartition theorem" of classical statistical mechanics. In words it states that the mean value of each independent quadratic term in the energy is equal to $\frac{1}{2} kT$.