# Generalized Fluxes and Einstein relation (kinetic theory)

In physics (specifically, the kinetic theory of gases) the **Einstein relation** (also known as **Wright Sullivan relation**[1]) is a previously unexpected connection revealed independently by William Sutherland in 1904,[2][3][4] Albert Einstein in 1905,[5] and by Marian Smoluchowski in 1906[6] in their works on Brownian motion. The more general form of the equation is[7]

$$D = \mu \, k_B T,$$

where

$D$ is the diffusion coefficient; $\mu$ is the "mobility", or the ratio of the particle's terminal drift velocity to an applied force, $\mu = v_d/F$; $k_B$ is Boltzmann's constant; $T$ is the absolute temperature.

This equation is an early example of a fluctuation-dissipation relation.[8]

Two frequently used important special forms of the relation are:

$$D = \frac{\mu_q \, k_B T}{q}$$

(**electrical mobility equation**, for diffusion of charged particles[9])

$q$ is the electrical charge of a particle;
$\mu_q$ is the electrical mobility of the charged particle;

$$J = -D\nabla C - \mu C \nabla E$$

## Electrical mobility equation

For a particle with electrical charge $q$, its electrical mobility $\mu_q$ is related to its generalized mobility $\mu$ by the equation $\mu = \mu_q/q$. The parameter $\mu_q$ is the ratio of the particle's terminal drift velocity to an applied electric field. Hence, the equation in the case of a charged particle is given as

$$D = \frac{\mu_q \, k_\text{B} T}{q},$$

## Semiconductor

In a semiconductor with an arbitrary density of states, i.e. a relation of the form $p = p(\varphi)$ between the density of holes or electrons $p$ and the corresponding quasi Fermi level (or electrochemical potential) $\varphi$, the Einstein relation is[12][13]

$$D = \frac{\mu_q p}{q \frac{dp}{d\varphi}},$$

where $\mu_q$ is the electrical mobility (see section below for a proof of this relation). An example assuming a parabolic dispersion relation for the density of states and the Maxwell–Boltzmann statistics, which is often used to describe inorganic semiconductor materials, one can compute (see density of states):

$$p(\varphi) = N_0 e^{\frac{q\varphi}{k_\text{B}T}},$$

where $N_0$ is the total density of available energy states, which gives the simplified relation:

$$D = \mu_q \frac{k_\text{B} T}{q}.$$

The net flux of particles due to the drift current is

$$\mathbf{J}_\text{drift}(\mathbf{x}) = \mu(\mathbf{x}) F(\mathbf{x}) \rho(\mathbf{x}) = -\rho(\mathbf{x}) \mu(\mathbf{x}) \nabla U(\mathbf{x}),$$

i.e., the number of particles flowing past a given position equals the particle concentration times the average velocity.

The flow of particles due to the diffusion current is, by Fick's law,

$$\mathbf{J}_\text{diffusion}(\mathbf{x}) = -D(\mathbf{x}) \nabla \rho(\mathbf{x}),$$

where the minus sign means that particles flow from higher to lower concentration.

Now consider the equilibrium condition. First, there is no net flow, i.e. . $\mathbf{J}_{\text{drift}} + \mathbf{J}_{\text{diffusion}} = 0$ Second, for non-interacting point particles, the equilibrium density $\rho$ is solely a function of the local potential energy $U$, i.e. if two locations have the same $U$ then they will also have the same (e.g. see Maxwell-Boltzmann statistics as discussed below.) That means, applying the chain rule,

$$\nabla\rho = \frac{\mathrm{d}\rho}{\mathrm{d}U}\nabla U.$$

Therefore, at equilibrium:

$$0 = \mathbf{J}_{\text{drift}} + \mathbf{J}_{\text{diffusion}} = -\mu\rho\nabla U - D\nabla\rho = \left(-\mu\rho - D\frac{\mathrm{d}\rho}{\mathrm{d}U}\right)\nabla U.$$

As this expression holds at every position $\mathbf{x}$, it implies the general form of the Einstein relation:

$$D = -\mu\frac{\rho}{\frac{\mathrm{d}\rho}{\mathrm{d}U}}.$$

The relation between $\rho$ and $U$ for classical particles can be modeled through Maxwell-Boltzmann statistics

$$\rho(\mathbf{x}) = Ae^{-\frac{U(\mathbf{x})}{k_{\mathrm{B}}T}},$$

$A$

where $\frac{\mathrm{d}\rho}{\mathrm{d}U} = -\frac{1}{k_{\mathrm{B}}T}\rho.$ is a constant related to the total number of particles. Therefore

Under this assumption, plugging this equation into the general Einstein relation gives:

$$D = -\mu\frac{\rho}{\frac{\mathrm{d}\rho}{\mathrm{d}U}} = \mu k_{\mathrm{B}}T,$$

which corresponds to the classical Einstein relation.

## References


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