

Alternative Derivation of the Einstein Relation

Advanced

In this derivation we consider the *forces* acting on carriers and the currents resulting from these forces.

- The important point to know is that within the general framework of mechanics and thermodynamics, forces are generalized and expressed as the (space) derivatives of thermodynamic potentials.
- In particular, diffusion currents due to concentration gradients of the diffusing species may be seen as an expression of a **chemical force** F_{chem} that acts on particles. We call it chemical because it tends to change particle numbers.
- The value of the chemical force is always given by the derivative of the [chemical potential](#); looking at a one-dimensional case we thus have

$$F_{\text{chem}, x} = F = - \frac{d\mu_{\text{chem}}}{dx} = - \frac{dE_F}{dx}$$

- Of course, we will never confuse μ_{chem} , the chemical potential, with μ , the carrier mobility!

Looking at the most general case with only *local equilibrium* in the bands, we use the [Quasi-Fermi energies](#), E_F^e and E_F^h , given by

$$E_F^e = E_C - kT \cdot \ln \frac{N^{\text{eff}}}{n_e}$$

$$E_F^h = E_C + kT \cdot \ln \frac{N^{\text{eff}}}{n_h}$$

- We thus have for the chemical forces

$$F^e = - \frac{dE_F^e}{dx} = - \frac{dE_C}{dx} + \frac{kT}{n^e} \cdot \frac{dn^e}{dx}$$

$$F^h = - \frac{dE_F^h}{dx} = - \frac{dE_C}{dx} + \frac{kT}{n^h} \cdot \frac{dn^h}{dx}$$

- In what follows we drop the indexes "e" and "h" and write only one set of equations for the conduction band (i.e. for electrons). For holes everything is the same, both equations can be retrieved at the end by proper indexing.

We allow for the band edges to be functions of x , i.e. $E_C = E_C(x)$ and $E_V = E_V(x)$. What then determines the numerical value of the band edge energy (for some defined zero point of the energy)? There are two factors:

- The particular kind of semiconductor or crystal considered - this defines the band structure in general. We call this part E_{Cryst} , and note, while E_{Cryst} is constant in semiconductors of one kind of material (and omitted from formulas), it generally may be a function of x . Examples are materials with compositions that change gradually (e.g. **Si-Ge** alloys, or **GaAlAs** with "sliding" **Ge** or **Al** concentration, respectively).
- External or internal electrical field $E_x = -dV(x)/dx$ due to the electrostatic potential $V(x)$ that must be superimposed on the band energies as $-|e|V$ with $|e|$ = magnitude of the elementary charge. In the following we drop the magnitude signs for the sake of convenience. (*We will write the electrical field E_x in pink here, to avoid confusion with the various energies*).

We thus can write

$$\frac{dE_C}{dx} = \frac{dE_{\text{Cryst}}}{dx} + e \cdot E_x$$

- This yields for the force

$$F_{\text{chem}} = - \frac{dE_{\text{Cryst}}}{dx} - e \cdot E_x - \frac{kT}{n} \cdot \frac{dn}{dx}$$

The chemical force will cause a particle movement exactly as an electrical force (which is now a part of the chemical force). The result is the same as in the basic treatment of the [electrical conductivity](#): There will be a constant average drift velocity in the direction of the force and we obtain

- $\langle v_{\text{chem}} \rangle$ = average velocity due to the chemical force = **const.** · F_{chem} .
- For an electrical field E_x in x -direction, we had
 $\langle v_{\text{elect}} \rangle$ = average velocity due to the electrical force $F_{\text{elect}} = e \cdot E_x$.
- $\langle v_{\text{elect}} \rangle$ must be a constant and we defined $\langle v_{\text{elect}} \rangle / E_x =$ mobility μ , or

$$\frac{\langle v_{\text{elect}} \rangle}{F_{\text{elect}}} = \frac{\mu}{e}$$

Since the scattering processes that caused $\langle v_{\text{elect}} \rangle$ to be constant *are the same* for all forces, the proportionality constant between force and average velocity must be the same, too. We thus can write

- $\langle v_{\text{chem}} \rangle / F_{\text{chem}} = \mu / e$ or (dropping indexes for convenience again):

$$\langle v_{\text{chem}} \rangle = v = \frac{\mu}{e} \cdot F_{\text{chem}}$$

- The electrical current carried by this velocity is

$$j = e \cdot n \cdot \langle v_{\text{chem}} \rangle = n \cdot \mu \cdot \frac{dE(x)_{\text{Cryst}}}{dx} + e \cdot n \cdot \mu \cdot E_x(x) - \mu \cdot kT \cdot \frac{dn(x)}{dx}$$

If we now consider the usual case of a semiconductor with $E(x)_{\text{Cryst}} = \text{const.}$, and a zero net current ($j = 0$), we are left with

$$e \cdot n \cdot \mu \cdot E_x - \mu \cdot kT \cdot \frac{dn}{dx} = 0$$

- The second term is an (electrical) current due to a concentration gradient which, according to Ficks first law, *always* can be written as

$$j = - e \cdot D \cdot \frac{dn}{dx}$$

- We thus can *always* equate

$$D = \frac{\mu \cdot kT}{e}$$

- And this is the *Einstein-Smoluchowski relation*.

Substituting this in the equation above, we get [exactly the same equation as in the first derivation](#)

$$n \cdot \mu \cdot E_x = D \cdot \frac{dn}{dx}$$

The consideration of the currents caused by the *chemical force*, however, is *much more general*. The arguments used would also apply for the case where E_{Cryst} is not constant and we will come back to this when discussing heterojunctions or graded semiconductors.