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Einstein Relation for Quantum Systems

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The Einstein relation between the diffusion constant $\mathscr{D}$ and the mobility u is discussed for various quantum systems, proceeding from the analysis of the general thermodynamic relation. Comparison between the kinematic and the thermodynamic derivation reveals the possibility to use the Einstein relation in investigations of the particle energy distribution in nonequilibrium conditions.

KEY WORDS: Diffusion constant; mobility; quasiparticles; fermions; bosons.

1. The Einstein relation,$^{(1)}$ that gives the connection between the diffusion constant $\mathscr{D}$ and the mobility u, had played an important role in formulation of the principles of the molecular-kinetic theory of matter[2] and still remains topical (see, for example, Refs. 2 and 3). It had allowed to find the size of molecules in liquids; moreover, it had established the relationship between the Brownian motion and the thermal motion of molecules in liquids. This relation is essential since it connects two different kinetic transport processes and therefore gives the possibility to determine one of the transport coefficients if the other is known or measured.

The Einstein relation

$$\mathscr{E}_n \equiv \frac{\mathscr{D}}{u} = kT \tag{1}$$

was derived for particles that obey the classical Boltzmann statistics (T is the temperature, k is the Boltzmann constant; starting from Section 2 we put $k = 1$).

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[2] Einstein had repeatedly discussed the relationship between the mobility and the diffusion constant (see Ref. 1).

Let us first give the derivation of Eq. (1) that follows the work of Einstein.$^{(1)}$ If 1 cm^3 contains n particles of the soluted substance, then the volume per one particle is

$$v = \frac{1}{n} \tag{2}$$

The force, acting on the soluted (chosen) particle due to the osmotic pressure p, i.e., is created by all other soluted particles, is equal to

$$\mathbf{F} = \int_{(S)} p\,\mathbf{dS} = -\int_{(v)} \nabla p\,dv \tag{3}$$

where S is the surface, surrounding this particle, $\mathbf{dS}$ is the area element oriented along the normal to the surface, v is the volume per one particle. The variation of the pressure gradient ∇p in the volume v is, naturally, taken to be small. Then

$$\mathbf{F} = -v\,\nabla p \tag{4}$$

The osmotic pressure that is created by the soluted particles is

$$p = nkT \tag{5}$$

According to (2), (4), and (5) in the isothermic case we have

$$\mathbf{F} = -kT\frac{\nabla n}{n} \tag{6}$$

The velocity $\mathbf{v}$ of the spherical particle with the radius a, subjected to the action of the force $\mathbf{F}$, is given, according to Stokes (see, e.g., Ref. 4), by the expression $\mathbf{F}/6\pi a\eta$, where η is the viscosity of the solvent. Hence the mobility of the particle is

$$u = (6\pi\eta a)^{-1} \tag{7}$$

On the other hand the current density of the soluted particles is $\mathbf{J} = \mathbf{vn}$. By substituting the Stokes expression for $\mathbf{v}$ and Eq. (6) for the force $\mathbf{F}$, and introducing the diffusion constant $\mathscr{D}$, we have

$$\mathbf{J} = -\mathscr{D}\,\nabla n, \qquad \mathscr{D} = kT/6\pi\eta a \tag{8}$$

By comparing Eqs. (8) and (7) we find the relation (1). Eq. (8) that connects $\mathscr{D}$, η, and a shows, that the measurement of the diffusion constant $\mathscr{D}$ and the viscosity η allows to determine the size a of the molecule. Such measurements were performed by Perren in 1908.

2. The relation (1) can be obtained in a more formal way.$^{(5)}$ Emergence of the current flow $\mathbf{J}$ of the solution particles is the consequence of the deviation from the equilibrium state that is caused by the dependence of the chemical potential μ of the soluted particles on the coordinates. In the linear approximation we have

$$J_i = -\gamma_{ik} \frac{\partial \mu}{\partial x_k} \tag{9}$$

where γ_{ik} is the tensor of transport coefficients. The anisotropic form of (9) is used, since we want to apply further the Einstein relation to crystals. When the particles are in the external field, i.e., are subjected to the action of the force $\mathbf{F} \doteq -\nabla U$,

$$\mu = \mu_0(n, T) + U \tag{10}$$

where μ_0 is the chemical potential at $U \equiv 0$. According to (9) and (10)

$$J_i = -\gamma_{ik} \left[\left(\frac{\partial \mu_0}{\partial n} \right)_T \frac{\partial n}{\partial x_k} - \mathscr{F}_k \right]$$

By the definition, the tensor of diffusion constants is

$$\mathscr{D}_{ik} = \gamma_{ik} \left(\frac{\partial \mu_0}{\partial n} \right)_T \tag{10'}$$

while the tensor of the mobilities is

$$u_{ik} = \gamma_{ik} \frac{1}{n} \tag{10''}$$

Hence

$$\mathscr{D}_{ik} = n \left(\frac{\partial \mu}{\partial n} \right)_T u_{ik} \tag{11}$$

We have omitted the subscript 0 for μ, keeping in mind, however, that μ is the chemical potential at $U \equiv 0$.

For the dilute solution of noninteracting particles (cf. Ref. 6, Section 87)

$$\mu = T \ln \frac{n}{N} \tag{12}$$

(N is the number of the solvent particles per unit volume). It follows from (11) and (12) that the relation (1) connects the tensor of the mobilities with the tensor of diffusion constants and that the proportionality factor is a scalar, no matter where the soluted particles move (in the isotropic liquid or in the anisotropic crystal).

We stress that for the dilute solution the relation (1) does not depend on statistics of the soluted particles. This is quite natural since Eq. (12) does not take into account the interaction between particles or the quantum correlations in their motion.

Interaction between the soluted particles leads to the appearance in the chemical potential μ of the additional term n/N which is linear in concentration (see Ref. 6); when such term is taken into account it modifies the Einstein relation (1):

$$\mathscr{E}_n = T\left(1 + \beta\frac{n}{N}\right) \tag{13}$$

where $\beta = \beta(p, T)$ is some function of pressure and temperature. Thus, investigation of the concentration dependence of the Einstein relation can be useful in studies of interaction between particles in a solution. Especially, we can mention the influence of the correlation of the ionic motion in electrolytes (or the charged particles in plasmas) that is caused by the Coulomb interaction and leads to the nonanalytic (square root) dependence of the mobility of ions on their concentration (Ref. 7, Section 26). Effects of mutual entrainment of ions with opposite charges (or ions and electrons) also require generalization of the Einstein relation (see Ref. 19).

The relation (1) can be used to describe self-diffusion in solids. In order to proceed in this case, in the derivation of the Einstein relation, from Eq. (12) we should interpret μ as the chemical potential of the mobile (activated) atoms or vacancies with the help of which the self-diffusion process is realized in solids. This example shows that the formal derivation of Eq. (11) requires certain commentaries that clarify the particular physical situation.

3. Equation (11) permits to generalize the Einstein relation (1) [we have already used it in derivation of Eq. (13)]. The proportionality between the mobility and the diffusion constant is used in the physics of electron conductors since the calculation of the diffusion constant is much more illuminating than the calculation of the mobility (see, for example, Refs. 7, Section 90; 8, Section 26; and 9, Chap. 29). In recent years much attention was paid to some rather exotic (in any case, at a first glance) objects, such as quantum crystals with anomalously narrow bands of certain quasipar-

ticles (impuritons and the vacancy quasiparticles)(10); the illuminated crystals that contain many excitons (under the appropriate conditions the exciton gas can become degenerate[3])(11); ferro- and antiferromagnets where the high density of magnons is artificially maintained(14); finally, active research is carried out to create the degenerate Bose gas of hydrogen atoms in the presence of a magnetic field.(15) All these phenomena make the problem of calculating the Einstein number $\mathscr{E}_n$ for the degenerate gases of Fermi or Bose particles (or quasiparticles) highly interesting. According to Eqs. (11) and (1) the Einstein number is related to the derivative of the chemical potential

$$\mathscr{E}_n = n\left(\frac{\partial\mu}{\partial n}\right)_T \tag{14}$$

4. We start with our analysis from the case where the density n of particles (or quasiparticles) can be taken as a parameter that does not depend on temperature T. All the exotic objects listed above, as well as electrons in metals or doped semiconductors at low temperatures, satisfy such condition. Then the temperature dependence of $\mathscr{E}_n$ can be defined by the ratio

$$\mathscr{E}_n(T) = \int_0^\infty \frac{\nu(\varepsilon)\,d\varepsilon}{\exp[(\varepsilon-\mu)/T] \pm 1} \Bigg/ \frac{\partial}{\partial\mu}\int_0^\infty \frac{\nu(\varepsilon)\,d\varepsilon}{\exp[(\varepsilon-\mu)/T] \pm 1} \tag{15}$$

where the chemical potential $\mu = \mu(n, T)$ should be found from the normalization condition

$$\int_0^\infty \frac{\nu(\varepsilon)\,d\varepsilon}{\exp[(\varepsilon-\mu)/T] \pm 1} = n \tag{16}$$

while the density of states $\nu(\varepsilon)$ is specified by the particular set-up of the problem.

Usually $\nu(0) = 0$ (e.g., in three-dimensional gases of particles and quasiparticles). This allows to rewrite Eq. (15) in a slightly different form:

$$\mathscr{E}_n(T) = \int_0^\infty \frac{\nu(\varepsilon)\,d\varepsilon}{\exp[(\varepsilon-\mu)/T] \pm 1} \Bigg/ \int_0^\infty \frac{\nu'(\varepsilon)\,d\varepsilon}{\exp[(\varepsilon-\mu)/T] \pm 1} \tag{17}$$

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[3] The investigation of the exciton motion under the action of the field of the nonhomogeneous deformation was performed in Ref. 12, while in Ref. 13 the role of the electronic wind in the motion of excitons was analyzed.

We discuss first the case of the temperatures that are high as compared with the degeneracy temperature T_0 ($T \gg T_0$). By expanding into powers of $\exp[(\varepsilon - \mu)/T]$ we find from Eq. (17)

$$\mathscr{E}_n(T) \approx T \left\{ 1 \pm e^{\mu/T} \int_0^\infty \nu(\varepsilon)\, e^{-2\varepsilon/T}\, d\varepsilon \Big/ \int_0^\infty \nu(\varepsilon)\, e^{-\varepsilon/T}\, d\varepsilon \right\} \tag{18}$$

where the chemical potential should be determined from the zeroth approximation

$$e^{\mu/T} \approx \frac{n}{\int_0^\infty \nu(\varepsilon)\, e^{-\varepsilon/T}\, d\varepsilon}$$

Thus

$$\mathscr{E}_n(T) \approx T \left\{ 1 \pm \int_0^\infty \nu(\varepsilon)\, e^{-2\varepsilon/T}\, d\varepsilon \Big/ \left[\int_0^\infty \nu(\varepsilon)\, e^{-\varepsilon/T}\, d\varepsilon \right]^2 \right\} \tag{19}$$

and we can see that for the Fermi gas (the upper sign) $\mathscr{E}_n$ is greater than the classical value $\mathscr{E}_n^{(\mathrm{cl})} = T$, while for the Bose gas (the lower sign) $\mathscr{E}_n < \mathscr{E}_n^{(\mathrm{cl})}$. To make the expression (19) more explicit we have to specify $\nu(\varepsilon)$. For the gas of free particles

$$\nu(\varepsilon) = \frac{g\sqrt{2}\, m^{3/2}}{\pi^2 \hbar^3}\, \varepsilon^{1/2} \equiv a\varepsilon^{1/2} \tag{20}$$

where m is the particle mass, $g = 2S + 1$, S is the spin of a particle, and

$$\mathscr{E}_n(T) \approx T \left\{ 1 \pm \left(\frac{T_{\mathrm{qua}}}{T} \right)^{3/2} \right\}, \qquad T_{\mathrm{qua}} = \frac{\pi\hbar^2}{m} \left(\frac{n}{4g} \right)^{2/3} \tag{21}$$

For the gas of quasiparticles (with a fixed density) Eq. (20) holds if temperature satisfies the conditions

$$T_{\mathrm{qua}} \ll T \ll \Delta\varepsilon \tag{22}$$

where $\Delta\varepsilon$ is the bandwidth. Certainly, this implies that the band should be sufficiently wide and that the number of particles inside it should be small: $(\pi\hbar^2/m)(n/4g)^{2/3} \ll \Delta\varepsilon$.

When the band is narrow, another extremal situation is possible:

$$T \gg \Delta\varepsilon \tag{23}$$

Then, if the "band capacity" $\int_0^{\Delta\varepsilon} \nu(\varepsilon)\, d\varepsilon$ is denoted as N_Δ,

$$\mathscr{E}_n \approx T \left(1 \pm \frac{n}{N_\Delta} \right), \qquad n \ll N_\Delta \tag{24}$$

The inequality $n \ll N_\Delta$ represents the condition under which the expansion in terms of $e^{\mu/T}$ is valid:

$$e^{\mu/T} \approx n \Big/ \int_0^{\Delta\varepsilon} e^{-\varepsilon/T}\, \nu(\varepsilon)\, d\varepsilon \approx n \Big/ \int_0^{\Delta\varepsilon} \nu(\varepsilon)\, d\varepsilon = \frac{n}{N_\Delta} \ll 1$$

It should be stressed that the correction to $\mathscr{E}_n^{(\mathrm{cl})}$ appearing in Eq. (24), does not vanish with the increase of temperature [cf. Eq. (21)]. On the contrary, it becomes significant at high temperatures when the finiteness of the bandwidth is particularly essential. If density of particles satisfies the condition

$$n \ll g \frac{(m\,\Delta\varepsilon)^{3/2}}{\hbar^3} \tag{25}$$

then the nonclassical expression (24) should be used at higher temperatures $(T \gg \Delta\varepsilon)$, while the classical result (21) with a certain correction becomes valid only when the condition (22) is satisfied.

5. Two-dimensional and one-dimensional gases have to be discussed in a separate way. Let us return to Eqs. (15) and (16) and assume n to be the number of particles per 1 cm^2 or 1 cm (correspondingly, n_2 and n_1). Our discussion will be limited to the case when the dispersion law is quadratic. Then for the two-dimensional gas

$$\nu_2 = \frac{gm}{2\pi\hbar^2} \tag{26}$$

while for the one-dimensional gas

$$\nu_1 = \frac{g\sqrt{m}}{2\pi\hbar\sqrt{2}} \frac{1}{\sqrt{\varepsilon}} \tag{27}$$

The independence of the density of states in the two-dimensional gas on energy allows to obtain the value of its chemical potential μ_2 for an arbitrary temperature:

(i) for fermions,

$$\mu_2^f = T \ln(e^{T_{\mathrm{qua}}^{(2)}/T} - 1), \qquad T_{\mathrm{qua}}^{(2)} = 2\pi\hbar^2 n_2/gm \tag{28}$$

(ii) for bosons,

$$\mu_2^b = T \ln(1 - e^{-T_{\mathrm{qua}}^{(2)}/T}) \tag{28'}$$

Note that the two-dimensional gas of bosons (and, hence, obviously the one-dimensional gas) does not exhibit the Bose–Einstein condensation[(6)]: at $T \to 0$ the chemical potential

$$\mu_2^b \sim Te^{-T_{\text{qua}}^{(2)}/T} \to 0$$

According to (14), (28), and (28′)

$$\mathscr{E}_n^{(2)} = \begin{cases} T_{\text{qua}}^{(2)}/(1 - e^{-T_{\text{qua}}^{(2)}/T}) & \text{for fermions} \\ T_{\text{qua}}^{(2)}/(e^{T_{\text{qua}}^{(2)}/T} - 1) & \text{for bosons} \end{cases} \tag{29}$$

The temperature dependence of the Einstein number in the case of two-dimensional gas is shown in Fig. 1.

For the one-dimensional gas at high temperatures

$$\mathscr{E}_n^{(1)} \approx T \left\{ 1 \pm \left(\frac{T_{\text{qua}}^{(1)}}{T} \right)^{1/2} \right\}, \qquad T \gg T_{\text{qua}}^{(1)} = 16\pi^2\hbar^2 n/g^2 m \tag{30}$$

As always, the uppers sign refers to fermions and the lower one refers to bosons. At low temperatures

$$\mathscr{E}_n^{(1)} = \begin{cases} (1/4)\, T_{\text{qua}}^{(1)} & \text{for fermions} \\ 8\pi^2 T^2/T_{\text{qua}}^{(1)} & \text{for bosons} \end{cases} \tag{31}$$

Qualitatively the dependence $\mathscr{E}_n^{(1)} = \mathscr{E}_n^{(1)}(T)$ resembles $\mathscr{E}_n^{(2)}(T)$. The principal difference is that the temperature dependence of $\mathscr{E}_n$ for bosons at $T \to 0$ is of the power type ($\mathscr{E}_n^{(1)} \sim T^2$), and not exponential $\mathscr{E}_n^{(2)} \sim T_{\text{qua}}^{(2)} e^{-T_{\text{qua}}^{(2)}/T}$.

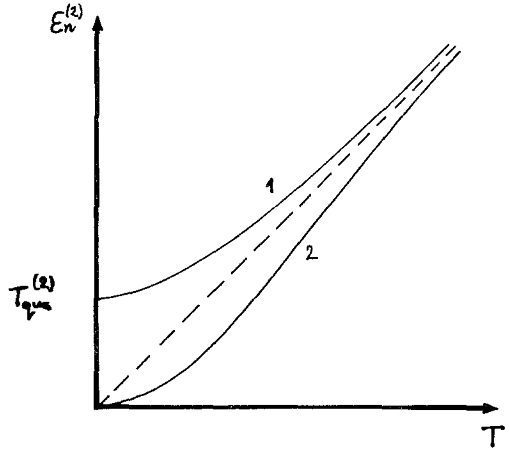

Fig. 1. Temperature dependence of the Einstein number for two-dimensional quantum gases (1, fermions; 2, bosons; the dashed line shows the classical value $\mathscr{E}_n^{\text{cl}} = T$).

6. Let us return to the three-dimensional gas. Behavior of fermions and bosons at low temperatures is drastically different and, naturally, it is revealed in the temperature dependence of the Einstein number $\mathscr{E}_n$. In the case of fermions at $T \ll T_{\text{qua}} \sim \varepsilon_F$

$$\mathscr{E}_n = \frac{n}{\nu_F}\left[1 - \frac{\pi^2 T^2}{6}\left(\frac{\nu'}{\nu}\right)'_F\right] \tag{32}$$

Here all the variables, such as the density of states ν and its derivatives ν' and ν'', are taken at the Fermi energy ε_F (defined[8] by the condition $N(\varepsilon_F) \equiv \int_0^{\varepsilon_F} \nu(\varepsilon)\, d\varepsilon = n$). If $\nu \sim \varepsilon^{1/2}$, then (see Ref. 6)

$$\mathscr{E}_n = \frac{2}{3}\varepsilon_F\left(1 + \frac{\pi^2 T^2}{12\varepsilon_F^2}\right), \qquad \varepsilon_F = (2\pi\hbar)^2\, n^{2/3}/2m(4\pi g)^{2/3} \tag{33}$$

These expressions are valid, as well, for the band electrons, if ε_F is close to the bottom of the band were $\nu \sim \varepsilon^{1/2}$. When the Fermi energy is close to top of the band, it would be natural to use the description in terms of the "holes." For holes the Einstein number is

$$\mathscr{E}_n^h = -n_h \frac{\partial \mu}{\partial n_h} \tag{33'}$$

where n_h is the density of holes (see Ref. 9). Here again $\mathscr{E}_n^h$ grows with the increase of temperature. Since $n_h \equiv N_\Delta - n \neq n$ we have $\mathscr{E}_n^h \neq \mathscr{E}_n$. Their difference follows from the definition of the mobility (10″). If we use the conductivity instead of the mobility, this ambiguity would disappear.

At low temperatures ($T \ll \varepsilon_F$) the dependence of $\mathscr{E}_n$ on magnetic field is also of interest. We would not dwell here on this question. Note only that the Einstein number should experience the thermodynamic oscillations analogous to the de-Haas–van-Alphen effect,[8] while both the diffusion constant $\mathscr{D}$ and the mobility u can have some additional oscillatory features, specific for the transport coefficients (for instance, this happens under the conditions of the magnetic breakdown[20] where the spectrum of oscillations of the conductivity are more rich than that of the magnetic susceptibility).

7. In the case of bosons at temperatures lower than the temperature T_{BE} of Bose–Einstein condensation the chemical potential is equal to zero.[6] At $T = T_{\text{BE}}$ the Einstein number vanishes together with μ.

Having in mind the gas of quasiparticles, it is interesting to study the Bose–Einstein condensation and properties of $\mathscr{E}_n$ without any particular assumption about the dependence of the density of states on energy. The condensation temperature T_{BE} is defined as the root of the equation

$$n = \int_0^\infty \frac{\nu(\varepsilon)\, d\varepsilon}{e^{\varepsilon/T_{\mathrm{BE}}} - 1} \tag{34}$$

which, as it seems, always has solutions if $\nu(0) = 0$ (this holds in the three-dimensional case). The dependence of T_{BE} on n is very sensible to the relationship between the band capacity N_Δ and the density of particles n. When the number of particles is small, $T_{\mathrm{BE}} \ll \Delta\varepsilon$, the density of states $\nu(\varepsilon)$ can be approximated by its form near the lower edge of the band $[\nu(\varepsilon) \sim \varepsilon^{1/2}]$ and the limits of integration can be put infinite. Naturally, this results in the "usual" value of the temperature of Bose–Einstein condensation[(6)]

$$T_{\mathrm{BE}} = \left(\frac{\pi^2 n}{g\alpha\sqrt{2}}\right)^{2/3} \frac{\hbar^2}{m}, \qquad \alpha = \Gamma(3/2)\,\zeta(3/2) \approx 1.3\sqrt{\pi} \tag{35}$$

(here m is the effective mass). At high densities of quasiparticles $T_{\mathrm{BE}} \gg \Delta\varepsilon$ and we can expand the exponent in (34) into a series. Then

$$T_{\mathrm{BE}} \approx n \bigg/ \int_0^{\Delta\varepsilon} \frac{\nu(\varepsilon)\, d\varepsilon}{\varepsilon} \gg \Delta\varepsilon \tag{36}$$

By taking the derivative of (16) in respect to temperture, we have

$$\frac{d\mu}{dT} \int_0^\infty \frac{\nu(\varepsilon)\, e^{(\varepsilon-\mu)/T}\, d\varepsilon}{(e^{(\varepsilon-\mu)/T} - 1)^2} = -\frac{1}{T} \int_0^\infty \frac{\nu(\varepsilon)(\varepsilon - \mu)\, e^{(\varepsilon-\mu)/T}\, d\varepsilon}{(e^{(\varepsilon-\mu)/T} - 1)^2} \tag{37}$$

It is seen that at $\mu \to 0$, i.e., for $T \to T_{\mathrm{BE}}$, the coefficient at $d\mu/dT$ diverges at lower limit, while the integral in the right side of the above equation remains finite at $\mu = 0$. After substitution of $\nu(\varepsilon)$ by the expression (20), we calculate the coefficient at $d\mu/dT$

$$\int_0^\infty \frac{\nu(\varepsilon)\, e^{(\varepsilon-\mu)/T}\, d\varepsilon}{(e^{(\varepsilon-\mu)/T} - 1)^2} \approx \frac{T_{\mathrm{BE}}^2 \alpha}{|\mu|^{1/2}} \int_0^\infty \frac{x^{1/2}\, dx}{(x+1)^2} = \frac{\pi}{2} \frac{T_{\mathrm{BE}}^2}{|\mu|^{1/2}} \alpha$$

Hence, taking into account (37),

$$\frac{1}{|\mu|^{1/2}} \frac{d|\mu|}{dT} = C, \qquad C = \frac{2}{\pi} \frac{1}{T_{\mathrm{BE}}^3 \alpha} \int_0^\infty \frac{\nu(\varepsilon)\varepsilon\, d\varepsilon}{(e^{\varepsilon/T_{\mathrm{BE}}} - 1)^2} \tag{38}$$

Consequently,

$$\mu \approx -(1/4)\, C^2 (T - T_{\mathrm{BE}})^2, \qquad T \gtrsim T_{\mathrm{BE}} \tag{39}$$

In the same approximation [according to (14)]

$$\mathscr{E}_n = B(T - T_{\mathrm{BE}}), \qquad B = \frac{1}{2} C^2 \frac{dT_{\mathrm{BE}}}{dn} n \tag{40}$$

i.e., the Einstein number linearly vanishes as $T \to T_{\mathrm{BE}}$. At $T_{\mathrm{BE}} \ll \Delta\varepsilon$ [see (35)] the coefficient B is constant and does not depend on the parameters of the solid

$$\left(B = \frac{4\gamma^2}{3\pi^2}, \text{ where } \gamma = \int_0^\infty \frac{x^{3/2}\, dx}{(e^x - 1)^2} = r\left(\frac{5}{2}\right)\left(\zeta\left(\frac{3}{2}\right) - \zeta\left(\frac{5}{2}\right)\right)\right)$$

at $T_{\mathrm{BE}} \gg \Delta\varepsilon$ [see (36)] the coefficient B is determined by the structure of the band

$$B \approx \frac{2}{\pi^2}\left(\frac{1}{a}\int_0^{\Delta\varepsilon} \frac{\nu(\varepsilon)\, d\varepsilon}{\varepsilon}\right)^2 \frac{1}{T_{\mathrm{BE}}} \tag{41}$$

We shall not discuss here the realizability of Bose–Einstein condensation in particular physical systems. In our calculations which yield Eqs. (31)–(41), we do not take into account the interaction of bosons (and the fluctuations of gas density too); hence they can be useful only under conditions when interaction and fluctuations are not essential. In close vicinity of the temperature of Bose–Einstein condensation such interactions and fluctuations surely play a decisive role in real physical systems and Eqs. (34)–(41) demonstrate only the tendency in the behavior of a physical system with decreasing temperature. [For example, according to Eq. (36) the temperature T_{BE} increases faster with growth of the density of quasiparticles n than one could expect, judging from the familiar "usual" relation (35), etc.]

8. Until now we have assumed that the density of particles (or quasiparticles) n is an independent on temperature parameter that determines the value of chemical potential μ [see (16)]. In the case of solids the situations are frequently encountered when the number of quasiparticles depends on temperature, and chemical potential is determined, for example, by the neutrality condition. This is the peculiar situation in an electron-hole semiconductor. Let us denote the density of electrons as n_e and the density of holes as n_h. Although electrons and holes have common chemical potential μ, their Einstein numbers are different (see Ref. 9, Chap. 29)

$$\mathscr{E}_n^e = n_e \frac{\partial \mu}{\partial n_e}, \qquad \mathscr{E}_n^h = -n_h \frac{\partial \mu}{\partial n_h} \tag{42}$$

The temperature dependence of $\mathscr{E}_n^e$ and $\mathscr{E}_n^h$ can be calculated most conveniently by using the formulae analogous to Eqs. (15) and (17) assuming $\mathscr{E}_n^{e,h} = \pm n_{e,h}(\partial\mu/\partial n_{e,h})$.

The difference consists only in the temperature dependence of $\mu = \mu(T)$. We shall analyze several special cases that will help us to find out which information the temperature dependence of Einstein numbers does carry.

We discuss first an electronic semiconductor of the n type with the energetic structure shown in Fig. 2; the donor level with the energy $-\varepsilon_g$ ($\varepsilon_g > 0$) has the δ-like density of states, at $T = 0$ it contains n_g electrons per cm^3. As a result of thermal excitation, electrons appear in the conduction band with the width $\Delta\varepsilon \gg T$. This validates the use of Eq. (20), where m should be considered, certainly, as an effective mass. The distance from the conduction band to the valency band is so large that excitation from the valency band can be completely neglected.

To calculate $\mathscr{E}_n^e = \mathscr{E}_n^e(T)$ we shall use Eq. (17) (with the upper sign) and, instead of the normalization condition (16), the neutrality condition

$$\frac{n_g}{e^{(\varepsilon_g+\mu)/T}+1} = \int_0^\infty \frac{\nu_e(\varepsilon)\, d\varepsilon}{e^{(\varepsilon-\mu)/T}+1} \tag{43}$$

will be taken for determination of $\mu = \mu(T)$. At both low temperatures ($T \ll \varepsilon_g$) and at high temperatures ($T \gg \varepsilon_g$, $\hbar^2 n_g^{2/3}/m$) electrons can be with good accuracy described by the classical statistics,

$$\mathscr{E}_n^e(T) \approx T\left(1 + \frac{1}{2\sqrt{2}}\, e^{\mu/T}\right)$$

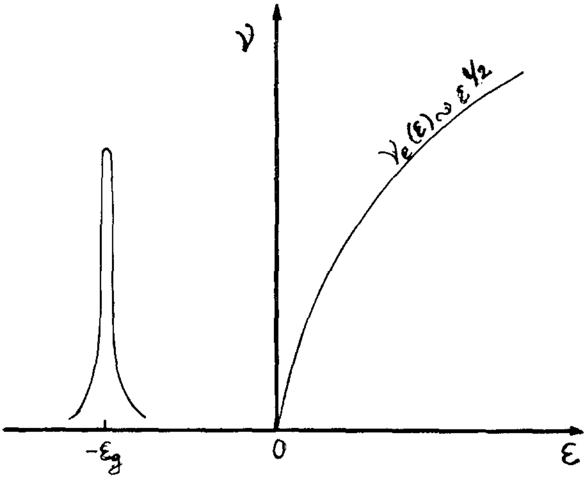

Fig. 2. Energetic structure of semiconductors of the n type.

[see (18)], and instead of μ we should substitute the approximate value of the chemical potential:

$$\mu \approx \begin{cases} -\dfrac{1}{2}\varepsilon_g + \dfrac{3}{4} T \ln \dfrac{T_g}{T}, \qquad T_g = 2^{1/3}\pi n_g^{2/3}\hbar^2/m, \qquad T \ll \varepsilon_g \\ \dfrac{3T}{2} \ln \dfrac{\tilde{T}_g}{T}, \qquad T \gg T_g \end{cases}$$

Hence

$$\begin{aligned} \mathscr{E}_n^e(T) &\approx T\left[1 + \sqrt{2}\left(\frac{T_g}{T}\right)^{3/4} e^{-\varepsilon_g/2T}\right], \qquad && T \ll \varepsilon_g \\ \mathscr{E}_n^e &\approx T\left[1 + \left(\frac{\tilde{T}_g}{T}\right)^{3/2}\right], && T \gg \varepsilon_g, T_g \end{aligned} \tag{44}$$

Here $\tilde{T}_g$ differs from T_g by a numerical factor of the order of unity. Note that in this case the classical Einstein relation is especially well satisfied at low temperatures: owing to the existence of a gap the correction to the classical value at $T \ll \varepsilon_g$ is exponentially small.

In the intermediate interval of temperatures $\mathscr{E}_n^e(T)$ can essentially differ from the classical value. The character of the function $\mathscr{F}(T) = \mathscr{E}_n^e/\mathscr{E}_n^{\text{cl}} = \mathscr{E}_n^e(T)/T$ depends on the relationship between T_g and ε_g; this function can be easily found at various values of parameters in Eq. (43). If positivity of the chemical potential is taken as a qualitative indication of degeneracy of the electron gas the quantitative criterion of existence of a degeneracy interval can be derived. According to (43), the chemical potential μ vanishes at the temperature $T_0 = x\varepsilon_g$ where x is determined by the equation

$$\frac{1}{e^{1/x} + 1} = \left(\frac{\varepsilon_g}{T_g}\right)^{3/2} x^{3/2}$$

Depending on the ratio ε_g/T_g, this equation has either two solutions (x_1 and x_2) or none. If $T_g \gg \varepsilon_g$ there are always two solutions $[x_1 \approx 2/(3\ln(T_g/\varepsilon_g))$, $x_2 \approx T_g/2^{2/3}\varepsilon_g]$, and a comparatively wide degeneracy interval $(x_1\varepsilon_g < T < x_2\varepsilon_g)$ is present, inside which $\mathscr{E}_n^e(T)$ differs considerably from $\mathscr{E}_n^{\text{cl}} = T$. On the boundaries of such an interval, according to (17), the ratio $\mathscr{E}_n^e/\mathscr{E}_n^{\text{cl}}$ is close to 2.

In the case of the intrinsic semiconductor (its energy structure is shown in Fig. 3) the chemical potential $\mu = \mu(T)$ is determined by the condition of equality of electron and hole numbers:

$$\int_0^\infty \frac{\nu_c(\varepsilon)\, d\varepsilon}{e^{(\varepsilon-\mu)/T} + 1} = \int_{-\infty}^{-\varepsilon_g} \frac{\nu_v(\varepsilon)\, d\varepsilon}{e^{(\mu-\varepsilon)/T} + 1} \tag{45}$$

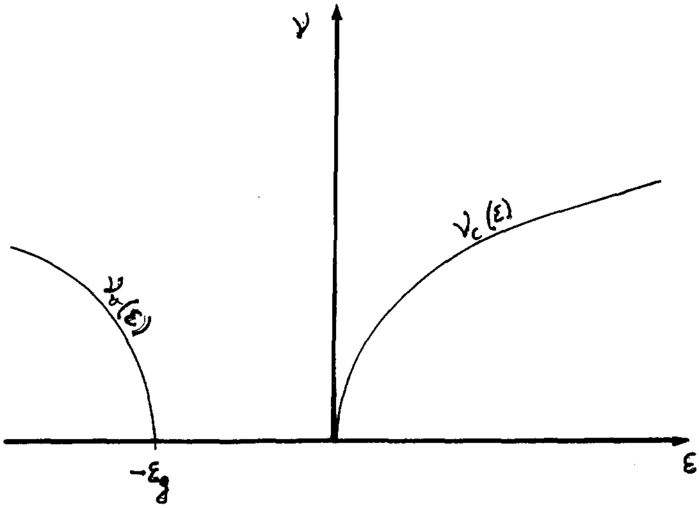

Fig. 3. Energetic structure of an intrinsic semiconductor ($\gamma_c(\varepsilon)$ is the density of states in the conduction band, $\nu_v(\varepsilon)$ is the density of states in the valency band).

the notations are given in Fig. 3, for $\nu_c(\varepsilon)$ and $\nu_v(\varepsilon)$ we have used Eq. (20) with an effective mass of an electron and a hole, correspondingly $[\nu_v(\varepsilon) = a_v(-\varepsilon_g - \varepsilon)^{1/2}]$. At low temperatures $(T \ll \varepsilon_g)$ the Einstein numbers for electrons and holes are close to the classical value, i.e., the difference $\mathcal{E}_n^{e,h}/T - 1$ is exponentielly small. Possibility (or impossibility) of significant deviations of $\mathcal{E}_n^{e,h}$ from the classical value at comparatively high temperatures is related to possibility (or impossibility) of degeneracy of electron or hole gases. If $m_c < m_v$, then the temperature can be found at which μ_e would vanish and this would, certainly, influence quantities $\mathcal{E}_n^e$ and $\mathcal{E}_n^h$ (see the remarks above).

We conclude this section with discussion of the gapless semiconductor$^{(16)}$; here the equation for determination of μ coincides with Eq. (45) with $\varepsilon_g = 0$. Assuming that the effective masses of electrons and holes are different, we have

$$\left(\frac{m_c}{m_v}\right)^{3/2} = \int_0^\infty \frac{x^{1/2}\,dx}{e^{\mu/T}e^x + 1} \Bigg/ \int_0^\infty \frac{x^{1/2}\,dx}{e^{-\mu/T}e^x + 1} \tag{46}$$

Hence, μ is the linear function of temperature $(\mu = \tilde{s}T)$, and the proportionality factor is determined by the ratio of effective masses: $\tilde{s} > 0$ for $m_v > m_c$ and $\tilde{s} < 0$ for $m_v < m_c$. For $m_c = m_v$ the chemical potential is equal to zero and $\mathcal{E}_n^{e,h}$ is approximately twice greater than the classical value [see Eq. (17)].

9. Until now we have assumed that the diffusing particles (or quasiparticles) represent an ideal gas [the exception is in the case corresponding to Eq. (13)]. In the general case it is impossible to take into account interactions between particles and special assumptions should be made. If the particles are fermions, then at low temperatures the most important role in their interactions plays Landau's Fermi-liquid interaction,(17) described by the correlation function $f(\mathbf{p}, \mathbf{p}')$ where $\mathbf{p}$ and $\mathbf{p}'$ are the momenta of interacting particles. The Einstein number for fermions (e.g., for atoms of He^3 diffusing through He^4) can be easily expressed in terms of the sound velocity in the Fermi-particles gas, taking into account their Fermi-liquid interaction. Indeed [see, e.g., Ref. 18, Eq. (66.2)]

$$n\frac{\partial\mu}{\partial n} = ms^2 \tag{47}$$

where s is a sound velocity in the Fermi-liquid, m is a mass of particles, unrenormalized by interaction. In the same reference [Ref. 18, Eq. (66.9)] the expression is given that defines the dependence of a squared speed velocity on the correlation function $f(\mathbf{p}, \mathbf{p}')$. Eq. (47) generalizes Eq. (33) at $T = 0$.

10. If a system of mobile particles in a condensed medium is not in the thermodynamic equilibrium state (e.g., hot electrons in a semiconductor), the thermodynamic relations cannot be applied. However, we can estimate the Einstein number from the kinetic treatment. By the order of magnitude

$$\mathscr{D} \sim l\langle v\rangle, \qquad u \sim l/\langle p\rangle \tag{48}$$

where l is the mean free path length of particles, and angular brackets mean averaging over the quasi-equilibrium distribution. Thus

$$\frac{\mathscr{D}}{u} \sim \langle v\rangle\langle p\rangle \sim \langle\varepsilon\rangle \tag{49}$$

i.e., the Einstein number is determined by the average energy of diffusing particles. Its measurement can serve as a source of information about the energy distribution of diffusing particles.

11. We do not intend to discuss in a detailed way the possibilities (and, of more importance, difficulties) of measurements of the mobility and the diffusion constant of uncharged particles or quasiparticles. However, we would like to make several remarks. If the number of particles (or quasiparticles) is conserved, their equilibrium distribution function is

$\{\exp[(\varepsilon-\mu)/T]+1\}^{-1}$. It is clear that at $T=\text{const}$ the flow of quasiparticles can be created only if $\nabla\mu\neq 0$. If $\nabla\mu$ is due to the nonhomogeneous distribution of particles (or quasiparticles), then $\nabla\mu=(\partial\mu/\partial n)\,\nabla n$ and there is a diffusive flow, while if $\nabla n=0$, then $-\nabla\mu$ should be interpreted as a generalized force **F** and this allows to determine the mobility.

Creation of the flow of uncharged particles (or quasiparticles) at $\nabla n=0$ is, seemingly, limited by existence (or absence) of the permanent source of particles (that should be included into the circuit, an element of which should be the investigated body), and not by the difficulty of action on an individual particle (or quasiparticle). For instance, if the energy of a particle (or quasiparticle) with the momentum **p** is

$$\varepsilon(\mathbf{p})=\varepsilon_0+\xi(\mathbf{p}) \tag{50}$$

then $-\nabla\varepsilon_0$ is the force, and ε_0 plays the role of a potential energy [cf. Eq. (10)]. The spectrum of magnons in a ferromagnet without account for the relativistic interactions is described by such an expression: $\varepsilon_0=\mu_B H$, where H is a magnetic field and μ_B is the Bohr magneton. The same spectrum is realized for atoms of hydrogen, polarized by the magnetic field. Even if the separate measurement of $\mathscr{D}$ and u turns out to be difficult, knowledge of the Einstein number is necessary in formulation of macroscopic equations that describe quasihydrodynamical processes in solids (in analogy with the description of motion of electrons, see, e.g., Ref. 9).

For many years I. M. Lifshitz had developed the concept of quasiparticles, repeatedly stressing similarities between quasiparticles and common particles and at the same time discovering the qualitative peculiarities in the behavior of quasiparticles that are revealed in properties of solids. We hope that the present paper belongs to that direction of the solid state theory which is forever associated with the name of Ilya Mikhailovich.

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