I.2.3 b Particle diffusion

Consider now "particles" immersed in a motionless and homogeneous medium, in which they can move around—microscopically, through scatterings on the medium constituents—without affecting the medium characteristics.[(12)] Examples are the motion of dust in the air, of micrometer-scale bodies in liquids, but also of impurities in a solid or of neutrons in the core of a nuclear reactor.

Let n denote the number density of the particles. The transport of particles can be described by *Fick's*[(i)] *law* (1855) [14]

$$\boxed{\vec{\mathcal{J}}_N = -D\,\vec{\nabla} n,} \tag{I.39a}$$

with $\vec{\mathcal{J}}_N$ the flux density of particle number and D the *diffusion coefficient*.

Remark: Relation (I.39a) is sometimes referred to as Fick's first law, the second one being actually the diffusion equation (I.40).

In the absence of temperature gradient and of collective motion of the medium, the general relation (I.31) yields for the particle number flux density

$$\vec{\mathcal{J}}_N = L_{NN}\vec{\nabla}\left(-\frac{\mu}{T}\right) \tag{I.39b}$$

with $L_{NN} \geq 0$. Relating the differential of chemical potential to that of number density with

$$\mathrm{d}\mu = \left(\frac{\partial \mu}{\partial n}\right)_T \mathrm{d}n,$$

(12) We shall come back to this physical setup in Chapter **??**.

(i) A. Fick, 1829–1901

the identification of Fick's law (I.39a) with formula (I.39b) yields

$$D = \frac{1}{T}\left(\frac{\partial \mu}{\partial n}\right)_T L_{NN}, \tag{I.39c}$$

where the precise form of the partial derivative depends on the system under study.

Diffusion equation

If the number of diffusing particles is conserved—which is for instance not the case for neutrons in a nuclear reactor[13]—and if the diffusion coefficient is independent of position, the associated continuity equation (I.18a) leads to the *diffusion equation*

$$\boxed{\frac{\partial n(t,\vec{r})}{\partial t} = D\,\triangle n(t,\vec{r}).} \tag{I.40}$$

To tackle this partial differential equation (considered on $\mathbb{R}^3$), one can introduce the Fourier transform of the number density with respect to space coordinates

$$\tilde{n}(t,\vec{k}) \equiv \int n(t,\vec{r})\,\mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}}\,\mathrm{d}^3\vec{r}.$$

This transform then satisfies for each $\vec{k}$ the ordinary differential equation

$$\frac{\partial \tilde{n}(t,\vec{k})}{\partial t} = -D\,\vec{k}^{\,2}\tilde{n}(t,\vec{k}),$$

where it was assumed that the number density and its spatial derivatives vanish at infinity at every instant. These assumptions respectively guarantee the finiteness of the overall particle number and the absence of particle flux at infinity.

The solution to the ordinary differential equation reads $\tilde{n}(t,\vec{k}) = \mathrm{e}^{-D\vec{k}^{\,2}t}\,\tilde{n}(0,\vec{k})$, with $\tilde{n}(0,\vec{k})$ the initial condition at $t=0$ in Fourier space. An inverse Fourier transform then yields

$$n(t,\vec{r}) = \int \mathrm{e}^{-D\vec{k}^{\,2}t}\,\tilde{n}(0,\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}}\,\frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}.$$

If the initial condition is $n(0,\vec{r}) = n_0\,\delta^{(3)}(\vec{r})$—which physically amounts to introducing a particle density n_0 at the point $\vec{r}=\vec{0}$ at time $t=0$—then the Fourier transform is trivially $\tilde{n}(0,\vec{k}) = n_0$, so that the inverse Fourier transform above is simply that of a Gaussian, which gives

$$n(t,\vec{r}) = \frac{n_0}{(4\pi Dt)^{3/2}}\,\mathrm{e}^{-\vec{r}^{\,2}/4Dt}. \tag{I.41}$$

The typical width of the particle number density increases with $\sqrt{t}$. This growth of the width is illustrated in Fig. I.1 in the case of one-dimensional diffusion—in which case the prefactor of the exponential function scales as $1/\sqrt{Dt}$.

Remark: In Eq. (I.41) or on Fig. I.1, one sees that at any time $t>0$ the Gaussian extends infinitely far away from the origin. This means that particles could diffuse infinitely quickly away from where they were situated at $t=0$, in blatant violation of the main principle of Special Relativity: The equation (I.40) allows faster-than-light diffusion, it does not respect *causality*.

I.2.3 c Electrical conduction

Another example of particle transport is that of the moving charges in an electrical conductor in the presence of an electric field $\vec{\mathscr{E}} = -\vec{\nabla}\Phi$, with Φ the electrostatic potential. The latter is assumed to vary very slowly at the mesoscopic scale, so as not to spoil the local equilibrium assumption. If q denotes the electric charge of the carriers—assuming a single species of moving charges—, then

[13] There, one should also include various source and loss terms, to account for the production of neutrons through fission reactions, or their "destruction" through reactions with the nuclear fuel, with the nuclear waste present in the reactor, or with the absorber bars that moderate the chain reaction, or their natural decay.

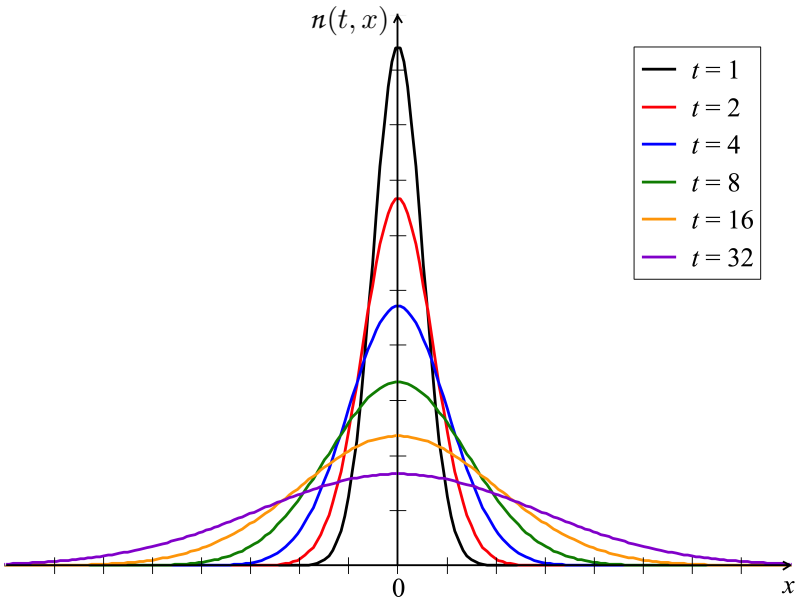

Figure I.1 – One-dimensional diffusion: starting from $n(t=0,x) = n_0\,\delta(x)$, the number density $n(t,x) = n_0\,\mathrm{e}^{-x^2/4Dt}/\sqrt{4\pi Dt}$ is displayed at various times t (in arbitrary units).

the electric charge flux density, traditionally referred to as *current density*, is simply related to the number flux density of the moving charges through

$$\vec{J}_{\text{el.}} = q\vec{\mathcal{J}}_N. \tag{I.42a}$$

The relation between electric field and current density in a mesoscopically isotropic conductor at constant temperature in the absence of magnetic field is (the microscopic version of) *Ohm's*[(j)] *law*

$$\boxed{\vec{J}_{\text{el.}} = \sigma_{\text{el.}}\vec{\mathscr{E}}} \tag{I.42b}$$

with $\sigma_{\text{el.}}$ the (isothermal) *electrical conductivity*.

To relate the electrical conductivity to the kinetic coefficients of § I.2.1, and more specifically to L_{NN} since $\vec{J}_{\text{el.}}$ is proportional to $\vec{\mathcal{J}}_N$, one needs to determine the intensive variable conjugate to particle number—or equivalently, thanks to the local equilibrium assumption, conjugate to particle number density. Now, if e denotes the (internal) energy density in the absence of electrostatic potential, then the energy density in presence of Φ becomes $e + nq\Phi$: meanwhile, the particle number density n remains unchanged. The entropy per unit volume then satisfies—as can most easily be checked within the grand-canonical ensemble of statistical mechanics—the identity

$$s(e,n,\Phi) = s(e - nq\Phi, n, 0),$$

which yields

$$\frac{\partial s}{\partial n} = -\frac{\mu + q\Phi}{T} \equiv -\frac{\mu_\Phi}{T}, \tag{I.43}$$

with μ the chemical potential at vanishing electric potential. μ_Φ is referred to as *electrochemical potential*.

Assuming a uniform temperature in the conductor, the linear relation (I.31) for the flux of particle number then reads

$$\vec{\mathcal{J}}_N = L_{NN}\vec{\nabla}\left(-\frac{\mu + q\Phi}{T}\right). \tag{I.44}$$

[(j)] G. S. Ohm, 1789–1854

Invoking again the uniformity of temperature, this gives

$$\vec{\mathcal{J}}_N = -\frac{1}{T}\left(\frac{\partial\mu}{\partial n}\right)_T L_{NN}\vec{\nabla}n - \frac{q}{T}\,L_{NN}\vec{\nabla}\Phi,$$

where the first term is the same as in § I.2.3 b, while the second can be rewritten with the help of the electric field. If the particle-number density is uniform, the first term vanishes, and the identification with Eqs. (I.42a) and (I.42b) yields the electrical conductivity

$$\sigma_{\text{el.}} = \frac{q^2}{T}\,L_{NN}. \tag{I.45}$$

Einstein relation

Equations (I.39c) and (I.45) show that the diffusion coefficient D and the electrical conductivity σ are both related to the same kinetic coefficient L_{NN}, so that they are related to each other:

$$D = \frac{\sigma_{\text{el.}}}{q^2}\left(\frac{\partial\mu}{\partial n}\right)_T. \tag{I.46}$$

Let $\mu_{\text{el.}}$ denote the *electrical mobility* of the charge carriers, which is the proportionality factor between the mean velocity $\vec{v}_{\text{av.}}$ they acquire in an electric field $\vec{\mathscr{E}}$ and this field

$$\vec{v}_{\text{av.}} = \mu_{\text{el.}}\vec{\mathscr{E}}. \tag{I.47}$$

Obviously, the determination of $\mu_{\text{el.}}$ requires a microscopic model for the motion of the charges.

At the macroscopic level, the electric current density is simply the product of the mean velocity of charges times the charge density, i.e.

$$\vec{J}_{\text{el.}} = nq\vec{v}_{\text{av.}} = nq\mu_{\text{el.}}\vec{\mathscr{E}},$$

which after identification with Ohm's law (I.42b) gives $\sigma_{\text{el.}} = nq\mu_{\text{el.}}$. Together with Eq. (I.46), one obtains

$$D = \frac{\mu_{\text{el.}}}{q}\,n\left(\frac{\partial\mu}{\partial n}\right)_T. \tag{I.48}$$

For a classical ideal gas, one has $\left(\frac{\partial\mu}{\partial n}\right)_T = \frac{k_BT}{n}$, which gives

$$D = \frac{\mu_{\text{el.}}}{q}\,k_BT, \tag{I.49}$$

which is a special case of a general relation derived by A. Einstein[(k)] in his 1905 paper on Brownian motion [15].

I.2.3 d Thermoelectric effects

We now turn to a first example of systems in which several quantities can be transported at the same time, namely that of isotropic electrical conductors, in which both heat and particles—corresponding to the charge carriers—can be transferred simultaneously from one region to the other.

For the sake of simplicity, we consider a single type of moving particles, with electric charge q. Throughout the section it will be assumed that their number density is uniform, i.e. $\vec{\nabla}n$ vanishes. On the other hand, these charges are able to move collectively, resulting in an electric current density $\vec{J}_{\text{el.}} = q\vec{\mathcal{J}}_N$. In the system reigns a slowly spatially varying electrostatic potential Φ, which results as seen in § I.2.3 c in the replacement of the chemical potential μ by the electrochemical potential μ_Φ defined by Eq. (I.43).

[(k)] A. Einstein, 1879–1955

In the linear regime, the transports of particles and energy are governed by the constitutive equations [Eq. (I.31)]

$$\vec{\mathcal{J}}_N = L_{NN}\vec{\nabla}\left(-\frac{\mu_\Phi}{T}\right) + L_{NE}\vec{\nabla}\left(\frac{1}{T}\right), \tag{I.50a}$$

$$\vec{\mathcal{J}}_E = L_{EN}\vec{\nabla}\left(-\frac{\mu_\Phi}{T}\right) + L_{EE}\vec{\nabla}\left(\frac{1}{T}\right), \tag{I.50b}$$

where Curie's symmetry principle has already been accounted for, while Onsager's reciprocal relation reads $L_{NE} = L_{NE}$ since both particle number and energy are invariant under time reversal.

Instead of $\vec{\mathcal{J}}_E$, it is customary to consider the *heat flux* (density) $\vec{\mathcal{J}}_Q$ defined as

$$\vec{\mathcal{J}}_Q = T\vec{\mathcal{J}}_S = \vec{\mathcal{J}}_E - \mu_\Phi\vec{\mathcal{J}}_N, \tag{I.51}$$

where the second identity follows from Eq. (I.27a).
Inspecting the entropy production rate (I.27b)

$$\sigma_S = \vec{\mathcal{J}}_Q \cdot \vec{\nabla}\left(\frac{1}{T}\right) - \frac{1}{T}\,\vec{\mathcal{J}}_N \cdot \vec{\nabla}\mu_\Phi, \tag{I.52}$$

one finds that the affinities conjugate to $\vec{\mathcal{J}}_Q$ and $\vec{\mathcal{J}}_N$ are $\vec{\nabla}(1/T)$ and $-(1/T)\vec{\nabla}\mu_\Phi$, respectively. Using these new fluxes and affinities as variables, we can introduce alternative linear relations

$$\vec{\mathcal{J}}_N = -L_{11}\frac{1}{T}\,\vec{\nabla}\mu_\Phi + L_{12}\vec{\nabla}\left(\frac{1}{T}\right), \tag{I.53a}$$

$$\vec{\mathcal{J}}_Q = -L_{21}\frac{1}{T}\,\vec{\nabla}\mu_\Phi + L_{22}\vec{\nabla}\left(\frac{1}{T}\right), \tag{I.53b}$$

with new kinetic coefficients L_{jk}, which are related to the original ones by

$$\begin{aligned} &L_{11} = L_{NN}, \\ &L_{12} = L_{NE} - \mu_\Phi L_{NN}, \quad L_{21} = L_{EN} - \mu_\Phi L_{NN}, \\ &L_{22} = L_{EE} - \mu_\Phi\big(L_{EN} + L_{NE}\big) + \mu_\Phi^2 L_{NN}. \end{aligned} \tag{I.53c}$$

Again a reciprocal relation $L_{21} = L_{12}$ holds when $L_{EN} = L_{NE}$.

Heat conduction

Let us first investigate the transport of heat in a situation where the particle number flux vanishes, $\vec{\mathcal{J}}_N = \vec{0}$, i.e. for an open electric circuit $\vec{\mathcal{J}}_{\text{el.}} = \vec{0}$. Equation (I.53a) gives

$$\vec{\nabla}\mu_\Phi = -\frac{1}{T}\frac{L_{12}}{L_{11}}\,\vec{\nabla}T. \tag{I.54}$$

Inserting this identity in the expression of the heat flux (I.53b) then yields

$$\vec{\mathcal{J}}_Q = -\frac{L_{11}L_{22} - L_{12}L_{21}}{T^2\,L_{11}}\,\vec{\nabla}T. \tag{I.55}$$

Since $L_{11} = L_{NN} \geq 0$ and $L_{11}L_{22} - L_{12}L_{21} = L_{NN}L_{EE} - L_{NE}L_{EN} \geq 0$, the ratio is a non-negative number. Now, since the particle flux vanishes, $\vec{\mathcal{J}}_Q = \vec{\mathcal{J}}_E$. The comparison of Eq. (I.55) with Fourier's law (I.37a) allows us to interpret the prefactor of $\vec{\nabla}T$ in relation (I.54) as the *heat conductivity* κ. With the help of the relations (I.53c) it can be rewritten as

$$\kappa = \frac{L_{11}L_{22} - L_{12}L_{21}}{T^2\,L_{11}} = \frac{L_{NN}L_{EE} - L_{NE}L_{EN}}{T^2\,L_{NN}}. \tag{I.56}$$

This result differs from the expression (I.37c) of the heat conductivity in an insulator, which is not unexpected since in the case of a electric conductor, both phonons and moving charges contribute to the transport of heat.

Seebeck effect

Consider again the case of an open circuit, $\vec{\mathcal{J}}_N = \vec{0}$. In such a circuit, a temperature gradient induces a gradient of the electrochemical potential, see Eq. (I.54). This constitutes the *Seebeck*[(1)] *effect* (1821). The relationship is traditionally written in the form

$$\frac{1}{q}\,\vec{\nabla}\mu_\Phi = -\epsilon_S\,\vec{\nabla}T, \tag{I.57a}$$

which defines the *Seebeck coefficient* ϵ_S of the conductor.[(14)] Since the number density of moving charges is assumed to be uniform, $\vec{\nabla}\mu_\Phi = q\vec{\nabla}\Phi = -q\vec{\mathscr{E}}$, so that Eq. (I.57a) can be recast as

$$\vec{\mathscr{E}} = \epsilon_S\,\vec{\nabla}T, \tag{I.57b}$$

with $\vec{\mathscr{E}}$ the electric field.

Comparing Eqs. (I.54) and (I.57a), one finds at once

$$\epsilon_S = \frac{1}{qT}\frac{L_{12}}{L_{11}}. \tag{I.58}$$

The Seebeck effect is an instance of indirect transport, since its magnitude, measured by ϵ_S, is proportional to the cross-coefficient L_{12}.

To instantiate the Seebeck effect, one can use a circuit consisting of two conductors A and B made of different materials, a "thermocouple", whose junctions are at different temperatures T_2 and

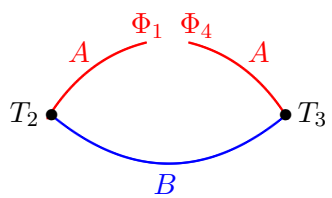

Figure I.2 – Schema of a thermocouple to evidence the Seebeck effect.

T_3, as illustrated in Fig. I.2. There appears then between the points 1 and 4 a voltage

$$\Phi_4 - \Phi_1 = \frac{1}{q}\int_1^4 \vec{\nabla}\mu_\Phi \cdot \mathrm{d}\vec{\ell} = \int_{T_2}^{T_3} \left(\epsilon_S^{(A)} - \epsilon_S^{(B)}\right) \mathrm{d}T.$$

This voltage can be measured with a high-resistance (so as not to close the circuit) voltmeter,[(15)] so that the Seebeck coefficient of one of the materials, say B, can be assessed when all other quantities (T_2, T_3, $\epsilon_S^{(A)}$) are known. Conversely, when using materials whose coefficients are known, this thermocouple allows the measurement of temperature differences.

Remark: Similar phenomena were recently discovered in magnetic materials, either conductors or insulators. Thus, in ferromagnetic materials, a so-called *spin Seebeck effect* was discovered [16], in which a temperature gradient induces a gradient in the "spin voltage" $\mu^\uparrow - \mu^\downarrow$, where $\mu^\uparrow$ resp. $\mu^\downarrow$ denotes the electrochemical potential of spin up resp. down electrons.[(16)]

(14) This coefficient, characteristic of the conducting material, is often denoted by S, which I wanted to avoid here.

(15) One can easily convince oneself that the temperature of the voltmeter is irrelevant.

(16) For a review on "spin caloritronics"—the interplay of heat and spin transport—see Ref. [17]. The theory of the spin Seebeck effect is reviewed in Ref. [18].

(1) T. J. Seebeck, 1770–1831

An exact analogue of the "usual" spin-independent electric Seebeck effect is the *magnetic Seebeck effect* theorized in Ref. [19], in which a temperature gradient induces a magnetic field in a material with magnetic dipoles [20].

Peltier effect

The *Peltier*[(m)] *effect* (1834) consists in the observation that in a conductor at uniform temperature, a current density $\vec{J}_{\text{el.}}$ is accompanied by a heat flux. This relation is usually written as

$$\vec{\mathcal{J}}_Q = \Pi\, \vec{J}_{\text{el.}}, \tag{I.59}$$

which defines the *Peltier coefficient* Π of the conducting material.

Setting $\vec{\nabla} T = \vec{0}$ in Eqs. (I.53a)–(I.53b) and eliminating $(1/T)\vec{\nabla}\mu_\Phi$ between the two equations leads at once to

$$\Pi = \frac{1}{q}\frac{L_{21}}{L_{11}}. \tag{I.60}$$

This is again an indirect transport phenomenon, somehow "reverse" to the Seebeck effect since it involves the reciprocal kinetic coefficient L_{21} instead of L_{12}.

Consider the junction between two different conducting materials A and B at the same temperature depicted in Fig. I.3. An electric current $\vec{J}_{\text{el.}}$ crosses the junction without change, as dictated by local charge conservation. In each conductor, this current is accompanied by heat fluxes $\vec{\mathcal{J}}_Q^{(A)}$

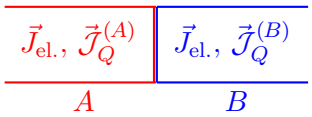

Figure I.3 – Schema of an isothermal junction to evidence the Peltier effect.

and $\vec{\mathcal{J}}_Q^{(B)}$, which differ since $\Pi^{(A)} \neq \Pi^{(B)}$. To ensure energy conservation, a measurable amount of heat

$$\left.\frac{\mathrm{d}Q}{\mathrm{d}t}\right|_{\text{Peltier}} = \left(\Pi^{(A)} - \Pi^{(B)}\right) J_{\text{el.}}$$

is released per unit time and unit cross-sectional area at the junction, with $J_{\text{el.}} \equiv \left|\vec{J}_{\text{el.}}\right|$. Note that $\mathrm{d}Q/\mathrm{d}t$ can be negative, which means that heat is actually absorbed from the environment at the junction.

Comparing now the Seebeck coefficient (I.58) with the Peltier coefficient (I.60), one sees that the relation $L_{21} = L_{12}$—which follows from Onsager's reciprocal relation between L_{EN} and L_{NE}—leads to

$$\Pi = \epsilon_S T, \tag{I.61}$$

which is known as *second Kelvin*[(n)] *relation* (or sometimes *second Thomson relation*[(17)]).

Coming back to the fluxes (I.53a)–(I.53b) in the most general case of non-vanishing gradients in temperature as well as in electrochemical potential, and eliminating $(1/T)\vec{\nabla}\mu_\Phi$ between the two relations, one find with the help of Eqs. (I.56), (I.60) and (I.61) the heat flux

$$\vec{\mathcal{J}}_Q = -\kappa\, \vec{\nabla} T + \epsilon_S\, T\, q\, \vec{\mathcal{J}}_N. \tag{I.62}$$

The first term corresponds to thermal conduction, the second to convection.

[(17)] ... which is historically more accurate, since William Thomson had not yet been ennobled as Lord Kelvin when he empirically found this relation in 1854.

[(m)] J. Peltier, 1785–1845 [(n)] W. Thomson, Lord Kelvin, 1824–1907