Theory of condensed matter

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Contents

5 Electronic and ionic transport

5.1 Diffusion and Einstein relation

In this chapter we are dealing with the diffusion of charged particles in condensed matter and the corresponding electric conduction phenomena. Such theoretical considerations are traditionally called *transport theory* as the focus is on the *transport of charged particles* from one region in space to another with or without an applied electric field. Charged particles, which give rise to conduction phenomena in the presence of such a field can be electrons in a metal or semiconductor on the one side; on the other side mobile ions in a solid or liquid matrix ($\equiv$ host material).

Electric conduction phenomena due to charged particles are intimately related to the diffusion of such particles due to the thermal excitation of the material. This is the reason why we start with a reconsideration of diffusion and random walk which we first encountered in subsection 2.3.3 in connection with the random-walk description of polymer materials. Here we start from a different angle and consider the diffusion of a density profile $n(\mathbf{r}, t)$ from an initial disturbed pattern $n(\mathbf{r}, t = 0)$ towards its uniform value $n = N/V$. At finite temperature T a pattern different from n will give rise to a current, which is proportional to the *density gradient*:

$$\mathbf{j}(\mathbf{r}, t) = -D\nabla n(\mathbf{r}, t) \tag{5.1}$$

where D is the *diffusion coefficient*. (5.1) is called *Fick's law*. On the other hand, due to particle conservation, the current density is related to the time dependence of $n(\mathbf{r}, t)$ via the *continuity equation*

$$\nabla \cdot \mathbf{j}(\mathbf{r}, t) + \frac{\partial}{\partial t} n(\mathbf{r}, t) \tag{5.2}$$

Taking the divergence of Fick's law (5.1) we have

$$-\nabla \cdot \mathbf{j}(\mathbf{r}, t) = \frac{\partial}{\partial t} n(\mathbf{r}, t) = D\nabla^2 n(\mathbf{r}, t) \tag{5.3}$$

This is identical to the *diffusion equation* (2.109), which we derived from a completely different starting point, namely from a 3-dimensional random walk of a particle. We see that Fick's law, together with the continuity equation is equivalent to assuming that the particles which form the density distribution $n(\mathbf{r}, t)$ perform a random walk. The special solution $n(\mathbf{r}, t) = G(\mathbf{r}, t)$ with the initial condition

$$G(\mathbf{r}, t = 0) = \delta(\mathbf{r}) \tag{5.4}$$

has been shown to be (see (2.111))

$$G(\mathbf{r}, t) = \left[\frac{1}{\sqrt{4\pi Dt}}\right]^3 e^{-r^2/4Dt} \tag{5.5}$$

or, Fourier- and Laplace-transformed

$$G(\mathbf{k}, p) = \int_0^\infty dt e^{-pt} \int d^3\mathbf{r} e^{i\mathbf{k}\mathbf{r}} G(\mathbf{r}, t) = \frac{1}{p + Dk^2} \tag{5.6}$$

Thei initial condition (5.4) becomes

$$G(\mathbf{k}, t = 0) = 1. \tag{5.7}$$

The general solution is then given by

$$n(\mathbf{k}, p) = n(\mathbf{k}, t = 0)G(\mathbf{k}, p) \tag{5.8}$$

or, back transformed into the real space and time domain

$$n(\mathbf{r}, t) = \int d^3\mathbf{r}' n(\mathbf{r}', t = 0)G(\mathbf{r} - \mathbf{r}', t) \tag{5.9}$$

We now assume that the particles, which perform the random walk within the thermally excited medium (which is assumed to be in thermal equilibrium) carry a charge q and that there exists a small applied uniform electric field $\mathbf{E}$ throughout the material, such that the *non-diffusive* part of the current density, i.e. the *current-induced part* depends linearly on $\mathbf{E}$:

$$\mathbf{j}(\mathbf{E}) = \sigma\mathbf{E} \tag{5.10}$$

(Ohm's law). The *electric conductivity* is now related to the diffusion coefficient D by the famous *Einstein relation*

$$\sigma = \frac{\partial n}{\partial \mu} q^2 D \tag{5.11}$$

where n is the equilibrium density and μ the chemical potential. The Einstein relation (5.11) follows from the *time-dependent version of the fluctuation-dissipation theorem* (see 2.30), which is the central theorem of non-equilibrium thermodynamics. The explicit form of the μ derivative of the density depends on the *statistics*, which the particles under consideration obey. Diffusing ions (except protons) usually obey classical (Boltzmann) statistics, electrons (at room temperature and below) obey Fermi statistics. We have for the two statistics

$$\frac{\partial n}{\partial \mu} = \begin{cases} \frac{n}{k_B T} & \text{Boltzmann statistics} \\ \\ N(E_F) & \text{Fermi statistics, } T \to 0 \end{cases} \tag{5.12}$$

where $N(E_F)$ is the electronic density of states at the Fermi energy $E_F = \mu(T \to 0)$. The $T \to 0$ limit is called the *degenerate* limit.

5.2   Ionic diffusion in crystals

We now consider interstitial diffusion in a crystal, i.e. we assume that the sites the diffusing ions may occupy form a lattice, which we - for simplicity - assume to be a simple cubic one. We furthermore assume that the concentration of the diffusing ions is low so that we can neglect blocking phenomena due to occupied sites. In this limit the problem reduces to that of a random walk of a single ion. The equation of motion for the occupation probability of a site i follows from (2.96) with $t \gg \tau$

$$\frac{d}{dt}P_i(t) = \sum_{\substack{j \\ \text{n.N.}}} [\underbrace{-WP_i(t)}_{\substack{\text{hops} \\ \text{away from site } i}} \underbrace{+WP_i(t)}_{\substack{\text{hops} \\ \text{towards site } i}}] \tag{5.13}$$

$$P_i(t) = \lim_{\tau/t \to 0} P(\mathbf{r}_i, t) \qquad W = \frac{1}{2\tau}$$

Here W is the probability per unit time to perform a diffusion step ("hop") in any direction.
(5.13) is solved easily by going to reciprocal space $P_{\mathbf{k}} = \sum_\ell e^{i\mathbf{r}_\ell \mathbf{k}} P_\ell(t)$ and by performing a Laplace transform $P_{\mathbf{k}}(p) = \int_0^\infty e^{-pt} P_{\mathbf{k}}(t)$:

$$pP_{\mathbf{k}}(p) - 1 = W\big[6 + E(k)\big]$$

$$\Rightarrow \quad P_{\mathbf{k}}(p) = \frac{1}{p + W\big[6 + E(\mathbf{k})\big]} \tag{5.14}$$

$$E(\mathbf{k}) = -2\cos(k_x a) - 2\cos(k_y a) - 2\cos(k_z a)$$

where we have used the initial condition $P_{\mathbf{k}}(t=0) = 1$ corresponding to $P_i(t=0) = \delta_{i,0}$. $E(\mathbf{k})$ is just the tight-binding band structure with $E_0 = 0$ and $t = 1$. If we now become interested in length scales much larger than the lattice constant a we perform the limit $ka \ll 1$ and obtain

$$P_{\mathbf{k}}(p) = \frac{1}{p + \big[6 - 6 + k^2 a^2\big]W} = \frac{1}{p + Dk^2} \tag{5.15}$$

This is the solution of a diffusion equation wit diffusion constant

$$D = a^2 W \tag{5.16}$$

We emphasize again that the hopping motion of a particle on an interstitial lattice is equivalent to a random walk on such a lattice and becomes a diffusive motion in the continuum limit.

5.3 Ionic diffusion in disordered solids

The process discussed in the previous subsection describes a diffusion process of small ions (like H^+ or Li^+ ions) in a crystalline host. However, most of the materials (e.g. materials for solid-state batteries), which allow for small-ion diffusion are disordered. The hopping probability per unit time from a a potential energy minimum at site i to anoter one at site j W_{ij} is given by the *Arrhenius-Kramers relation*

$$W_{ij} = \nu_0 e^{-\epsilon_{ij}/k_B T} \tag{5.17}$$

where ϵ_{ij} is the energy barrier, which must be overcome to go from i to j, and ν_0 is the so-called *attempt frequency*, which describes the oscillatory motion of the particle inside the potential well and is of the order of a phonon frequency. The *disorder* in our model now enters via the assumption of a *distribution of energy barriers* $P(\epsilon)$, which may be a Gaussian or something else. The equation of motion for the hopping particles now becomes

$$\frac{\mathrm{d}}{\mathrm{d}t} P_i(t) = \sum_{\substack{j \\ \text{n.N.}}} \big[-W_{ij} P_i(t) + W_{ij} P_i(t) \big] \tag{5.18}$$

We now exploit a *mathematical analogy* between eq. (4.52) of the "scalar" phonon problem in paragraph 4.4.1 and (5.18), in order to be able to use the 2-site version of the CPA developed in this paragraph:

Scalar phonon problem	Hopping problem
$\left(\dfrac{\mathrm{d}}{\mathrm{d}t}\right)^2$	$\dfrac{\mathrm{d}}{\mathrm{d}t}$
$z = -\omega^2 + i\epsilon$	$p = i\omega + \epsilon$
K_{ij}	W_{ij}

$$\tag{5.19}$$

Defining $\Gamma(p)$ as the *frequency dependent hopping probability in the effective medium* we can use *mutatis mutandis*[1] the CPA equation (4.61) to calculate $\Gamma(p)$ from $P(W)$:

$$\Gamma(p) = \int_0^\infty \mathrm{d}\epsilon P(\epsilon) \frac{W(\epsilon)}{1 + \big(W(\epsilon) - \Gamma(p)\big)\frac{2}{Z\Gamma(p)}\big(1 - pG_{ii}(p)\big)}$$

(5.20)

$$G_{ii}(p) = \frac{1}{\Gamma(p)}G_{ii}^{(0)}(p) = \sum_{\mathbf{k}\in BZ} \frac{1}{p + \Gamma(p)\big(6 + E(\mathbf{k})\big)} \xrightarrow{ka\ll 1} \frac{1}{p + \Gamma(p)k^2}$$

In the continuum limit we obviously deal with a *frequency dependent diffusivity*

$$D(p) = \Gamma(p)a^2\,,$$

(5.21)

which leads, via the *Nernst-Einstein relation*

$$\sigma(p) = \frac{n}{k_B T}q^2 D(p) = \sigma'(\omega) + i\sigma''(\omega)$$

(5.22)

to a *frequency-dependent* dynamic conductivity. The latter is related by electrodynamics to the *frequency-dependent permittivity*

$$\epsilon(p) = \epsilon'(\omega) + \epsilon''(\omega) = \frac{\sigma(p)}{p}$$

(5.23)

The mathematical analogy (5.19) and the CPA scheme (5.20) already imply the following important and far-reaching conclusions:

- The disorder leads to a *frequency-dependent* conductivity.

- The frequency dependence of the *ac conductivity* $\sigma'(\omega)$ starts, where in the analogous phonon problem $\mathbf{k}$ would cease to be a "good quantum number", i.e. near the "boson peak".

Indeed, in all disordered "fast ion conductors", in which small ions contribute the conduction mechanism, one encounters such a frequency dependence which is very often of the form $\sigma(p) \propto p^x$ with $x \overset{\sim}{<} 1$. Such a dependence, indeed, is also obtained from the CPA equation (5.20) if a sufficient broad distribution $P(\epsilon)$ is taken.

5.3.1 Percolation picture for the dc conductivity

From the beginning of transport measurements of disordered fast-ion conductors the experimentalists associated the frequency dependence of the ac conductivity with the disorder and discussed it either in terms of independent different parallel conduction channels ("parallel equivalent network") or in terms of hopping processes in series ("serial equivalent network"). In both cases the disorder would lead to a *dc conductivity* $\sigma(o) = \sigma'(0)$, which does *not* obey an Arrhenius law

$$\sigma(0) = \sigma_0 e^{-E_A/k_B T}$$

(5.24)

where E_A is the so-called *activation energy*. In contrast, in all disordered fast-ion conductors such a temperature dependence is observed to a very good accuracy. This apparent contradiction is solved on the one hand by the fact known to electro-engineers that in a complex impedance network both parallel and serial equivalent circuits are wrong, on the other hand by the following argumentation using our CPA

---

[1]lat.: after the appropriate changes made

theory. In the *dc* limit $p \rightarrow 0$ we obtain for the quantity $\Gamma(0)$, which is proportional to the *dc* conductivity

$$
\begin{aligned}
\Gamma(0) \equiv \Gamma &= \left\langle \frac{W}{1 + \frac{W}{\Gamma} - \frac{1}{3}} \right\rangle = \left\langle \frac{W}{\frac{2}{3} + \frac{W}{\Gamma}} \right\rangle \\
&= \Gamma \left\langle \frac{1}{\frac{2\Gamma}{3W} + 1} \right\rangle
\end{aligned}
\tag{5.25}
$$

$$
\Rightarrow \quad 1 = \int d\epsilon \, P(\epsilon) \frac{1}{1 + \frac{2\Gamma}{3\nu_0} e^{\epsilon/k_B T}}
$$

We now make the ansatz

$$
\Gamma = \frac{3}{2} \nu_0 e^{-E^*/k_B T}
\tag{5.26}
$$

and obtain from (5.25)

$$
\boxed{1 = \int d\epsilon \, P(\epsilon) \frac{1}{1 + e^{(\epsilon - E^*)/k_B T}}}
\tag{5.27}
$$

From (5.27) we conclude

- The apparent activation energy E^* becomes independent of T for $T \ll E^*/k_B$;

- In this limit (which holds at room temperature) there is always an Arrhenius law, independent of $P(\epsilon)$

In the low-temperature limit the activation energy is given by

$$
1 = \int_0^{E^*} d\epsilon \, P(\epsilon)
\tag{5.28}
$$

This equation allows for the following interpretation:
Let us consider the hopping problem as a compex conductance problem: All hopping probabilities are modelled as conductances between the appropriate sites with values $G_{ij} = W_{ij}$. We now put all conductances away and sort them according to their magnitude. We then start to re-insert them, beginning with the small conductances i.e. large resistances. We then put larger conductances in up to a limiting value $G_{ij} = \nu_0 e^{-E/k_B T}$, where E is the minimum allowed energy barrier. If we increase E, more and more sites become connected by conducting paths until — at a *threshold energy* E_{thr} — a *conducting path* leads through the whole network. The model construction we just described is called *percolation construction*. According to this construction, which can be mathematically (approximately) described by equation (5.28), the observed activation energy $E_A = E^*$ is a little larger than E_{thr} such that just a current can penetrate through the disordered network. The considerations of the present little paragraph are at the heart of the theory of hopping conductivity in disordered systems developed by Sir Nevill Mott and Michael Pollak.

5.4 Electron transport in metals

5.4.1 Scattering, diffusion and Drude formula
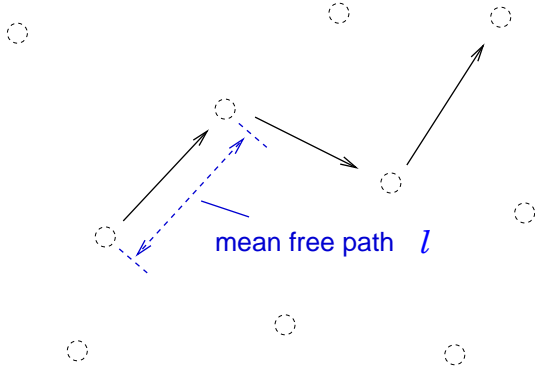
Scattering path of a nearly free electron

We now consider nearly free electrons in a metal, which are occasionally scattered by an impurity or a lattice vibration (phonon), which passes by (see our figure). The electronic velocity is its momentum $p_F = \hbar k_F$, divided by its mass

$$v_F = \frac{1}{m}\hbar k_F \qquad (5.29)$$

So, during the repeated scattering the electron performs a kind of random walk, and we make the ansatz

$$D = \frac{1}{3}\ell^2 \frac{1}{\tau} \qquad (5.30)$$

Here ℓ is the mean-free path of the electron, i.e. the length an electron moves freely (on average) without being scattered. $1/\tau$ is the (average) scattering rate per uni time, which is related to ℓ via

$$\ell = v_F \tau\,, \qquad (5.31)$$

so that we have

$$D = \frac{1}{3}\ell v_F = \frac{1}{3}v_F^2 \tau\,. \qquad (5.32)$$

From the degenerate version of the Einstein relation (5.11) we obtain

$$\sigma = N(E_F)e^2 D = \frac{3}{2}\frac{n}{E_F}e^2 \frac{1}{3}\frac{\hbar^2 k_F^2}{m^2}\tau = \frac{1}{m}ne^2\tau \qquad (5.33)$$

This is the *Drude formula* for the electric conductivity of a metal, which can be derived from kinetic theory as well. We shall do so in the next paragraph. Here we have emphasized the random-walk aspect, which states, that a repeated scattering process is equivalent to a diffusion mechanism.

5.4.2 Boltzmann equation

We now consider the repeated scattering process of electrons in a metal more formally. As the transport phenomena do not involve wave functions but electronic densities and currents one considers Wigner's *generalized phase space function*

$$
\begin{aligned}
f_{\mathbf{k},s}(\mathbf{r},t) &= \sum_{\mathbf{q}} e^{i\mathbf{qr}}\psi_s^*\left(\mathbf{k}-\frac{\mathbf{q}}{2}\right)\psi_s\left(\mathbf{k}+\frac{\mathbf{q}}{2}\right) \\
&= \int \mathrm{d}^3\vec{\rho}\, e^{i\vec{\rho}\mathbf{k}}\psi_s^*\left(\mathbf{r}-\frac{\vec{\rho}}{2}\right)\psi_s\left(\mathbf{r}+\frac{\vec{\rho}}{2}\right)
\end{aligned} \qquad (5.34)
$$

$\mathbf{r}, \vec{\rho}$ are center-of-mass and relative coordinates, resp.:

$$\mathbf{r} = \frac{1}{2}\left[\mathbf{r}_1 + \mathbf{r}_2\right] \qquad \vec{\rho} = \mathbf{r}_2 - \mathbf{r}_1 \qquad (5.35)$$

The scattering of a wave of wave vector $\mathbf{k}$ can be accounted for by making a bilance of "scattering in and out of the $\mathbf{k}$ channel" in the following manner:

$$\left.\frac{\partial}{\partial t}f_{\mathbf{k},s}(\mathbf{r},t)\right|_{\text{coll}} = -\frac{1}{V}\sum_{\mathbf{k}',s'}W_{\mathbf{k}\mathbf{k}'}^{ss'}f_{\mathbf{k},s}\left[1 - f_{\mathbf{k}',s'}\right] + \frac{1}{V}\sum_{\mathbf{k}',s'}W_{\mathbf{k}'\mathbf{k}}^{s's}f_{\mathbf{k}',s'}\left[1 - f_{\mathbf{k},s}\right] \qquad (5.36)$$

The index "coll" means that this is the collisional change of the electronic phase space density due to collisions with an impurity or a phonon.

We now disregard the spin index and consider the quantities $\mathbf{r}$ and $\mathbf{p} = \hbar\mathbf{k}$ in $f_{\mathbf{k}}(\mathbf{r}, t) \equiv f(\mathbf{p}, \mathbf{r}, t)$ as classical quantities $\mathbf{r}(t)$ and $\mathbf{p}(t)$. Then the collisional change of $f(\mathbf{p}, \mathbf{r}, t)$ should be equal to the *total time derivative* of $f(\mathbf{p}, \mathbf{r}, t)$:

$$
\begin{aligned}
\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} &= \frac{\partial f}{\partial t} + \sum_{\alpha=1}^{3} \frac{\partial f}{\partial p_\alpha}\frac{\partial p_\alpha}{\partial t} + \sum_{\alpha=1}^{3}\frac{\partial f}{\partial x_\alpha}\frac{\partial x_\alpha}{\partial t} \\
&= \frac{\partial f}{\partial t} + \mathbf{F}\cdot\nabla_{\mathbf{p}} f + \mathbf{v}\cdot\nabla_{\mathbf{r}} f
\end{aligned}
\tag{5.37}
$$

(5.37), together with the spinless version of (5.36) form the celebrated *Boltzmann equation* of electronic transport. $\mathbf{F}$ is the force on the electron, which — in "semiclassical approximation" — is taken to be the Lorentz force

$$
\mathbf{F} = -e\big[\mathbf{E} + \mathbf{v}\times\mathbf{B}\big]
\tag{5.38}
$$

In the *relaxation time approximation* one writes (see exercise 9.1)

$$
\begin{aligned}
\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} &= -\frac{1}{\tau}(f - f_0) \\
\text{with} \qquad \frac{1}{\tau} &= \frac{1}{V}\sum_{\mathbf{k}'} W_{\mathbf{k}\mathbf{k}'}\big(1 - \mathbf{e}_{\mathbf{k}}\cdot\mathbf{e}_{\mathbf{k}}'\big)\bigg|_{|\mathbf{k}|=|\mathbf{k}'|=k_F}
\end{aligned}
\tag{5.39}
$$

Here f_0 is the equilibrium Fermi distribution. We now call $f - f_0 = f_1$ and assume that f_1 is created by the small external electric field $\mathbf{E}$, so that f_1 can be neglected in the force term. We further assume an uniform spatial distribution of the scattered electrons, i.e. $\nabla_{\mathbf{r}} f = 0$, and no explicit time dependence, i.e. $\partial f/\partial t = 0$, so that we get the following strongly simplified version of the Boltzmann equation

$$
\mathbf{F}\cdot\nabla_{\mathbf{p}} f_0 = -\frac{f_1}{\tau}
\tag{5.40}
$$

We re-arrange $\nabla_{\mathbf{p}} f_0$ as

$$
\nabla_{\mathbf{p}} f_0 = \underbrace{\nabla_{\mathbf{p}} E}_{\mathbf{v}}\,\frac{\partial f}{\partial E}
\tag{5.41}
$$

$$
\Rightarrow \qquad f_1 = \tau\left(-\frac{\partial f}{\partial E}\right)\mathbf{v}\cdot\mathbf{F} = -e\tau\left(-\frac{\partial f}{\partial E}\right)\mathbf{v}\cdot\mathbf{E}
$$

For the field-induced current density we finally obtain

$$
\begin{aligned}
\mathbf{j} &= -\frac{2e}{V}\sum_{\mathbf{k}} f_1 \mathbf{v} \\
&= \frac{2e^2\tau}{V}\sum_{\mathbf{k}}\left(-\frac{\partial f}{\partial E}\right)\underbrace{\mathbf{v}\cdot\mathbf{E}\mathbf{v}}_{v^2\mathbf{e}_z \quad \text{if } \mathbf{j}||EE||\mathbf{e}_z}
\end{aligned}
\tag{5.42}
$$

from which we obtain the quantum Drude formula

$$
\boxed{
\begin{aligned}
\sigma &= \frac{2e^3\tau}{3V}\sum_{\mathbf{k}}\left(-\frac{\partial f}{\partial E}\right)v^2 \\
&\xrightarrow{\text{Exercise 9.2}} \frac{ne^2\tau}{m^*} \qquad \text{for } E = \frac{\hbar^2 k^2}{2m^*}
\end{aligned}
}
\tag{5.43}
$$

5.4.3 Quantum interference effects

We consider again the scattering of the electrons as a random walk and construct a time variable along the walk as we have done in discussing the polymer chains. in terms of this time variable the diffusivity is given as

$$D = \lim_{t \to \infty} \frac{1}{2t} \langle r^2(t) \rangle = \lim_{t \to \infty} \int d^3 \mathbf{r} \frac{r^2}{2t} P(\mathbf{r}, t) \tag{5.44}$$

where $P(\mathbf{r}, t)$ is the diffusion probability density. Defining ϵ to be the Laplace variable (instead of p) we have

$$D = \lim_{\epsilon \to 0} \frac{\epsilon^2}{2} \langle r^2(\epsilon) \rangle = \lim_{\epsilon \to 0} \frac{\epsilon^2}{2} \int d^3 \mathbf{r} r^2 P(\mathbf{r}, \epsilon) \tag{5.45}$$

Now there exists a relation by Kubo and Greenwood

$$
\begin{aligned}
D &\propto \lim_{\epsilon \to 0} \frac{\epsilon^2}{2} \int d^3 \mathbf{r} r^2 P_{\text{quantum}}(\mathbf{r}, \epsilon) \\
&\text{with} \quad P_{\text{quantum}}(\underbrace{\mathbf{r}_1 - \mathbf{r}_2}_{\mathbf{r}}, \epsilon) = \langle G_+(\mathbf{r}_1 - \mathbf{r}_2, \epsilon) G_-(\mathbf{r}_2 - \mathbf{r}_1, \epsilon) \rangle_{disorder}
\end{aligned}
\tag{5.46}
$$

$G_\pm(\mathbf{r}_1, \mathbf{r}_2, \epsilon) = < \mathbf{r}_1 | \mathcal{G} | \mathbf{r}_2 >= < \mathbf{r}_1 | \dfrac{1}{E \mp i\epsilon - \mathcal{H}} | \mathbf{r}_2 >$ is our old friend, the Green's function, which can be represented as a multiple-scattering expansion with respect to the fluctuating potential V as

$$
\begin{aligned}
\mathcal{G} &= \mathcal{G}_0 + \mathcal{G}_0 V \mathcal{G}_0 + \ldots \\
&= \mathcal{G}_0 T \mathcal{G}_0
\end{aligned}
\tag{5.47}
$$

The scattering operator T involves all possible scattering processes, which can be decomposed into scattering processes from specific impurities, located at a site i, associated with a single-site T matrix t_i. The Green's function can then be decomposed as (we drop all ϵs from now on)

$$G(\mathbf{r}, \mathbf{r}') = \sum_{\substack{\text{paths} \\ \text{from } \mathbf{r} \text{ to } \mathbf{r}'}} G_0(\mathbf{r}_{01}) t_1 G_0(\mathbf{r}_{12}) t_2 G_0(\mathbf{r}_{23}) \ldots t_{n-1} G_0(\mathbf{r}_{n-1,n}) \tag{5.48}$$

with $\mathbf{r}_0 = \mathbf{r}$ and $\mathbf{r}_n = \mathbf{r}'$.

If, now, we approximate $|G|^2$ in such a way that we put

$$\left| \sum_{\text{paths}} G_0 t_1 G_0 t_2 \ldots t_{n-1} G_0 \right|^2 \overset{?}{=} \sum_{\text{paths}} |G_0|^2 |t_1|^2 |G_0|^2 |t_2|^2 | \ldots |t_{n-1}|^2 |G_0|^2 \tag{5.49}$$

we obtain the diffusion propagator for $P_{\text{quantum}}(\mathbf{r}, \epsilon)$. with $\tau^{-1} \propto |t_i|^2$. By this procedure all interferences have been assumed to be cancelled out by the impurity averages, i.e. one has assumed that the $T_{ij} = A_{ij} e^{i\phi_{ij}}$ have all random phases ϕ_{ij}, which cancel out by the impurity average. As the free Green's functions have the form

$$G_0(r_{\nu,\nu+1}) \propto e^{i k_F r_{\nu,\nu+1}} \tag{5.50}$$

the phases ϕ_{ij} are just given by k_F times the length s_{ij} of the path from i to j. This fact leads to an *important exception* from the rule that the interference terms cancel out:

Assume that a multiple-scattering path contains a *loop*. As the positions of the impurities do not change in time, the phases along this path are fixed once forever. Let us now consider two paths one, which leads *clockwise* around the loop, the other *anticlockwise*. The phases along both paths are exactly the same so that we have for the intensities of the two processes
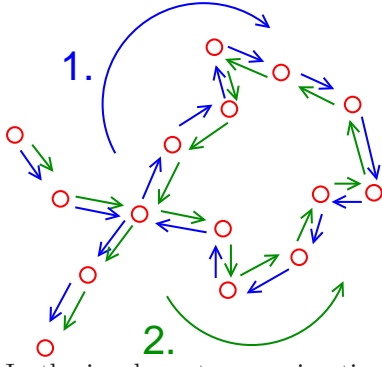
$$
\begin{aligned}
\left|T_1 + T_2\right|^2 &= \left|A_1 e^{i\phi_1} + A_2 e^{i\phi_2}\right|^2 \\
&= \left|A_1\right|^2 + \left|A_2\right|^2 + 2A_1 A_2 \underbrace{\cos(\phi_1 - \phi_2)}_{=1 \text{ for } \phi_1 = \phi_2} \\
&= 4\left|A_1\right|^2 \qquad \text{for } A_1 = A_2
\end{aligned}
$$

$$(5.51)$$

In the incoherent approximation (5.49) one would obtain $|T_1 + T_2|^2 = 2|A_1|^2$ instead. in the incoherent approximation, which treats the quantum propagator $P_{\mathrm{quantum}}(\mathbf{r}, \epsilon)$ as classical diffusion propagator the closed-loop interferences are missing. Obviously there must be a correction to the scattering rate due to the closed-loops:

$$\tau^{-1} = \tau_0^{-1} + \Delta\tau^{-1} \tag{5.52}$$

which is of the form

$$\Delta\tau^{-1} \propto \sum_{\text{loops}} \overset{\frown}{t_1 G_0 t_2 G_0} \cdots \sum_{\text{loops}} \overset{\frown}{t_1 G_0 t_2 G_0} \ldots \tag{5.53}$$

which can be approximated as

$$\Delta\tau^{-1} \propto G_{\mathrm{diff}}(\mathbf{r} = 0, \epsilon \to 0) = \lim_{\epsilon \to 0} \int_0^\infty \mathrm{d}t \frac{1}{\left[4\pi D_0 t\right]^{d/2}} e^{-\epsilon t} \tag{5.54}$$

where we have used the expression for the d dimensional diffusion propagator

$$G_{\mathrm{diff}}(\mathbf{r}, t) = \frac{1}{\left[4\pi D_0 t\right]^{d/2}} e^{-r^2/4Dt} \tag{5.55}$$

For evaluating the interference contribution (5.54) we first consider $d = 3$:

$$\int_0^\infty \mathrm{d}t\, t^{-3/2} e^{-\epsilon t} = \epsilon^{1/2}\Gamma(-1/2) \overset{\epsilon \to 0}{\longrightarrow} 0 \tag{5.56}$$

So the contribution vanishes, unless there is a *maximum loop length*, given by the *inelastic mean-free path* ℓ_{in} due to scattering from phonons. In this case ϵ is replaced by $\tau_{\mathrm{in}}^{-1} = v_F/\ell_{\mathrm{in}}$. Assuming[2] $\tau_{\mathrm{in}}^{-1} \propto T^p$ we obtain a correction with a temperature dependence $\propto T^{p/2}$.

Let us now consider the case $d = 2$. The integral $\int_0^\infty \frac{\mathrm{d}t}{t}$ certainly *diverges*. This is a first indication for a *disorder and interference induced localization transition in $d = 2$*, which we shall discuss in the next subsection. If we insert a minimal and maximal scattering time (the minimal one corresponding to the elastic mean-free path $\ell_0 = v_F \tau_0$) we obtain

$$\Delta\tau^{-1} \propto \ln \tau_{\mathrm{in}}/\tau_0 \propto -\ln T \tag{5.57}$$

Such a behavior is, indeed observed in two-dimensional devices.

5.4.4   Anderson localization

In 1958 P. W. Anderson published his famous paper "Absence of diffusion in certain random lattices", in which he showed that the diffusion coefficient of an electron in a random potential V can be zero if the spatial fluctuations measured by $< (V- < V >)^2 > /(< V >)^2$ exceed a certain critical value. This happens roughly when the mean free path due to the potential fluctuations becomes as short as the electronic wavelength or (equivalently) an interatomic distance. In 1979 Abrahams, Anderson, Licciardello and Ramakrishnan showed that this *localization* effect is due to a *quantum interference effect* first discussed by Langer and Neal in 1966. We just discussed this effect in the previous subjection.
We now discuss the Anderson localization transition (or *metal-nonmetal transition*) from the point of view of electrons in a random environment and present the scaling ideas of Abrabahams *et al.* .

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[2]The exponent p can vary between 2 and 5, depending on the type of material.

In his original paper Anderson considered a tight-binding Hamiltonian with a spatially fluctuating local energy ϵ_i representing the fluctuations of the external potentials:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_0 = \sum_i \epsilon_i |i><i| + t \sum_{\substack{ij \\ \text{n.N.}}} |i><j| \tag{5.58}$$

We assume that the on-site energies $\epsilon_i = \epsilon_i + \Delta\epsilon_i$ are random variables with average ϵ_0 and relative variance $\sigma_\epsilon = \langle(\Delta\epsilon_i)^2\rangle/\sigma_0^2$. In the subsection 3.2.6 we convinced ourselves that lear the lower band edge $\mathcal{H}_0$ can be represented by a free-electron Hamiltonian with effective mass $m^* = \hbar^2/2ta^2$, where a is the lattice constant of a simple-cubic lattice.

Anderson found that there exists a critical amount σ_c of disorder. For $\sigma_\epsilon < \sigma_c$ the mean-square displacements of the electrons increases linearly with time, whereas for $\sigma_\epsilon > \sigma_c$ it has an upper bound r_0^2:

$$\langle r^2(t)\rangle \quad \begin{cases} \propto t & \sigma_\epsilon < \sigma_c \quad \text{Diffusion} \\[2mm] \leq r_0^2 & \sigma_\epsilon > \sigma_c \quad \text{Localization} \end{cases} \tag{5.59}$$

r_0 is called *localization length*, and, in the localized state the electronic wave function has an envelope, which decays exponentially beyond r_0:
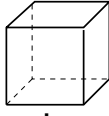
$$\psi(\mathbf{r}) = \sum_\alpha a_W(\mathbf{r})e^{-|\mathbf{r}-\mathbf{r}_\alpha|/r_0} \tag{5.60}$$

where $a_W(\mathbf{r})$ is a Wannier function and $\mathbf{r}_\alpha$ are some random points in the disordered material. The important point is, if one considers a piece of disordered material, the *conductance G* of the material will decay exponentially with the length L of a bar

$$G(L) \propto e^{-L/r_0} \tag{5.61}$$

We now turn to the *scaling argument of Abraham et al.*:
We consider the length dependence of the conductance a *metallic* piece of material of size L^d of resistivity ρ

$$d = 1 \qquad d = 2 \qquad d = 3$$

$$G \propto \frac{1}{\rho L} \qquad G \propto \frac{1}{\rho} \qquad G \propto \frac{L}{\rho} \tag{5.62}$$

We want to construct a dimensionless conductance and define

$$\frac{1}{G_0} = \frac{\hbar}{e^2} = \frac{1.05 \cdot 10^{-34}\text{Ws}^2}{(1.6)^2 \cdot 10^{-38}(\text{As})^2} = 410\Omega \tag{5.63}$$
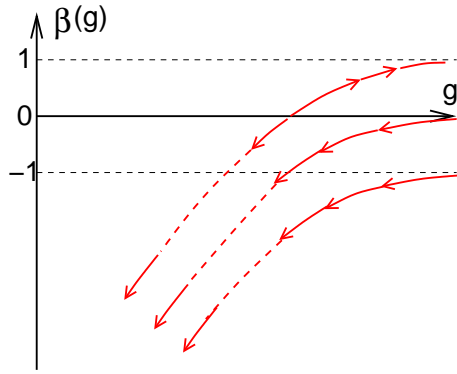
so that we have in the metallic regime

$$\lim_{L\to\infty} g(L) = \lim_{L\to\infty} \frac{G(L)}{G_0} \propto L^{d-2} \tag{5.64}$$

In the localized regime we expect

$$\lim_{L\to\infty} g(L) \propto e^{L/r_0} \to 0 \tag{5.65}$$

The *scaling hypothesis* now consists in postulating that in all dimension and whether there is localization or not $g(L)$ can be represented as

$$g(L) = g_0 L^\beta \qquad \text{or inversely} \qquad \beta(g) = \frac{\text{d}\ln g}{\text{d}\ln L} \tag{5.66}$$

where $\beta(g)$ is supposed to be a *universal* function of g. If $\beta(g)$ is known, one can desice from the *sign* of β, whether

$$\lim_{L\to\infty} g(L) \begin{cases} \longrightarrow \infty & \text{metallic for} \quad \beta > 0 \\[2ex] \longrightarrow 0 & \text{localized for} \quad \beta < 0 \end{cases}$$
$$(5.67)$$

How can $\beta(g)$ look like? For large g we have

$$\lim_{g\to\infty} \beta = d - 2 \qquad (5.68)$$

Abrahams *et al.* calculated the *corrections* to this asymptotic law:

$$\beta(g) = d - 2 - \frac{\text{cons.}}{g} \tag{5.69}$$

On the other hand, we have for small g $g(L) \propto e^{-L/r_0}$, from which follows

$$\lim_{g\to 0} \beta(g) = \ln g - \text{const.} \tag{5.70}$$

Result:

The scaling transformation (increasing L) leads to a *vanishing conductance* in $d = 1$ *and* in $d = 2$. This means that, in these dimensions, for *any* disorder there is always localization, i.e. $\lim_{L\to\infty} g(L) = 0$. In $d = 3$ this limit depends on the degree of disorder: if in a sample of a certain size L the dimensionless conductance is smaller than the critical one it will scale towards zero. If it is larger, it will scale towards infinity. The point, where $\beta(g)$ crosses the zero line is an *unstable fixed point* of the scaling transformation. These findings have been backed up by a field-theoretical treatment of the Anderson transition by F. Wegner and other authors. Within the field-theoretical formalism the scaling transformation corresponds to the *renormalization group transformation*.