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PHYS-E0421 Solid-State Physics (5cr), Spring 2019

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Lecture 4, 11/3/2019

Today's program

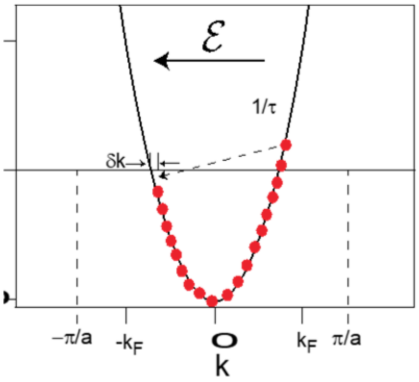
- Lecture topics
  - Boltzmann equation and electrical conductivity
  - Thermal conductivity (mostly electronic contribution)
  - Thermoelectric effects

Why is the Boltzmann equation needed?

Electrons in an external field in a metal:

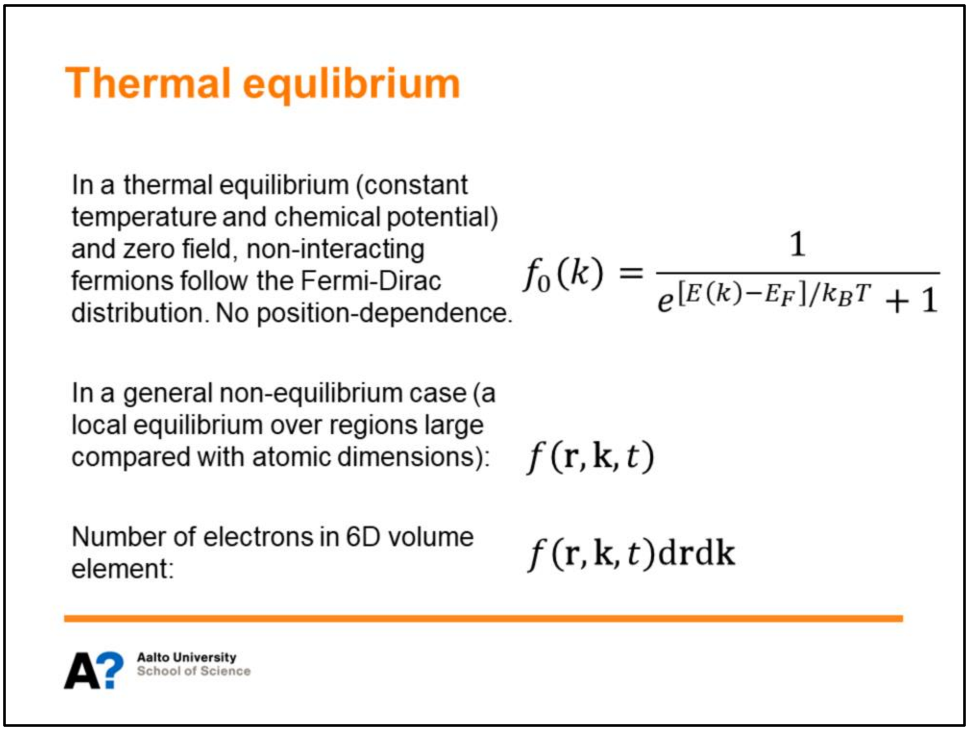
A balance between two mechanisms,

1. Driving electric field
2. Scattering from phonons and lattice defects



This is a non-equilibrium process. There might also be temperature gradients and variation in the chemical potential, which also affect transport phenomena.

How does the non-equilibrium distribution differ from the equilibrium one? How is it possible to build a more quantitative model?



Thermal equlibrium

In a thermal equilibrium (constant temperature and chemical potential) and zero field, non-interacting fermions follow the Fermi-Dirac distribution. No position-dependence.

$$f_0(k) = \frac{1}{e^{[E(k)-E_F]/k_B T} + 1}$$

In a general non-equilibrium case (a local equilibrium over regions large compared with atomic dimensions):

$$f(\mathbf{r}, \mathrm{k}, t)$$

Number of electrons in 6D volume element:

$$f(\mathbf{r}, \mathrm{k}, t)\mathrm{d}\mathbf{r}\mathrm{d}\mathrm{k}$$

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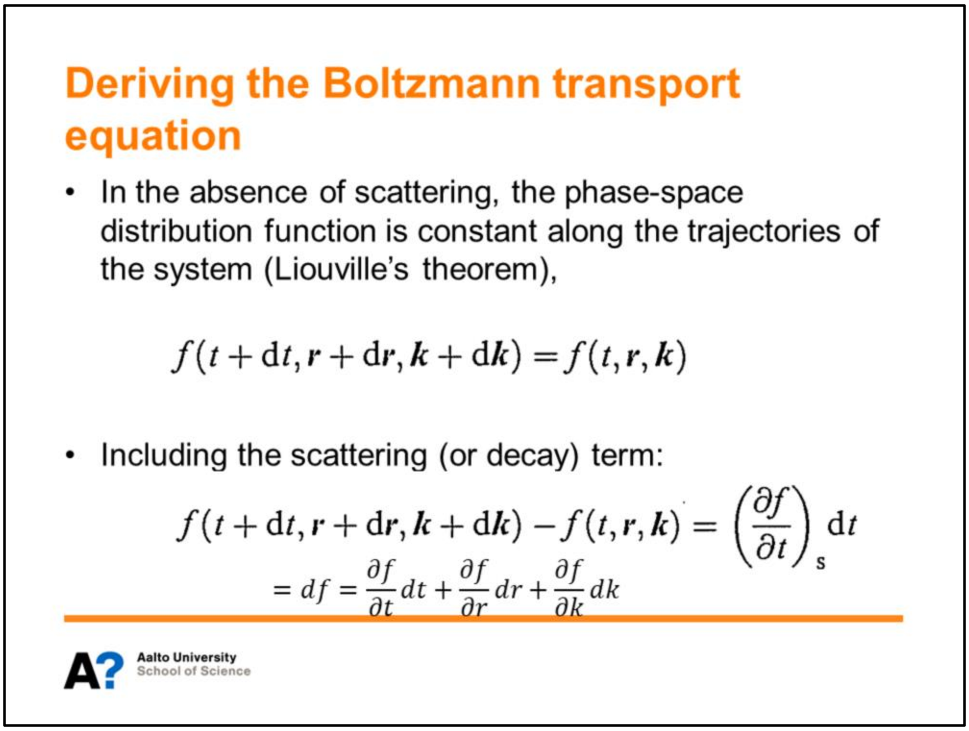
- Drawing 4.1, for f(E) vs f(k), f(k) only valid for a single band
- For well-defined k (or v), small delta-k needed => large extent in real space



Deriving the Boltzmann transport equation

- In the absence of scattering, the phase-space distribution function is constant along the trajectories of the system (Liouville's theorem),

$$f(t+\mathrm{d}t,\boldsymbol{r}+\mathrm{d}\boldsymbol{r},\boldsymbol{k}+\mathrm{d}\boldsymbol{k}) = f(t,\boldsymbol{r},\boldsymbol{k})$$

- Including the scattering (or decay) term:

$$f(t+\mathrm{d}t,\boldsymbol{r}+\mathrm{d}\boldsymbol{r},\boldsymbol{k}+\mathrm{d}\boldsymbol{k}) - f(t,\boldsymbol{r},\boldsymbol{k}) = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{s}} \mathrm{d}t$$

$$= df = \frac{\partial f}{\partial t}dt + \frac{\partial f}{\partial r}dr + \frac{\partial f}{\partial k}dk$$

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- (df/dt)s temporal change in f due to scattering
- In classical version, particles are in (t,r,p) instead of (t,r,k)

Deriving the Boltzmann transport equation

- Total derivative $$\frac{df(\mathbf{r},\mathbf{k},t)}{dt} = \frac{\partial f}{\partial t} + \nabla_r f \frac{d\mathbf{r}}{dt} + \nabla_k f \frac{d\mathbf{k}}{dt}$$

- Consider an electron in an electric field and the time evolving from *t* to *t+dt*. The semi-classical equations of motion give:

$$t \to t + dt$$

$$\mathbf{r} \to \mathbf{r} + d\mathbf{r} = \mathbf{r} + \mathbf{v}dt$$

$$\mathbf{k} \to \mathbf{k} + d\mathbf{k} = \mathbf{k} - \tfrac{e}{\hbar}\mathbf{E}dt$$

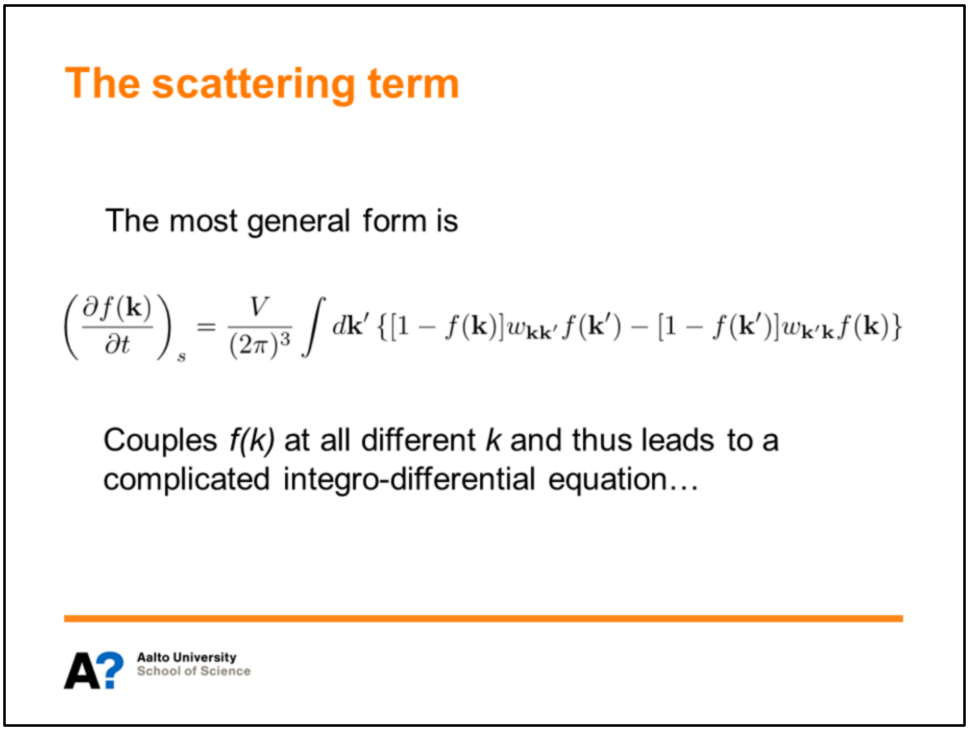
Deriving the Boltzmann transport equation

- Plugging in, we obtain

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \nabla_r f - \frac{e}{\hbar} \boldsymbol{E} \cdot \nabla_k f = \left(\frac{\partial f}{\partial t} \right)_s$$

- This is the general form of the so-called Boltzmann transport equation.
- With this we can try to solve *f*

- How to describe the scattering term in practice?



The scattering term

The most general form is

$$\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_s = \frac{V}{(2\pi)^3}\int d\mathbf{k}'\,\{[1-f(\mathbf{k})]w_{\mathbf{k}\mathbf{k}'}f(\mathbf{k}')-[1-f(\mathbf{k}')]w_{\mathbf{k}'\mathbf{k}}f(\mathbf{k})\}$$

Couples *f(k)* at all different *k* and thus leads to a complicated integro-differential equation…

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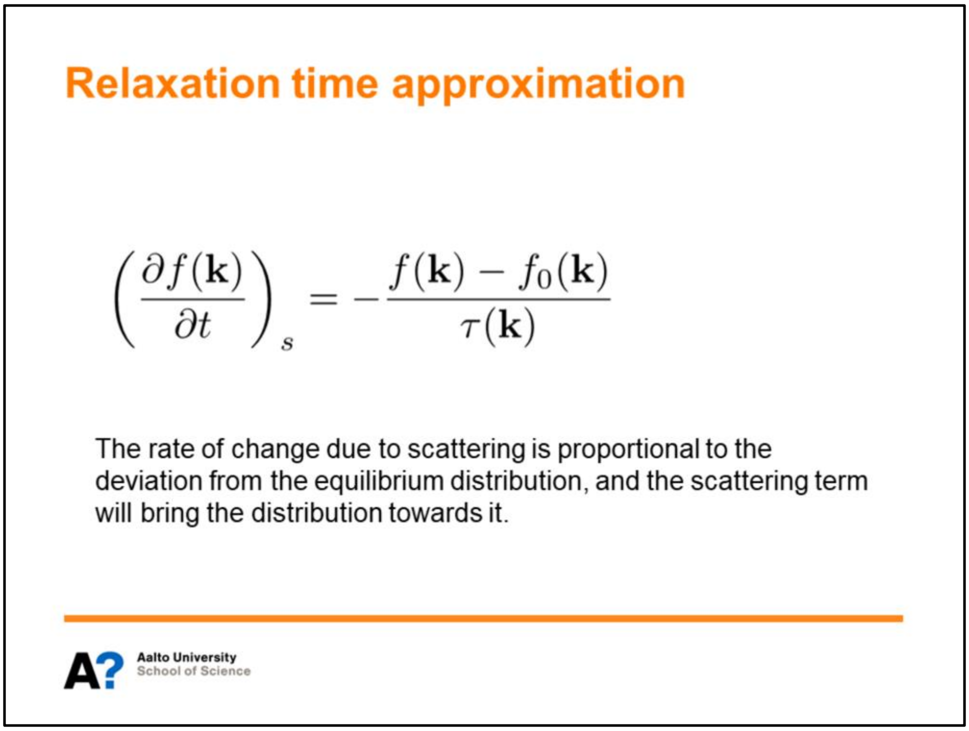
- Scattering to and from state k, can only take place when initial state is occupied and final state unoccupied



Relaxation time approximation

$$\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_s = -\frac{f(\mathbf{k}) - f_0(\mathbf{k})}{\tau(\mathbf{k})}$$

The rate of change due to scattering is proportional to the deviation from the equilibrium distribution, and the scattering term will bring the distribution towards it.

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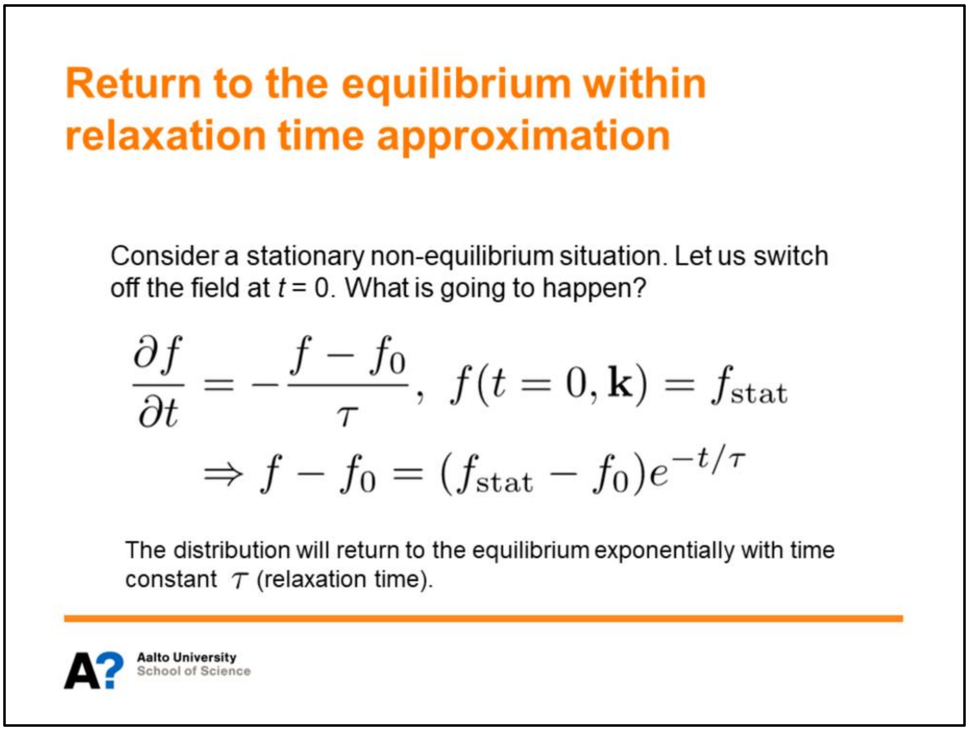
- Perhaps the most important ”physical assumption”, as asked in the homework.
- Only depends on k (no integral over other k’), we can solve BTE for each k separately



Return to the equilibrium within relaxation time approximation

Consider a stationary non-equilibrium situation. Let us switch off the field at $t = 0$. What is going to happen?

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}, \;\; f(t=0,\mathbf{k}) = f_{\mathrm{stat}}$$

$$\Rightarrow f - f_0 = (f_{\mathrm{stat}} - f_0)e^{-t/\tau}$$

The distribution will return to the equilibrium exponentially with time constant τ (relaxation time).

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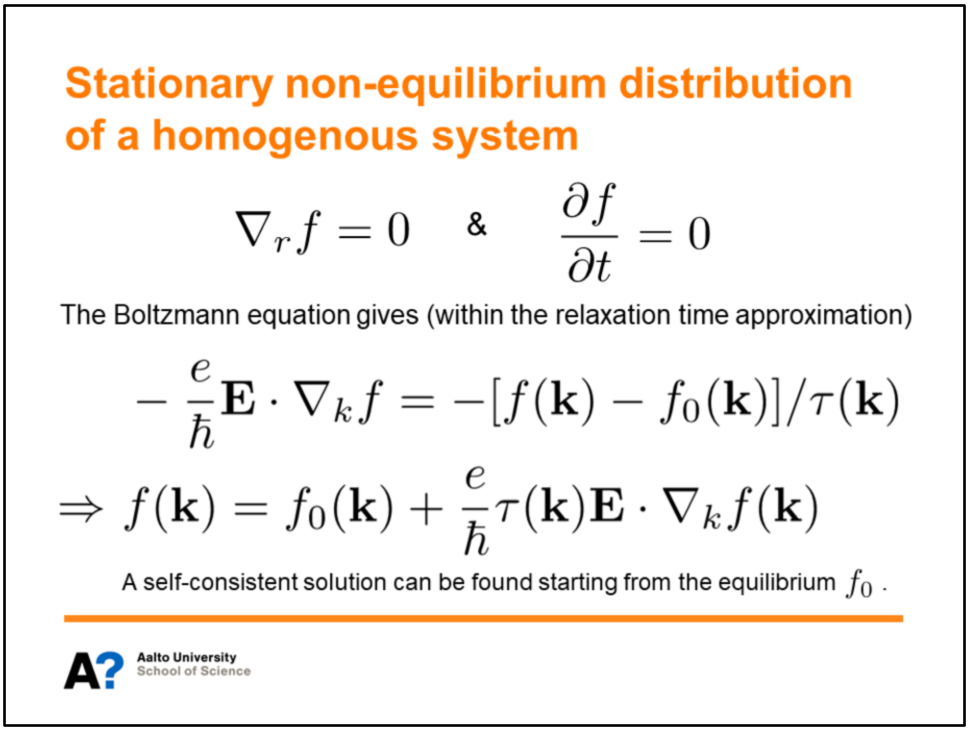

Stationary non-equilibrium distribution of a homogenous system

$$\nabla_r f = 0 \quad \& \quad \frac{\partial f}{\partial t} = 0$$

The Boltzmann equation gives (within the relaxation time approximation)

$$-\frac{e}{\hbar}\mathbf{E}\cdot\nabla_k f = -[f(\mathbf{k}) - f_0(\mathbf{k})]/\tau(\mathbf{k})$$

$$\Rightarrow f(\mathbf{k}) = f_0(\mathbf{k}) + \frac{e}{\hbar}\tau(\mathbf{k})\mathbf{E}\cdot\nabla_k f(\mathbf{k})$$

A self-consistent solution can be found starting from the equilibrium f_0 .

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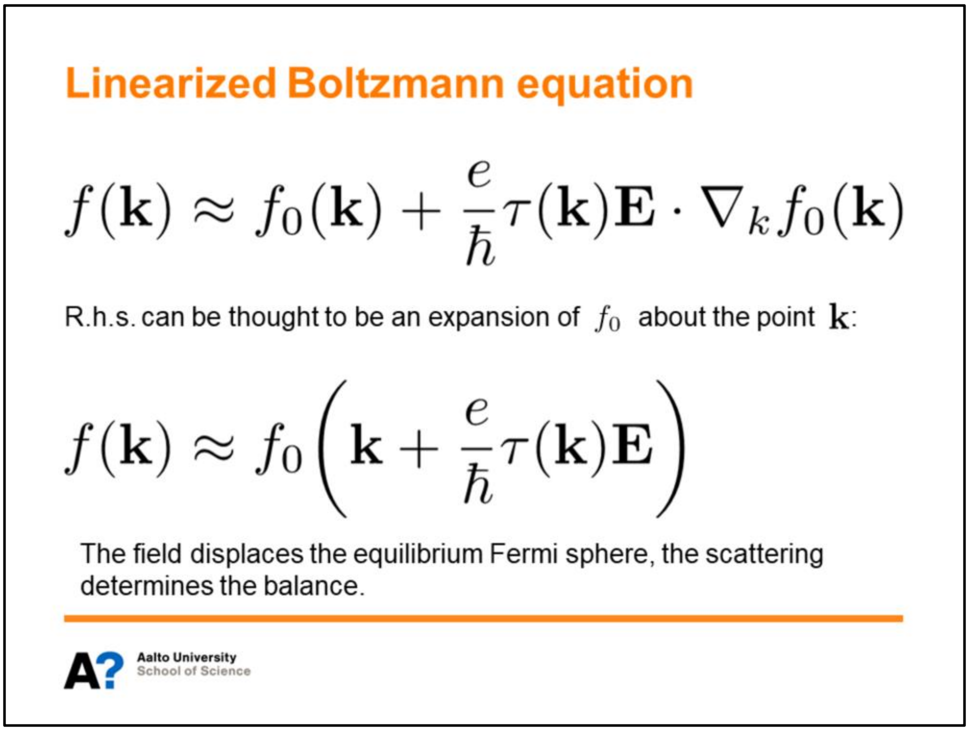
- Similar k-space-non-equilibrium distribution at all r.
- The solution still a bit difficult since f0(k) is a general function, either assume something about f(k) or ”linearize” the equation.



Linearized Boltzmann equation

$$f(\mathbf{k}) \approx f_0(\mathbf{k}) + \frac{e}{\hbar}\tau(\mathbf{k})\mathbf{E}\cdot\nabla_k f_0(\mathbf{k})$$

R.h.s. can be thought to be an expansion of f_0 about the point $\mathbf{k}$:

$$f(\mathbf{k}) \approx f_0\left(\mathbf{k} + \frac{e}{\hbar}\tau(\mathbf{k})\mathbf{E}\right)$$

The field displaces the equilibrium Fermi sphere, the scattering determines the balance.

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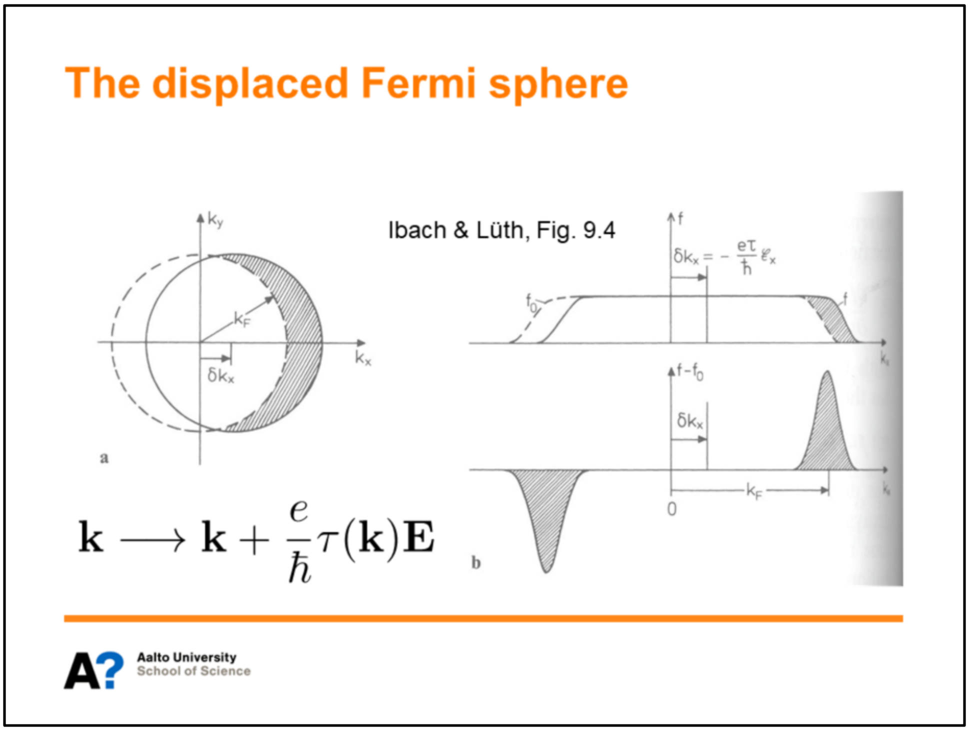
- Linearized means that f(k) is approximated by f0(k) in the second term
- f(k) is then already solved.
- If f(k) is plugged back into non-linearized version, it yields slightly different f(k), etc., but the change should be small (hopefully)
- Although we already knew that Fermi-surface is going to be displaced, now we know how much.



The displaced Fermi sphere

Ibach & Lüth, Fig. 9.4

$$\mathbf{k} \longrightarrow \mathbf{k} + \frac{e}{\hbar}\tau(\mathbf{k})\mathbf{E}$$

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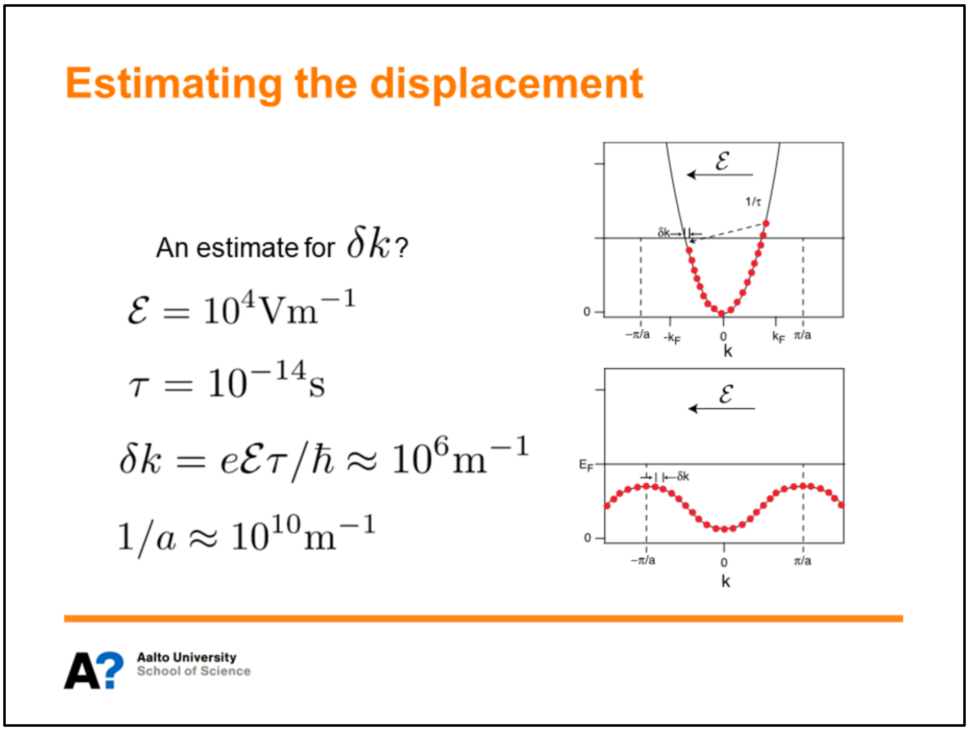
- f(k) is not exactly f0(k) displaced due to the different E(k) which means that the Fermi-Dirac distribution changes differently, i.e., in free electron mode the right side change becomes faster and left side change slower.
- The figure is a bit confusing: df/dk or df0/dk both give the two Gaussians, just displaced a bit in k.
- Both sides contribute to occupation asymmetry, electrons and missing electrons



Estimating the displacement

An estimate for δk?

$$\mathcal{E} = 10^4 \mathrm{Vm}^{-1}$$

$$\tau = 10^{-14} \mathrm{s}$$

$$\delta k = e \mathcal{E} \tau / \hbar \approx 10^6 \mathrm{m}^{-1}$$

$$1/a \approx 10^{10} \mathrm{m}^{-1}$$

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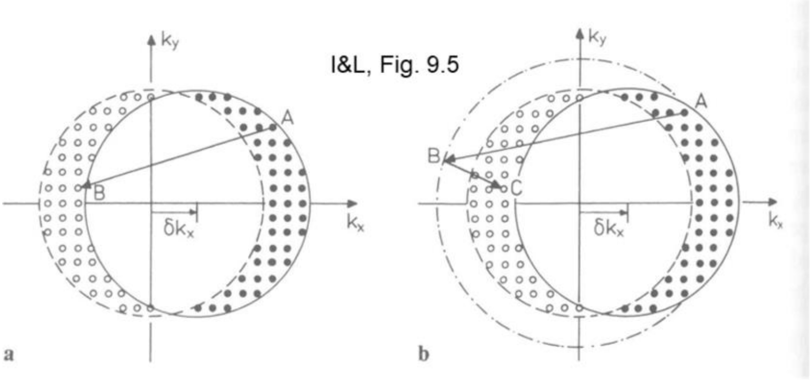
- So we should be safe with our assumption of small Fermi-surface displacement

The role of inelastic scattering



I&L, Fig. 9.5

Only inelastic processes (phonon scattering) can bring the system towards equilibrium. (All scattering causes resistance though!)

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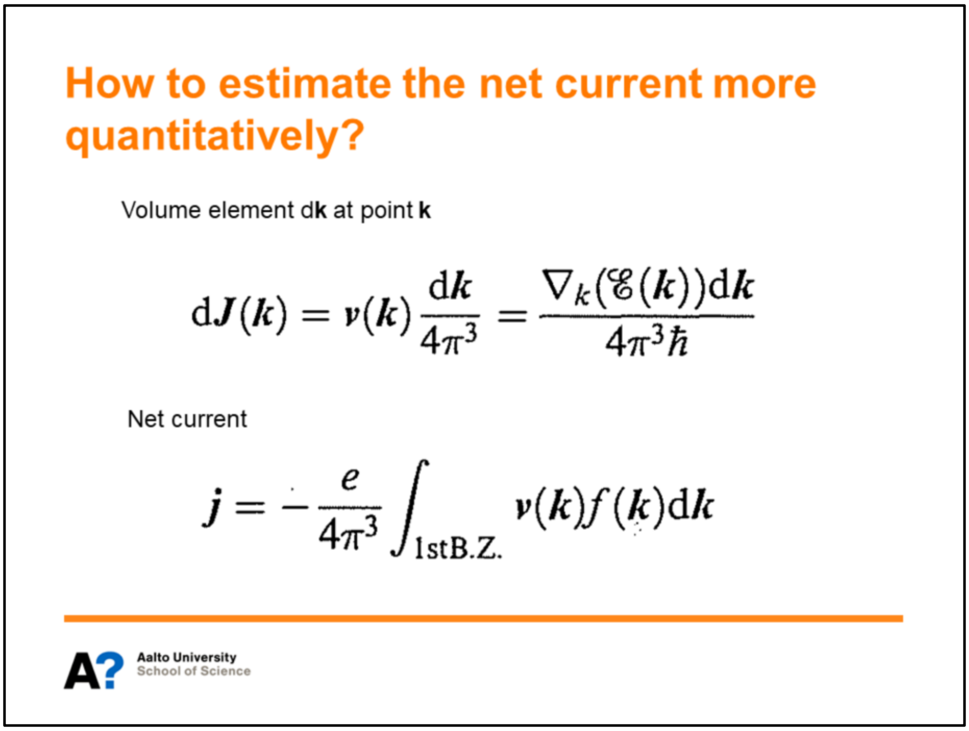

How to estimate the net current more quantitatively?

Volume element d**k** at point **k**

$$\mathrm{d}\boldsymbol{J}(\boldsymbol{k}) = \boldsymbol{v}(\boldsymbol{k})\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3} = \frac{\nabla_k(\mathcal{E}(\boldsymbol{k}))\mathrm{d}\boldsymbol{k}}{4\pi^3\hbar}$$

Net current

$$\boldsymbol{j} = -\frac{e}{4\pi^3}\int_{1\mathrm{stB.Z.}} \boldsymbol{v}(\boldsymbol{k})f(\boldsymbol{k})\mathrm{d}\boldsymbol{k}$$

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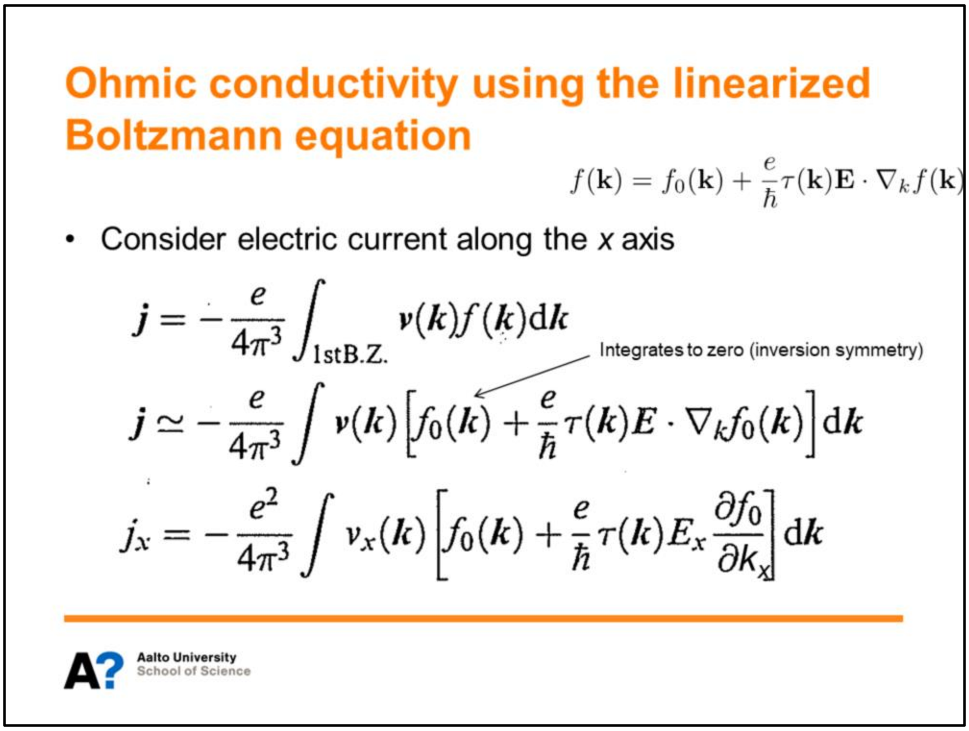
- dk/(8pi^3) counts for the density of allowed electron states. 1/(8pi^3) int_k dk f(k) = number of electrons/unit cell
- This has 4pi^3 since it already accounts for the spin. Alternatively we could have 2 electrons/state included in f(k)



Ohmic conductivity using the linearized Boltzmann equation

$$f(\mathbf{k}) = f_0(\mathbf{k}) + \frac{e}{\hbar}\tau(\mathbf{k})\mathbf{E}\cdot\nabla_k f(\mathbf{k})$$

- Consider electric current along the *x* axis

$$\boldsymbol{j} = -\frac{e}{4\pi^3}\int_{1\text{st B.Z.}} \boldsymbol{v}(\boldsymbol{k})f(\boldsymbol{k})\mathrm{d}\boldsymbol{k}$$

Integrates to zero (inversion symmetry)

$$\boldsymbol{j} \simeq -\frac{e}{4\pi^3}\int \boldsymbol{v}(\boldsymbol{k})\left[f_0(\boldsymbol{k}) + \frac{e}{\hbar}\tau(\boldsymbol{k})\boldsymbol{E}\cdot\nabla_k f_0(\boldsymbol{k})\right]\mathrm{d}\boldsymbol{k}$$

$$j_x = -\frac{e^2}{4\pi^3}\int v_x(\boldsymbol{k})\left[f_0(\boldsymbol{k}) + \frac{e}{\hbar}\tau(\boldsymbol{k})E_x\frac{\partial f_0}{\partial k_x}\right]\mathrm{d}\boldsymbol{k}$$

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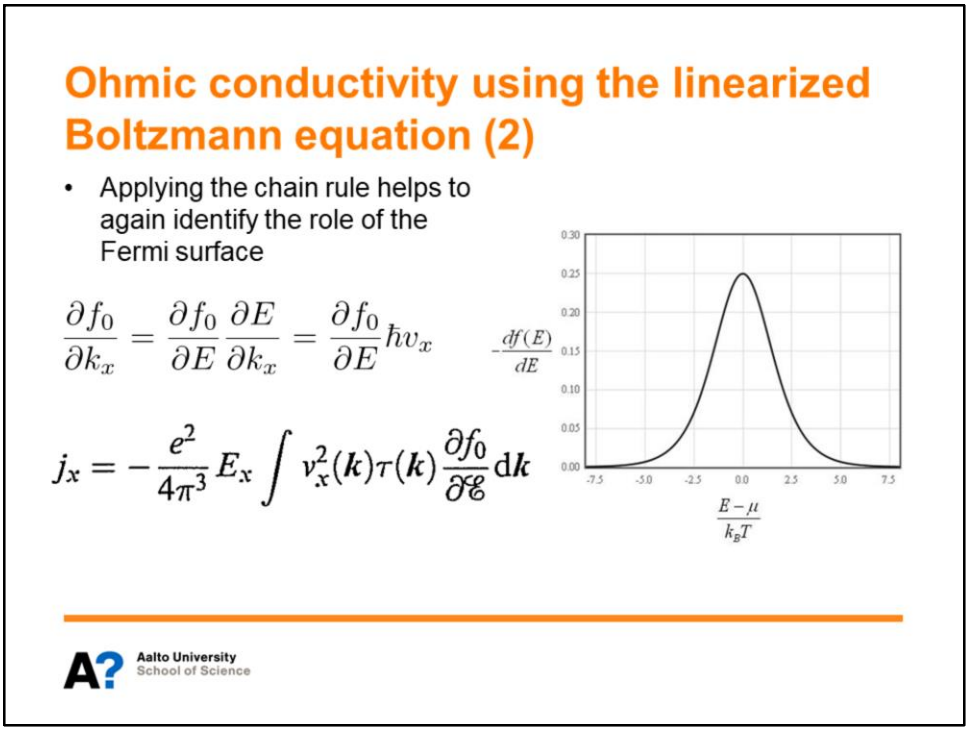
- j is still a vector, jx not
- Error in the book: the last term has df0/dx



Ohmic conductivity using the linearized Boltzmann equation (2)

- Applying the chain rule helps to again identify the role of the Fermi surface

$$\frac{\partial f_0}{\partial k_x} = \frac{\partial f_0}{\partial E}\frac{\partial E}{\partial k_x} = \frac{\partial f_0}{\partial E}\hbar v_x$$

$$j_x = -\frac{e^2}{4\pi^3}E_x \int v_x^2(\boldsymbol{k})\tau(\boldsymbol{k})\frac{\partial f_0}{\partial \mathcal{E}}\,\mathrm{d}\boldsymbol{k}$$

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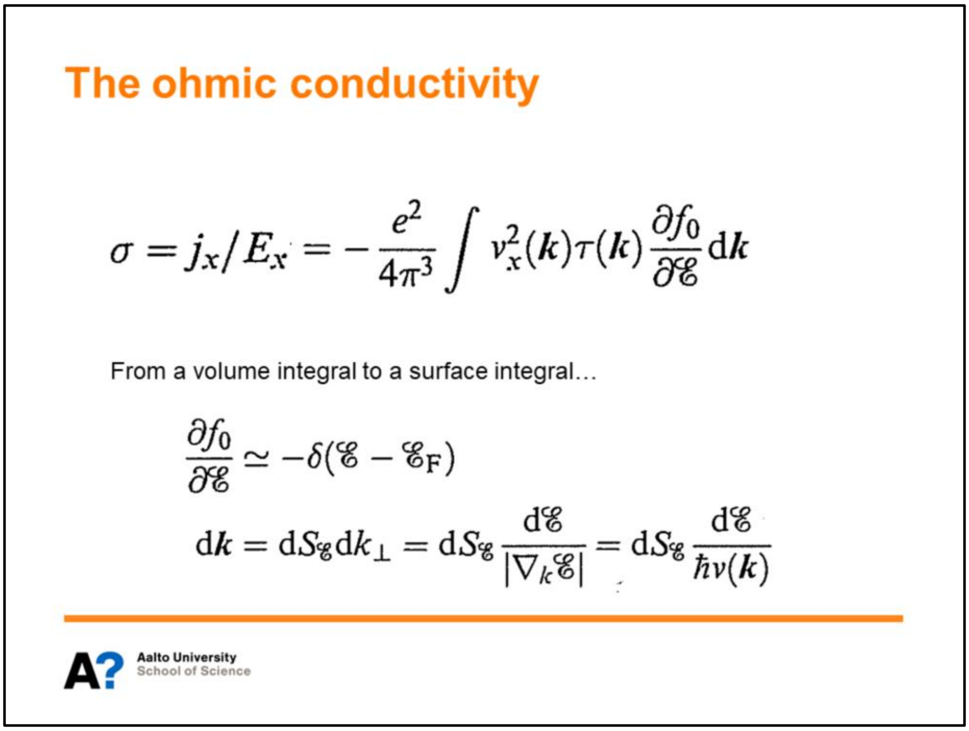
- Still considering only x-component of current density j_x.
- This could be done just as well, perhaps even in easier, without changing to energy variable: df0/dkx should become vx/v*delta(k-kF), where kF is Fermi wavevector…. I haven’t checked if this is true
- But let’s follow the book here.



The ohmic conductivity

$$\sigma = j_x/E_x = -\frac{e^2}{4\pi^3}\int v_x^2(\boldsymbol{k})\tau(\boldsymbol{k})\frac{\partial f_0}{\partial \mathscr{E}}\,\mathrm{d}\boldsymbol{k}$$

From a volume integral to a surface integral…

$$\frac{\partial f_0}{\partial \mathscr{E}} \simeq -\delta(\mathscr{E} - \mathscr{E}_\mathrm{F})$$

$$\mathrm{d}\boldsymbol{k} = \mathrm{d}S_{\mathscr{E}}\,\mathrm{d}k_\perp = \mathrm{d}S_{\mathscr{E}}\frac{\mathrm{d}\mathscr{E}}{|\nabla_k \mathscr{E}|} = \mathrm{d}S_{\mathscr{E}}\frac{\mathrm{d}\mathscr{E}}{\hbar v(\boldsymbol{k})}$$

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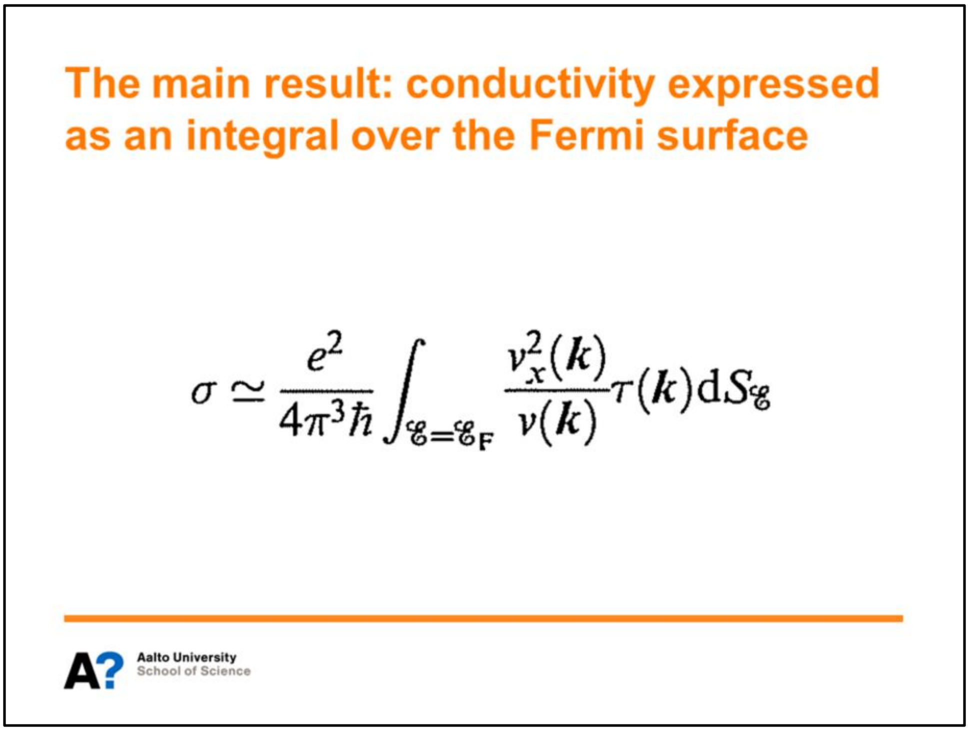
- Using dk/dE = hbar*v
- Calculating sigma_xx component of conductivity tensor (or independent of direction in isotropic materials)



The main result: conductivity expressed as an integral over the Fermi surface

$$\sigma \simeq \frac{e^2}{4\pi^3\hbar}\int_{\mathscr{E}=\mathscr{E}_\mathrm{F}} \frac{v_x^2(\boldsymbol{k})}{v(\boldsymbol{k})}\tau(\boldsymbol{k})\,\mathrm{d}S_{\mathscr{E}}$$

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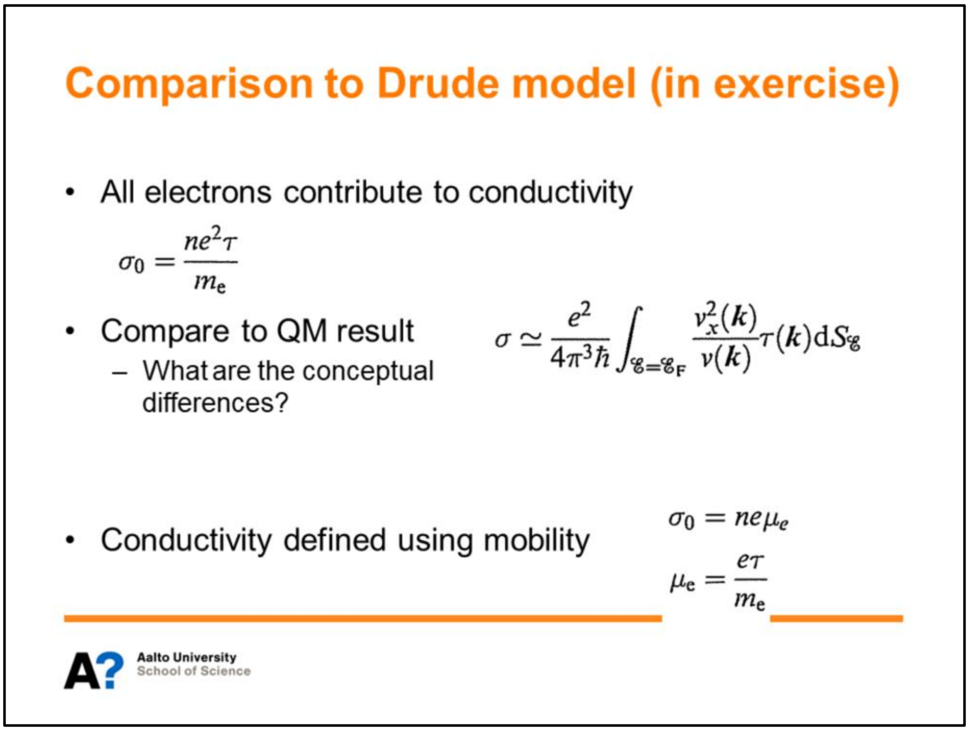
- If tau independent of k, it can be taken out of integral (and starts to look like Drude formula, cf. exercises)



Comparison to Drude model (in exercise)

- All electrons contribute to conductivity

$$\sigma_0 = \frac{ne^2\tau}{m_\mathrm{e}}$$

- Compare to QM result
  - What are the conceptual differences?

$$\sigma \simeq \frac{e^2}{4\pi^3\hbar}\int_{\mathcal{E}=\mathcal{E}_\mathrm{F}}\frac{v_x^2(\boldsymbol{k})}{v(\boldsymbol{k})}\tau(\boldsymbol{k})\,\mathrm{d}S_{\mathcal{E}}$$

- Conductivity defined using mobility

$$\sigma_0 = ne\mu_e$$

$$\mu_\mathrm{e} = \frac{e\tau}{m_\mathrm{e}}$$

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- Same tau? How is it possible if different number of electrons contribute?
  v~kF/m, S~kF^2, n~kF^3

Comparison between metals

- Velocity vs scattering vs Fermi-surface area
- What metals have highest conductivity?
- What have poor conductivity?

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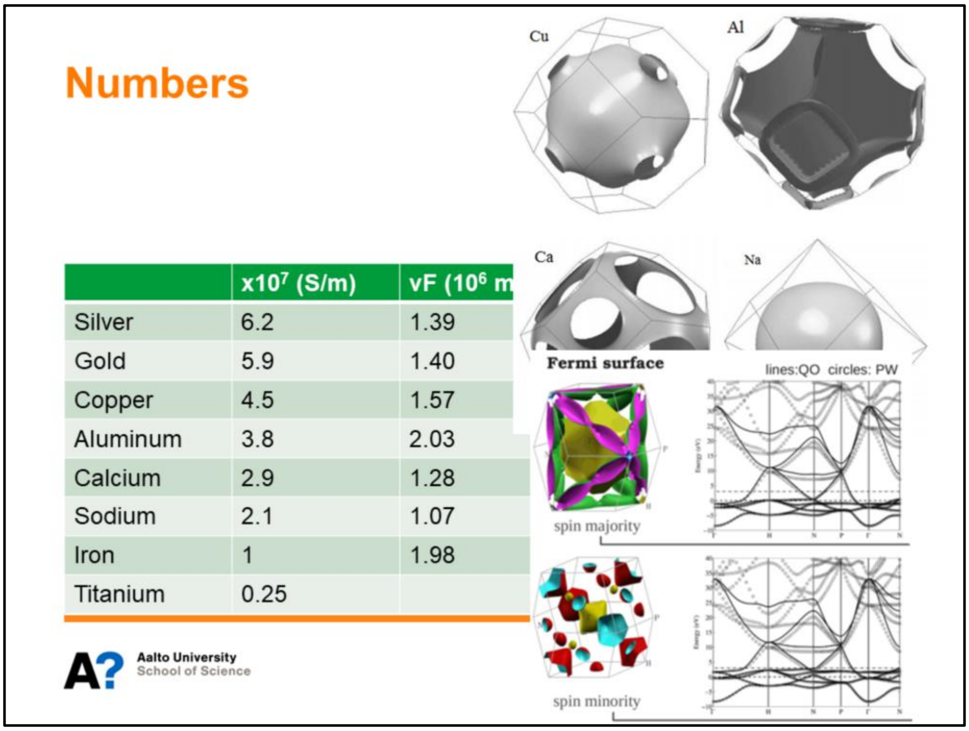

Numbers

	$x10^7$ (S/m)	vF (10^6 m
Silver	6.2	1.39
Gold	5.9	1.40
Copper	4.5	1.57
Aluminum	3.8	2.03
Calcium	2.9	1.28
Sodium	2.1	1.07
Iron	1	1.98
Titanium	0.25	

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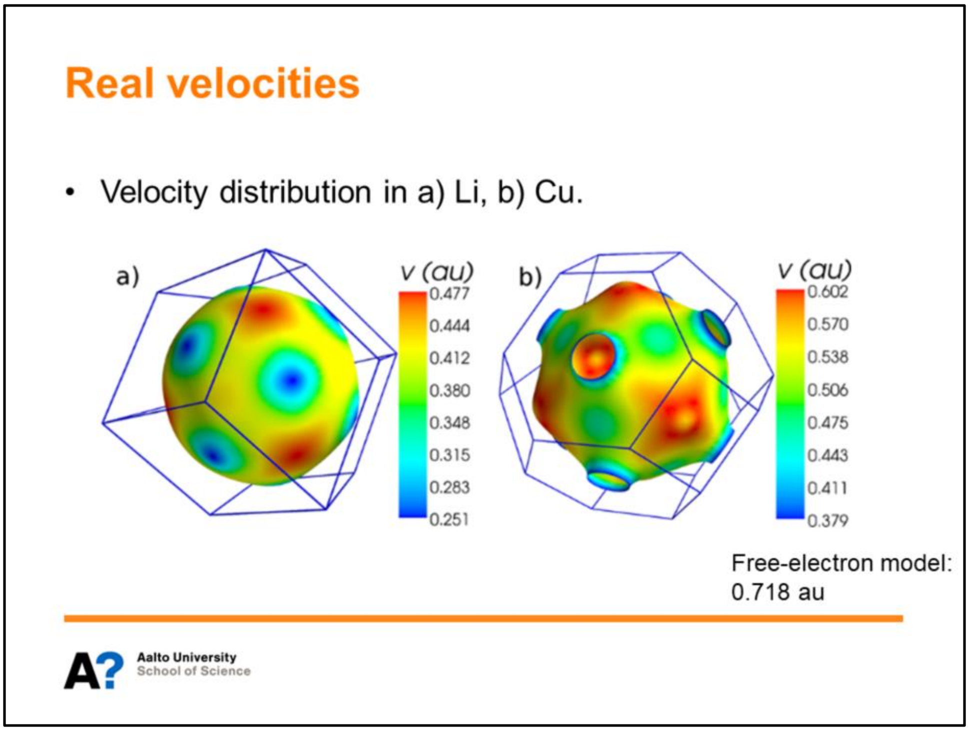
- Small differences overall, within about one order of magnitude
- Fermi velocity evaluated using free electron model. Doesn’t explain anything.
- Difference between noble metals, Ca and maybe Na can be explained with Fermi-surface area. Na has half the volume of BZ, Ca roughly similar but holey, noble metals close to BZ edges.
- Rest of the differences come from scattering (i.e., tau)… or from real velocities



Real velocities

- Velocity distribution in a) Li, b) Cu.

Free-electron model:
0.718 au

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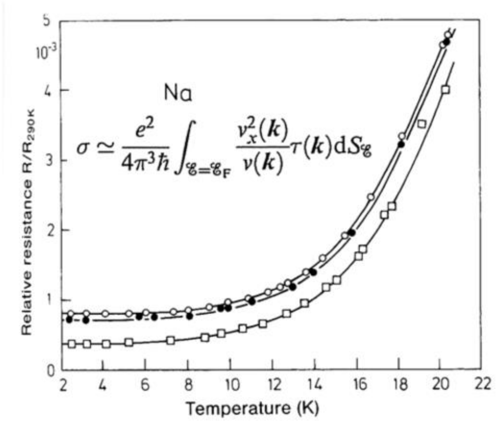
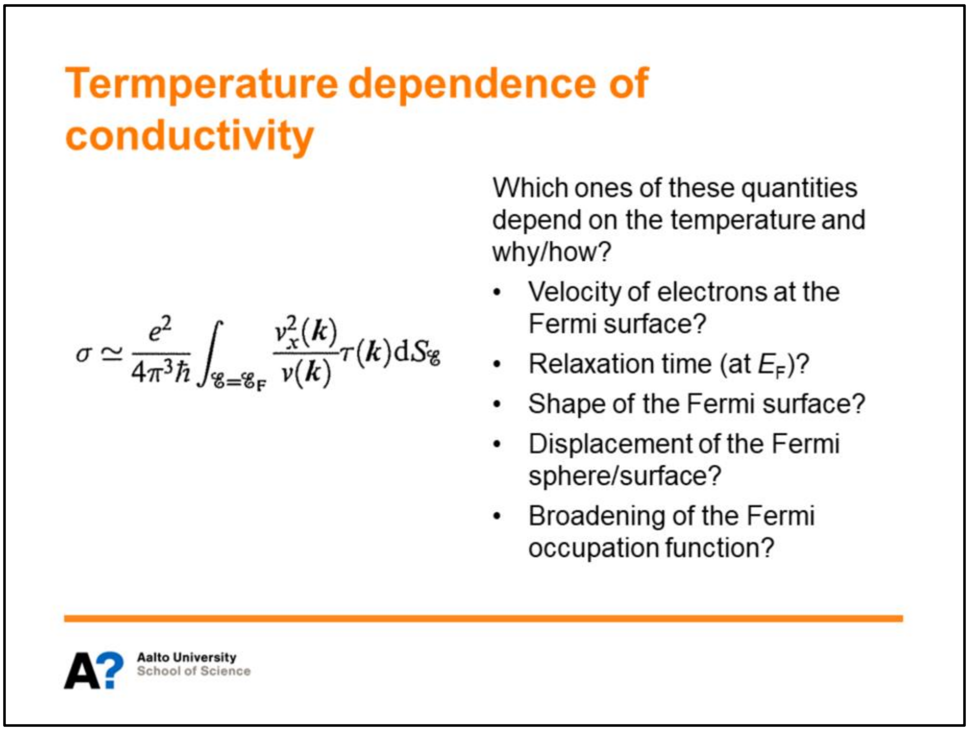
- Roughly factor of 2 variations
- (au) = (2.187*10^6 m/s)

The dependency of resistance/resistivity on the temperature



$$\sigma \simeq \frac{e^2}{4\pi^3\hbar}\int_{\mathscr{E}=\mathscr{E}_F} \frac{v_x^2(\boldsymbol{k})}{v(\boldsymbol{k})}\tau(\boldsymbol{k})\,\mathrm{d}S_{\mathscr{E}}$$



Termperature dependence of conductivity

$$\sigma \simeq \frac{e^2}{4\pi^3\hbar}\int_{\mathscr{E}=\mathscr{E}_\mathrm{F}} \frac{v_x^2(\boldsymbol{k})}{v(\boldsymbol{k})}\tau(\boldsymbol{k})\,\mathrm{d}S_{\mathscr{E}}$$

Which ones of these quantities depend on the temperature and why/how?

- Velocity of electrons at the Fermi surface?
- Relaxation time (at E_F)?
- Shape of the Fermi surface?
- Displacement of the Fermi sphere/surface?
- Broadening of the Fermi occupation function?

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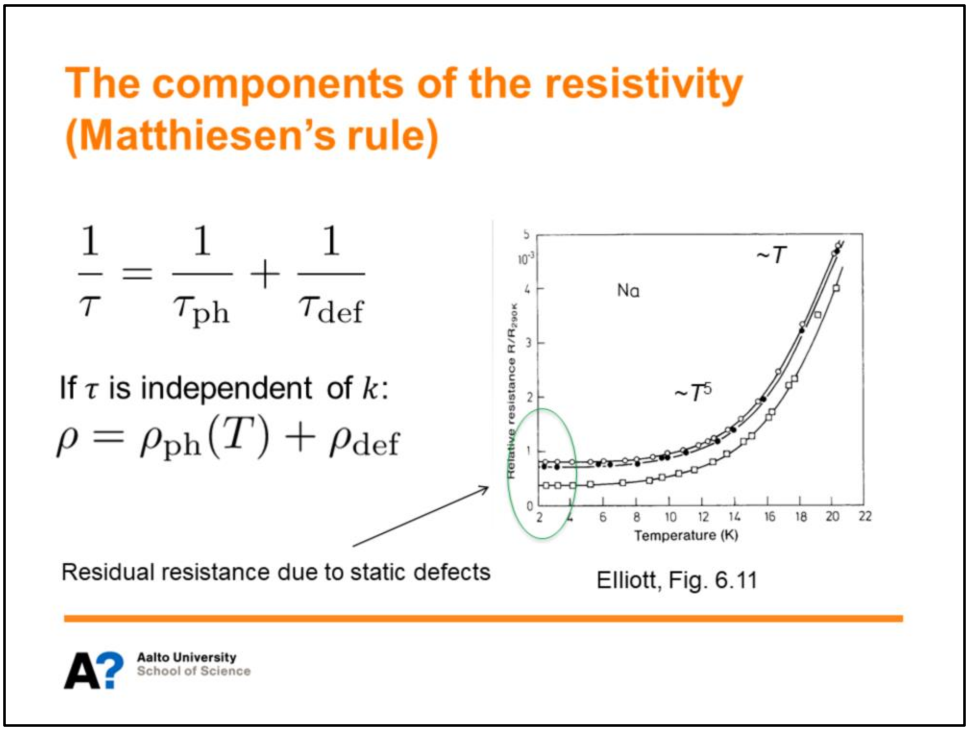
- Related to homework: v_F = hbar*k_F/m, estimate k_F quickly form pi/a, or better from (3*pi*n)^(1/3), where n is valence electron density



The components of the resistivity (Matthiesen's rule)

$$\frac{1}{\tau} = \frac{1}{\tau_{\mathrm{ph}}} + \frac{1}{\tau_{\mathrm{def}}}$$

If τ is independent of k:

$$\rho = \rho_{\mathrm{ph}}(T) + \rho_{\mathrm{def}}$$

Residual resistance due to static defects

Elliott, Fig. 6.11

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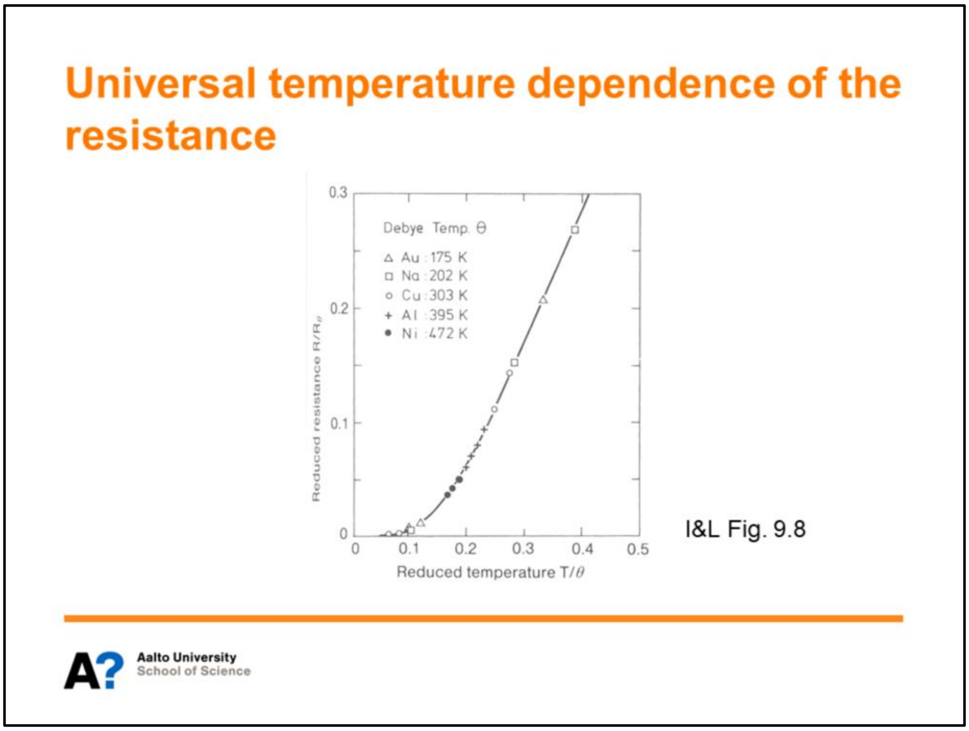
- Rates add up, and thus 1/tau add up. Resistivities add up if tau can be taken out of integral.
- Debye T of Na about 150 K



Universal temperature dependence of the resistance

I&L Fig. 9.8

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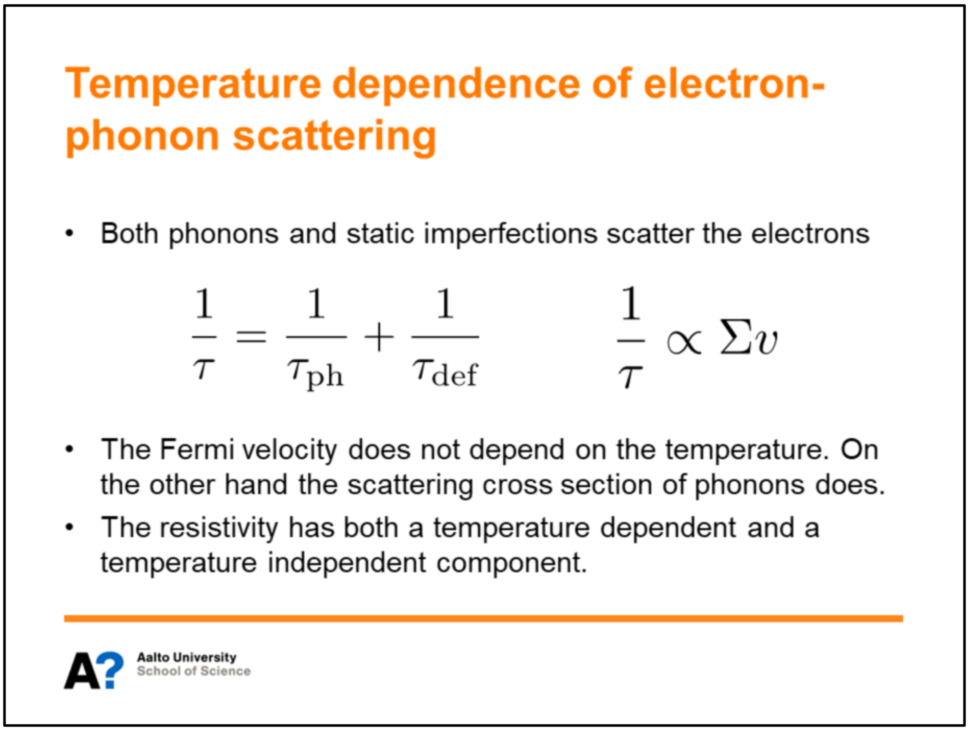
- In very pure materials



Temperature dependence of electron-phonon scattering

- Both phonons and static imperfections scatter the electrons

$$\frac{1}{\tau} = \frac{1}{\tau_{\mathrm{ph}}} + \frac{1}{\tau_{\mathrm{def}}} \qquad \frac{1}{\tau} \propto \Sigma v$$

- The Fermi velocity does not depend on the temperature. On the other hand the scattering cross section of phonons does.
- The resistivity has both a temperature dependent and a temperature independent component.

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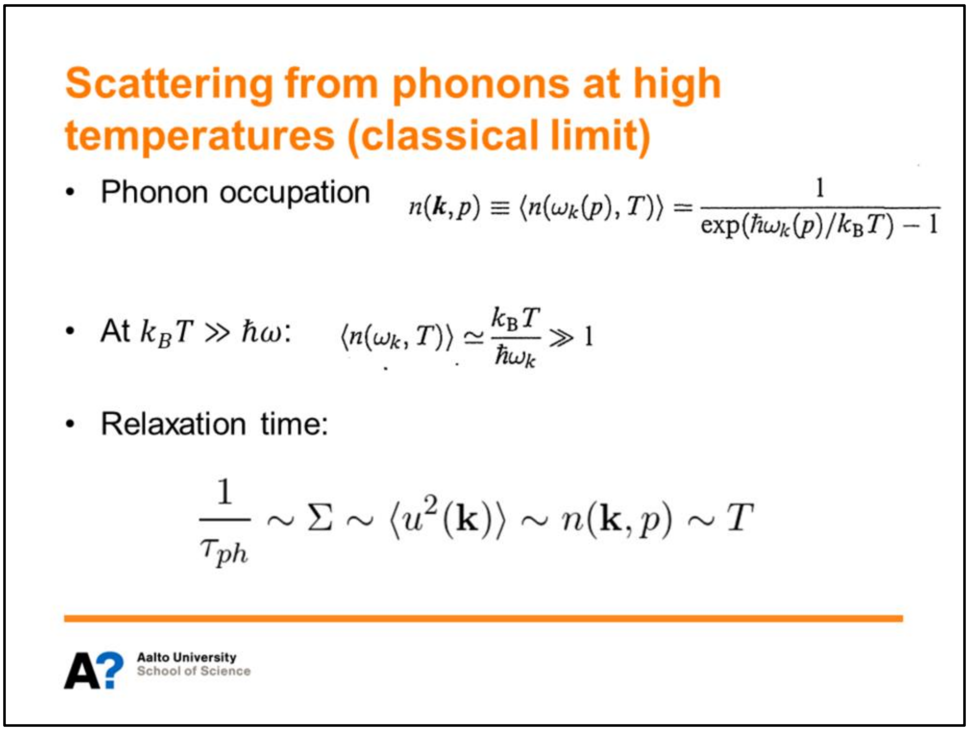
- Scattering cross section of defects does not depend on temperature.
- Off-topic: Scattering from magnetic impurities at low temperatures (the Kondo phenomenon), leading to increased resistance at T->0



Scattering from phonons at high temperatures (classical limit)

- Phonon occupation $n(\boldsymbol{k},p) \equiv \langle n(\omega_k(p),T)\rangle = \frac{1}{\exp(\hbar\omega_k(p)/k_\mathrm{B}T)-1}$
- At $k_B T \gg \hbar\omega$: $\langle n(\omega_k,T)\rangle \simeq \frac{k_\mathrm{B}T}{\hbar\omega_k} \gg 1$
- Relaxation time:

$$\frac{1}{\tau_{ph}} \sim \Sigma \sim \langle u^2(\mathbf{k})\rangle \sim n(\mathbf{k},p) \sim T$$

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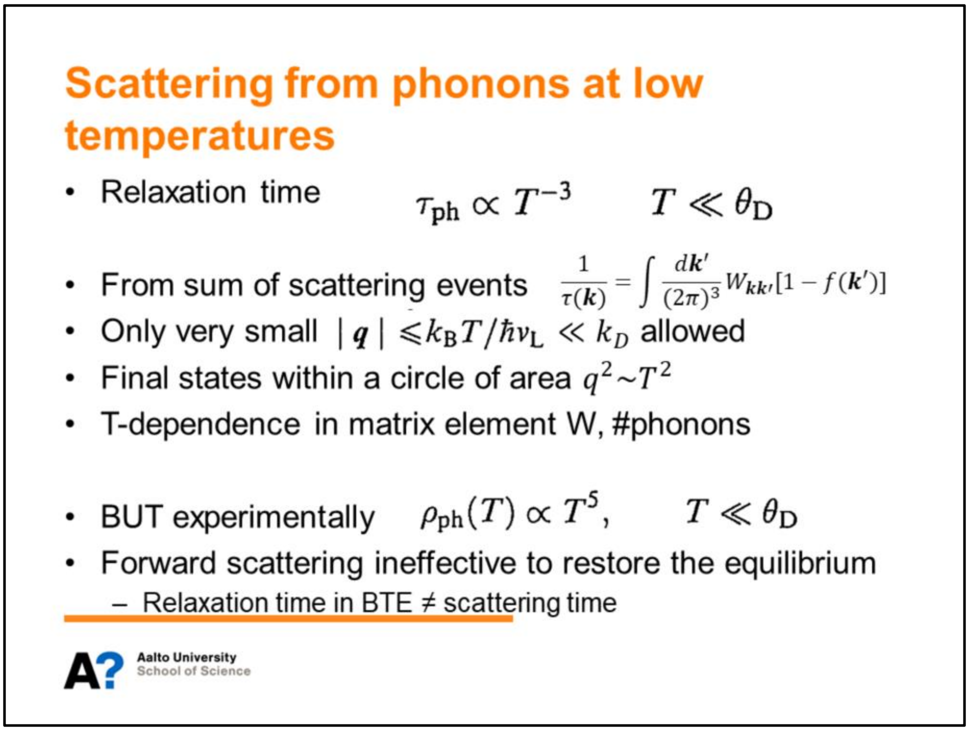
- Crossection is *area*, so it should depend on displacement *squared*
- For more on the displacement <u^2>, see Elliot section 4.2.6.



Scattering from phonons at low temperatures

- Relaxation time $\tau_{\text{ph}} \propto T^{-3}$ $T \ll \theta_{\text{D}}$
- From sum of scattering events $\frac{1}{\tau(\boldsymbol{k})} = \int \frac{d\boldsymbol{k}'}{(2\pi)^3} W_{\boldsymbol{k}\boldsymbol{k}'}[1 - f(\boldsymbol{k}')]$
- Only very small $|\boldsymbol{q}| \lesssim k_{\text{B}}T/\hbar v_{\text{L}} \ll k_D$ allowed
- Final states within a circle of area $q^2 \sim T^2$
- T-dependence in matrix element W, #phonons

- BUT experimentally $\rho_{\text{ph}}(T) \propto T^5$, $T \ll \theta_{\text{D}}$
- Forward scattering ineffective to restore the equilibrium
  - Relaxation time in BTE ≠ scattering time

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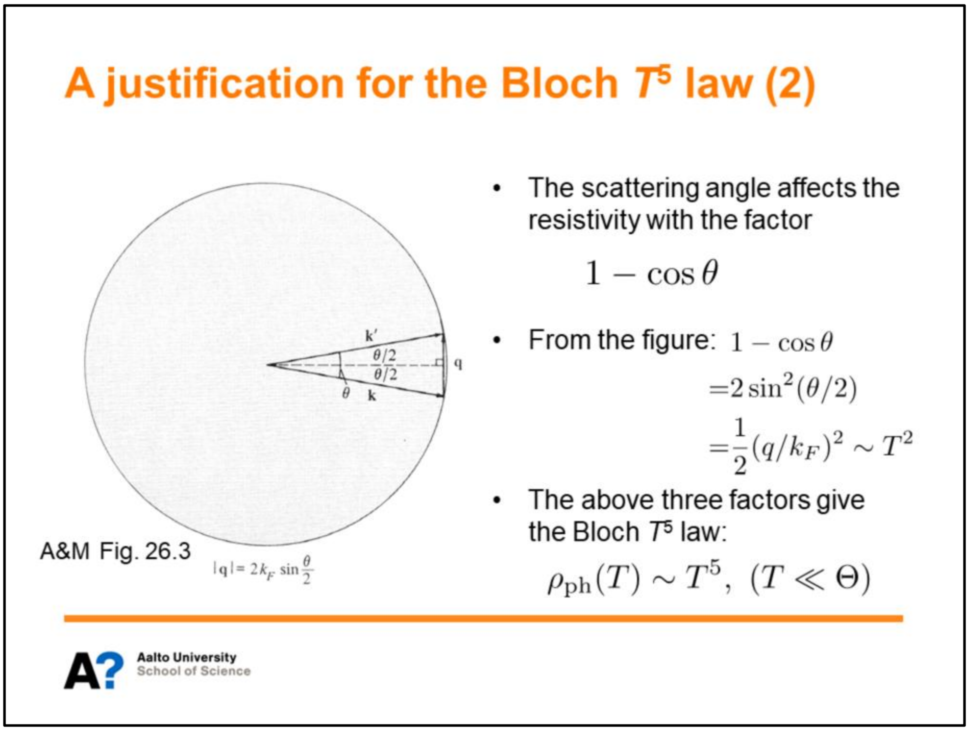
- Normal processes (G=0)
- Relaxation time in BTE is not the same as scattering time



A justification for the Bloch T^5 law (2)

- The scattering angle affects the resistivity with the factor

$$1 - \cos\theta$$

- From the figure: $1 - \cos\theta$

$$= 2\sin^2(\theta/2)$$

$$= \frac{1}{2}(q/k_F)^2 \sim T^2$$

- The above three factors give the Bloch T^5 law:

$$\rho_{\mathrm{ph}}(T) \sim T^5,\ (T \ll \Theta)$$

A&M Fig. 26.3

$|\mathbf{q}| = 2k_F \sin\frac{\theta}{2}$

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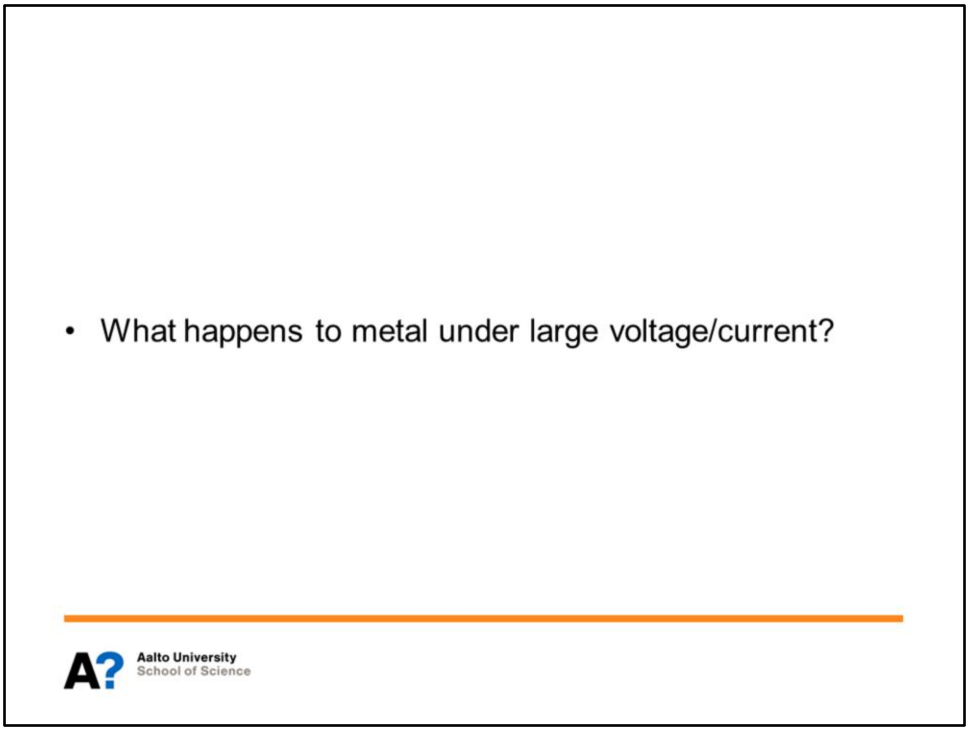
- Length of q at kT: omega = v*q, hbar*omega = k*T = hbar*v*q => q = k*T/(hbar*v), sound velocity of e.g. Na is 3200 m/s => at 10K q= 4e8 1/m, while pi/a = 8e9 1/m (if a=4 Å)



- What happens to metal under large voltage/current?

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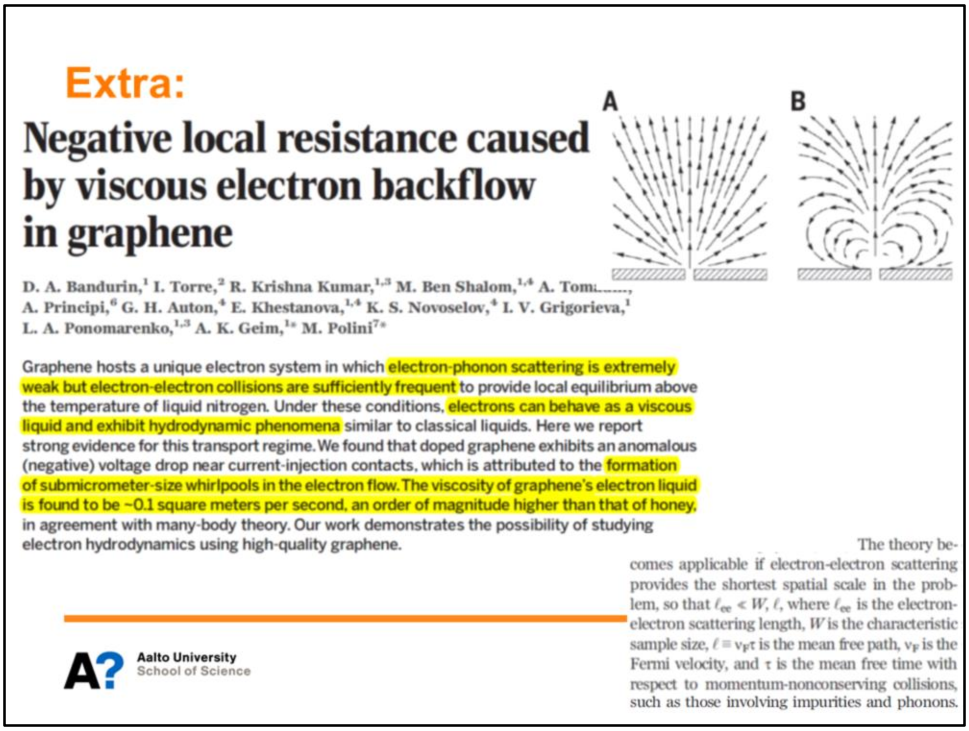
- The energy in inelastic collsions transferred to lattice.
- Most of collisions likely lead to creation of phonons, which in turn increase scattering



Extra:

Negative local resistance caused by viscous electron backflow in graphene

D. A. Bandurin,[1] I. Torre,[2] R. Krishna Kumar,[1,3] M. Ben Shalom,[1,4] A. Tom,
A. Principi,[6] G. H. Auton,[4] E. Khestanova,[1,4] K. S. Novoselov,[4] I. V. Grigorieva,[1]
L. A. Ponomarenko,[1,3] A. K. Geim,[1*] M. Polini[7*]

Graphene hosts a unique electron system in which electron-phonon scattering is extremely weak but electron-electron collisions are sufficiently frequent to provide local equilibrium above the temperature of liquid nitrogen. Under these conditions, electrons can behave as a viscous liquid and exhibit hydrodynamic phenomena similar to classical liquids. Here we report strong evidence for this transport regime. We found that doped graphene exhibits an anomalous (negative) voltage drop near current-injection contacts, which is attributed to the formation of submicrometer-size whirlpools in the electron flow. The viscosity of graphene's electron liquid is found to be ~0.1 square meters per second, an order of magnitude higher than that of honey, in agreement with many-body theory. Our work demonstrates the possibility of studying electron hydrodynamics using high-quality graphene.

The theory becomes applicable if electron-electron scattering provides the shortest spatial scale in the problem, so that $\ell_{ee} < W, \ell$, where ℓ_{ee} is the electron-electron scattering length, W is the characteristic sample size, $\ell \equiv v_F\tau$ is the mean free path, v_F is the Fermi velocity, and τ is the mean free time with respect to momentum-nonconserving collisions, such as those involving impurities and phonons.

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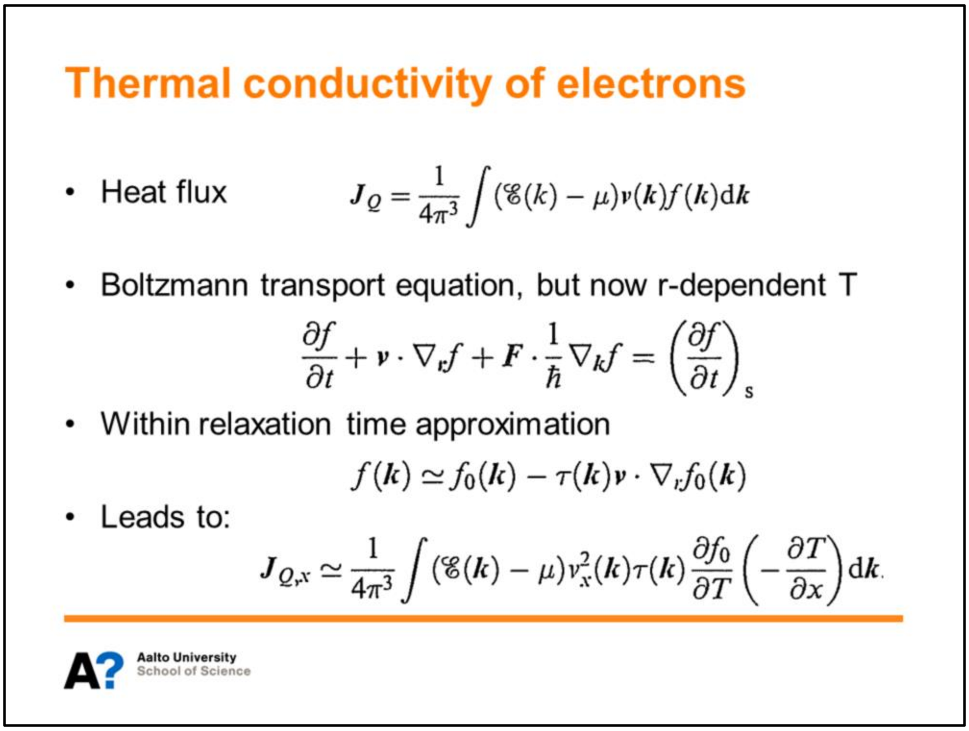
- Science 351, 1055 (2016)



Thermal conductivity of electrons

- Heat flux $$J_Q = \frac{1}{4\pi^3}\int (\mathscr{E}(k) - \mu)\boldsymbol{v}(\boldsymbol{k})f(\boldsymbol{k})\mathrm{d}\boldsymbol{k}$$
- Boltzmann transport equation, but now r-dependent T
$$\frac{\partial f}{\partial t} + \boldsymbol{v}\cdot\nabla_r f + \boldsymbol{F}\cdot\frac{1}{\hbar}\nabla_k f = \left(\frac{\partial f}{\partial t}\right)_s$$
- Within relaxation time approximation
$$f(\boldsymbol{k}) \simeq f_0(\boldsymbol{k}) - \tau(\boldsymbol{k})\boldsymbol{v}\cdot\nabla_r f_0(\boldsymbol{k})$$
- Leads to:
$$J_{Q,x} \simeq \frac{1}{4\pi^3}\int (\mathscr{E}(\boldsymbol{k}) - \mu)v_x^2(\boldsymbol{k})\tau(\boldsymbol{k})\frac{\partial f_0}{\partial T}\left(-\frac{\partial T}{\partial x}\right)\mathrm{d}\boldsymbol{k}.$$

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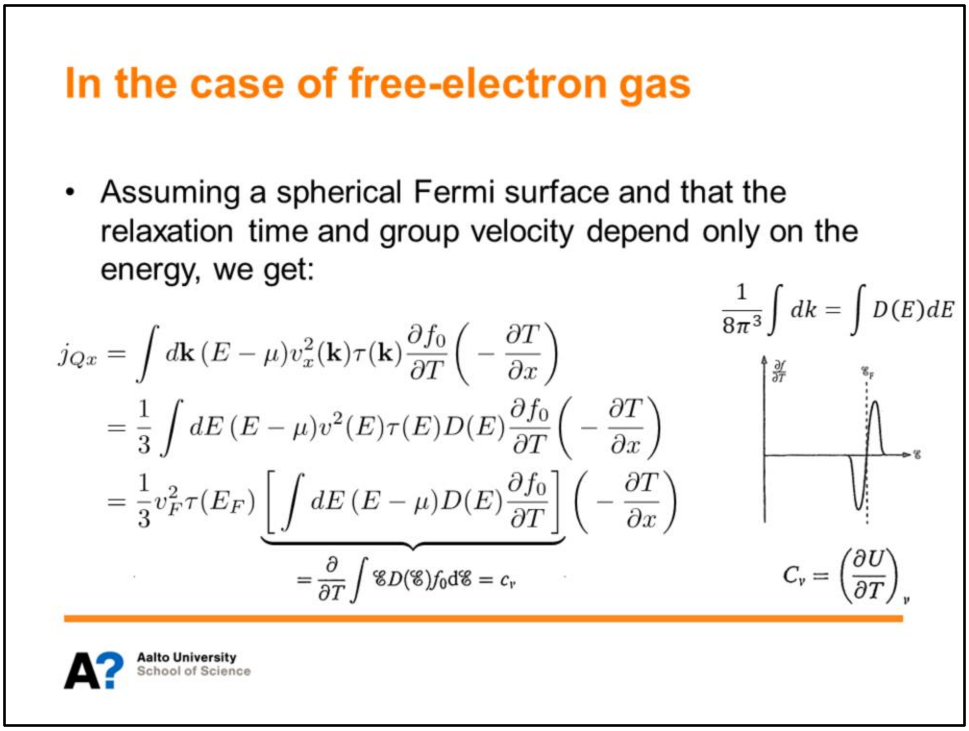
- F just some generic force affecting k, here F=0
- Finally, in the form suitable for extracting thermal conductivity…
- Drawing 4.2, electron and heat fluxes between two areas with different Fermi-Dirac distribution



In the case of free-electron gas

- Assuming a spherical Fermi surface and that the relaxation time and group velocity depend only on the energy, we get:

$$\frac{1}{8\pi^3}\int dk = \int D(E)dE$$

$$\begin{aligned} j_{Qx} &= \int d\mathbf{k}\,(E-\mu)v_x^2(\mathbf{k})\tau(\mathbf{k})\frac{\partial f_0}{\partial T}\left(-\frac{\partial T}{\partial x}\right) \\ &= \frac{1}{3}\int dE\,(E-\mu)v^2(E)\tau(E)D(E)\frac{\partial f_0}{\partial T}\left(-\frac{\partial T}{\partial x}\right) \\ &= \frac{1}{3}v_F^2\tau(E_F)\underbrace{\left[\int dE\,(E-\mu)D(E)\frac{\partial f_0}{\partial T}\right]}_{=\frac{\partial}{\partial T}\int \mathscr{E}D(\mathscr{E})f_0 d\mathscr{E} = c_v}\left(-\frac{\partial T}{\partial x}\right) \end{aligned}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

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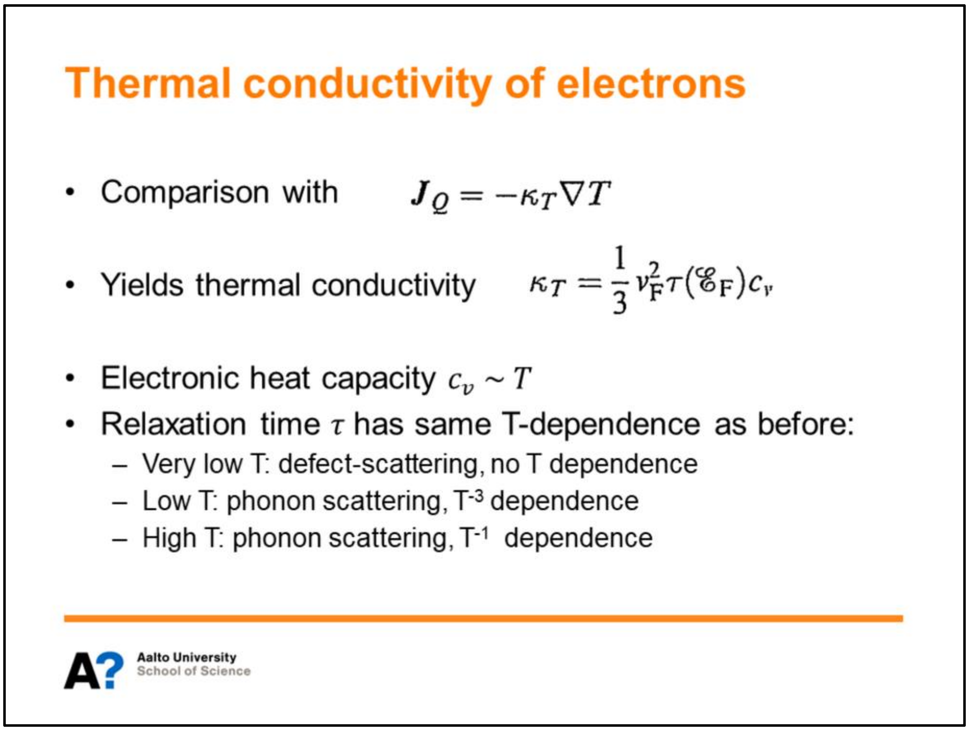
- Integral over 1st Brillouin zone
- f0 = f0(k)
- Change from dk to D(E)dE works only if symmetric distribution f(k)
- For discussion of electronic heat capacity of free electron gas, see Elliott section 5.1.3.1



Thermal conductivity of electrons

- Comparison with $J_Q = -\kappa_T \nabla T$
- Yields thermal conductivity $\kappa_T = \frac{1}{3} v_F^2 \tau(\mathscr{E}_F) c_v$
- Electronic heat capacity $c_v \sim T$
- Relaxation time τ has same T-dependence as before:
  - Very low T: defect-scattering, no T dependence
  - Low T: phonon scattering, T^{-3} dependence
  - High T: phonon scattering, T^{-1} dependence

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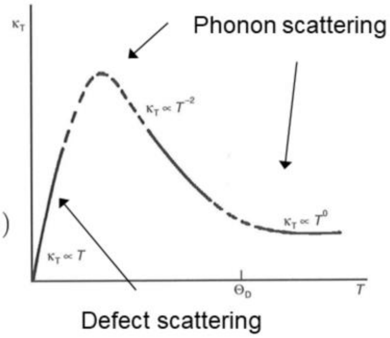
- Energy of electrons in Cv, describes how the energy of electrons changes as a function of T.
- Why not T^-5? Here, to restore f0, scattering needs to change energy, but not k. In electrical conductivity, to restore f0, the electrons needed to be taken to other side of the Fermi-surface (opposite k).
- Remember that both the extra energy in electrons and energy of phonons is ~kT
- Relaxation should still be different from scattering time. E.g., defect-scattering is elastic and thus it can’t lose energy.
- Somewhat surprisingly, it doesn’t seem to affect the T-dependence…

Temperature dependence of the thermal conductivity of electrons

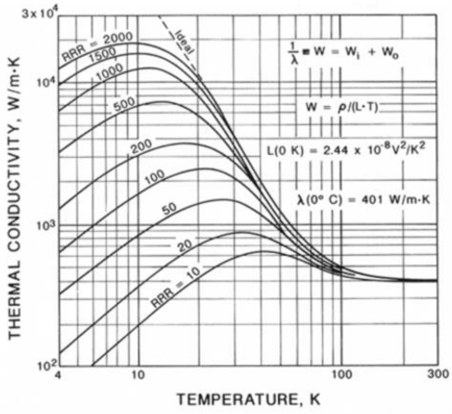
$$\kappa_T = \frac{1}{3} v_F^2 \tau(\mathscr{E}_F) c_v$$

- $c_v \propto T$
- Temperature dependence of $\tau(E_F)$ depends on the scattering mechanism

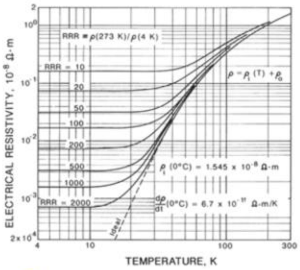


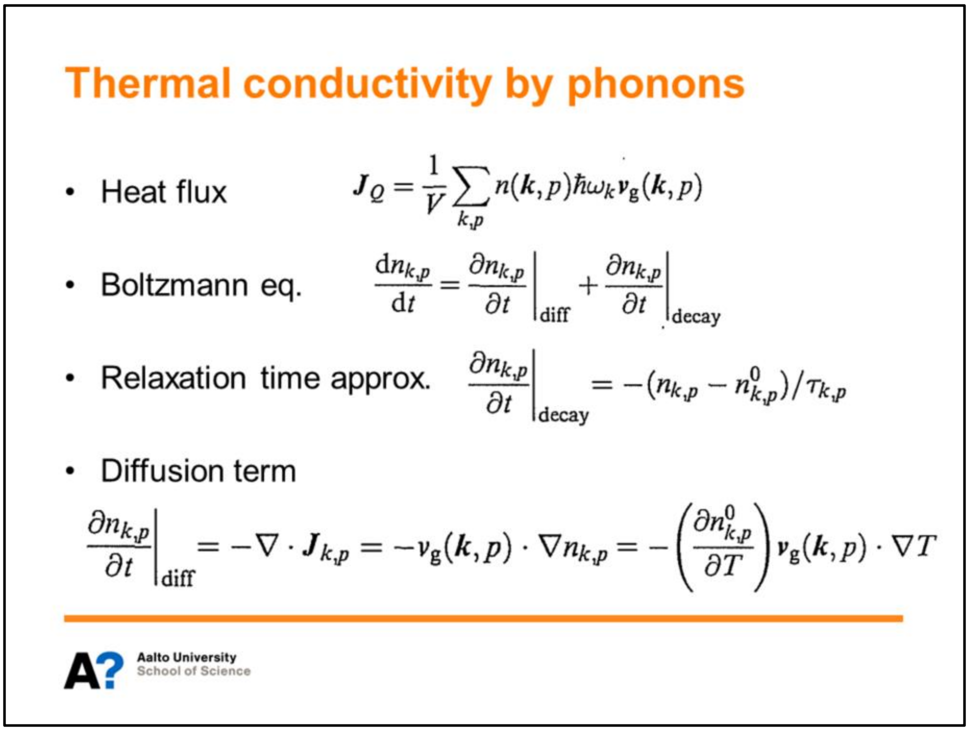
Thermal conductivity of copper

- RRR (residual resistance ratio) describes the purity of material $\mathrm{RRR} = \rho(273K)/\rho(4K)$



- Resistivity for comparison:





Thermal conductivity by phonons

- Heat flux $$\boldsymbol{J}_Q = \frac{1}{V}\sum_{k,p} n(\boldsymbol{k},p)\hbar\omega_k \boldsymbol{v}_\mathrm{g}(\boldsymbol{k},p)$$
- Boltzmann eq. $$\frac{\mathrm{d}n_{k,p}}{\mathrm{d}t} = \left.\frac{\partial n_{k,p}}{\partial t}\right|_\mathrm{diff} + \left.\frac{\partial n_{k,p}}{\partial t}\right|_\mathrm{decay}$$
- Relaxation time approx. $$\left.\frac{\partial n_{k,p}}{\partial t}\right|_\mathrm{decay} = -(n_{k,p} - n^0_{k,p})/\tau_{k,p}$$
- Diffusion term

$$\left.\frac{\partial n_{k,p}}{\partial t}\right|_\mathrm{diff} = -\nabla \cdot \boldsymbol{J}_{k,p} = -\boldsymbol{v}_\mathrm{g}(\boldsymbol{k},p)\cdot\nabla n_{k,p} = -\left(\frac{\partial n^0_{k,p}}{\partial T}\right)\boldsymbol{v}_\mathrm{g}(\boldsymbol{k},p)\cdot\nabla T$$

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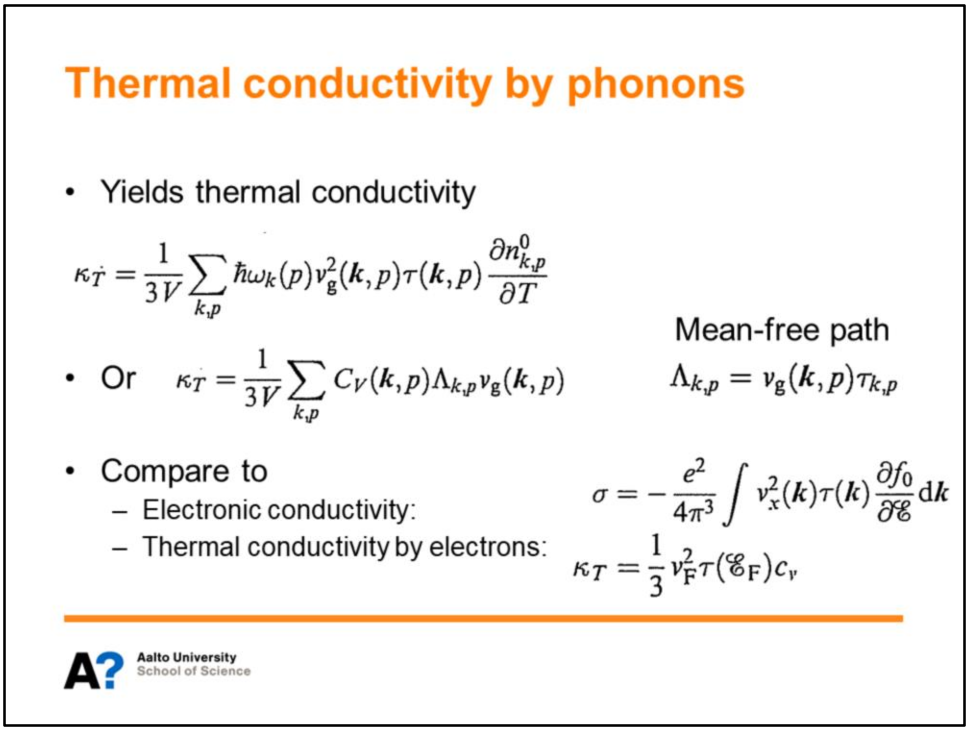
- Section 4.6.2.2 in Elliott
- Distribution to consider is the number of phonons n(k,p)



Thermal conductivity by phonons

- Yields thermal conductivity

$$\kappa_T = \frac{1}{3V}\sum_{k,p}\hbar\omega_k(p)v_{\mathrm{g}}^2(\boldsymbol{k},p)\tau(\boldsymbol{k},p)\frac{\partial n^0_{k,p}}{\partial T}$$

Mean-free path

- Or $\kappa_T = \frac{1}{3V}\sum_{k,p} C_V(\boldsymbol{k},p)\Lambda_{k,p}v_{\mathrm{g}}(\boldsymbol{k},p)$

$$\Lambda_{k,p} = v_{\mathrm{g}}(\boldsymbol{k},p)\tau_{k,p}$$

- Compare to
  - Electronic conductivity: $\sigma = -\frac{e^2}{4\pi^3}\int v_x^2(\boldsymbol{k})\tau(\boldsymbol{k})\frac{\partial f_0}{\partial \mathscr{E}}\mathrm{d}\boldsymbol{k}$
  - Thermal conductivity by electrons: $\kappa_T = \frac{1}{3}v_{\mathrm{F}}^2\tau(\mathscr{E}_{\mathrm{F}})c_v$

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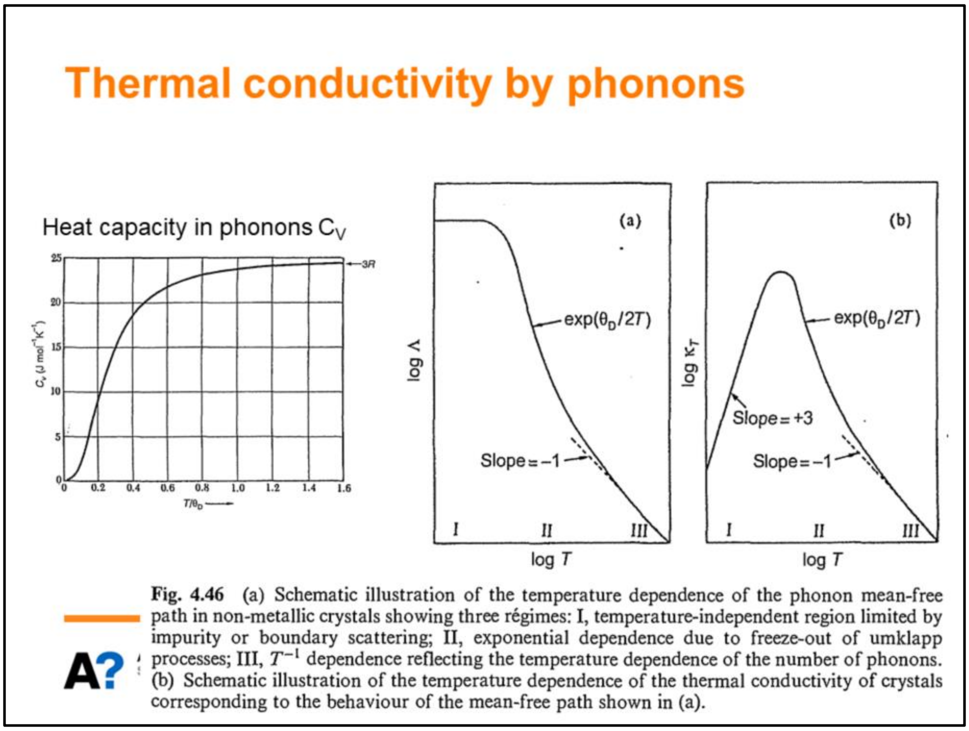
- Section 4.6.2.2 in Elliott
- With dn/dT we can’t do similar tricks around Fermi-level as with df/dT

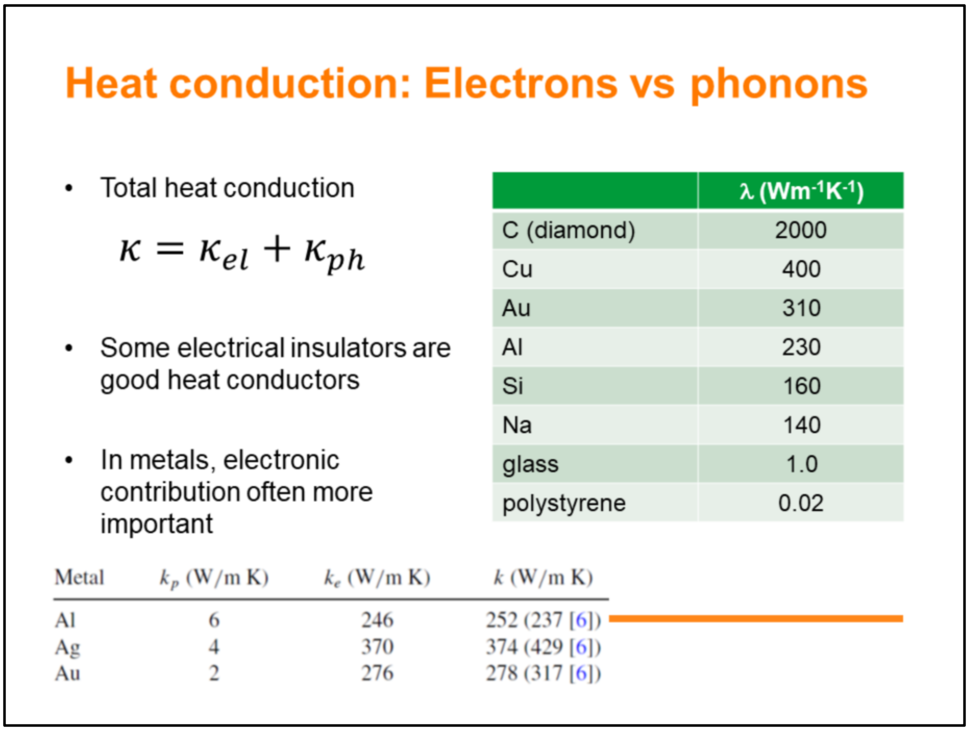


Thermal conductivity by phonons

Heat capacity in phonons C_V

Fig. 4.46 (a) Schematic illustration of the temperature dependence of the phonon mean-free path in non-metallic crystals showing three régimes: I, temperature-independent region limited by impurity or boundary scattering; II, exponential dependence due to freeze-out of umklapp processes; III, T^{-1} dependence reflecting the temperature dependence of the number of phonons. (b) Schematic illustration of the temperature dependence of the thermal conductivity of crystals corresponding to the behaviour of the mean-free path shown in (a).

- Non-metallic crystal, electronic contribution can be ignored
- At high T, tau similar to phonon number ~ 1/T and C_V = constant
- C_v at low T (T^3 dependence) can be obtained even with Debye model.
- Additional processes, umklapp and boundary scattering (due to very long mean free path)



Heat conduction: Electrons vs phonons

- Total heat conduction

$$\kappa = \kappa_{el} + \kappa_{ph}$$

- Some electrical insulators are good heat conductors
- In metals, electronic contribution often more important

	λ (Wm^{-1}K^{-1})
C (diamond)	2000
Cu	400
Au	310
Al	230
Si	160
Na	140
glass	1.0
polystyrene	0.02

Metal	k_p (W/m K)	k_e (W/m K)	k (W/m K)
Al	6	246	252 (237 [6])
Ag	4	370	374 (429 [6])
Au	2	276	278 (317 [6])

- Calculated comparison, experimental in parentheses, from Jain&McGaughey, Phys. Rev. B 93, 081206(R) (2016)

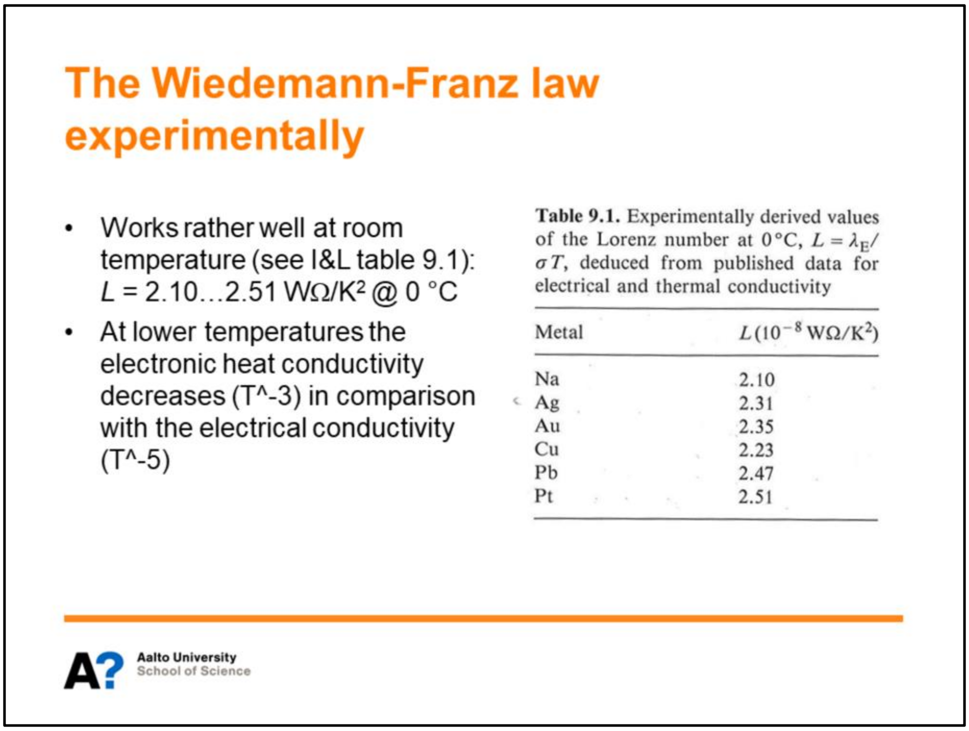
How are the heat and electric currents due to electrons related?

- Same particle flux, same quantities involved

$$\sigma \simeq \frac{e^2}{4\pi^3\hbar}\int_{\mathscr{E}=\mathscr{E}_\mathrm{F}} \frac{v_x^2(\boldsymbol{k})}{v(\boldsymbol{k})}\tau(\boldsymbol{k})\,\mathrm{d}S_{\mathscr{E}} \qquad \kappa_T = \frac{1}{3}v_\mathrm{F}^2\tau(\mathscr{E}_\mathrm{F})c_v$$

- Wiedemann-Franz law $\kappa_T/\sigma T = L$
- From free-electron gas: $L = \dfrac{\kappa_T}{\sigma_0 T} = \dfrac{\pi^2}{3}\left(\dfrac{k_\mathrm{B}}{e}\right)^2$

Lorenz number: $L = 2.45 \times 10^{-8}\,\mathrm{W\,\Omega\,K^{-2}}$



The Wiedemann-Franz law experimentally

- Works rather well at room temperature (see I&L table 9.1): $L = 2.10\ldots2.51\ \mathrm{W\Omega/K^2}$ @ 0 °C
- At lower temperatures the electronic heat conductivity decreases (T^-3) in comparison with the electrical conductivity (T^-5)

Table 9.1. Experimentally derived values of the Lorenz number at 0 °C, $L = \lambda_E/\sigma T$, deduced from published data for electrical and thermal conductivity

Metal	$L\,(10^{-8}\ \mathrm{W\Omega/K^2})$
Na	2.10
Ag	2.31
Au	2.35
Cu	2.23
Pb	2.47
Pt	2.51

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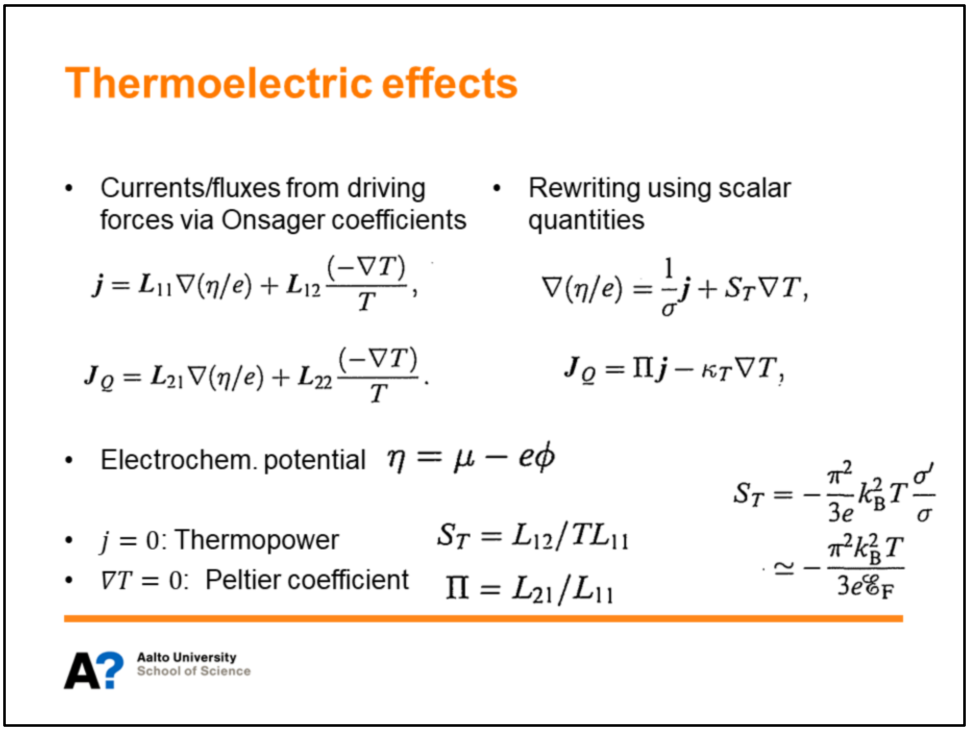
- At low T, there was the extra T^-2 factor in T-dependence of electrical conductivity due to the small angle (small k) scattering is ineffective at restoring equilibrium.
- And obviously valid only in cases where heat conductivity dominated by electronic contribution



Thermoelectric effects

- Currents/fluxes from driving forces via Onsager coefficients

$$\boldsymbol{j} = L_{11}\nabla(\eta/e) + L_{12}\frac{(-\nabla T)}{T},$$

$$\boldsymbol{J}_Q = L_{21}\nabla(\eta/e) + L_{22}\frac{(-\nabla T)}{T}.$$

- Rewriting using scalar quantities

$$\nabla(\eta/e) = \frac{1}{\sigma}\boldsymbol{j} + S_T\nabla T,$$

$$\boldsymbol{J}_Q = \Pi\boldsymbol{j} - \kappa_T\nabla T,$$

- Electrochem. potential $\eta = \mu - e\phi$
- $j = 0$: Thermopower $S_T = L_{12}/TL_{11}$
- $\nabla T = 0$: Peltier coefficient $\Pi = L_{21}/L_{11}$

$$S_T = -\frac{\pi^2}{3e}k_B^2 T\frac{\sigma'}{\sigma} \simeq -\frac{\pi^2 k_B^2 T}{3e\mathscr{E}_F}$$

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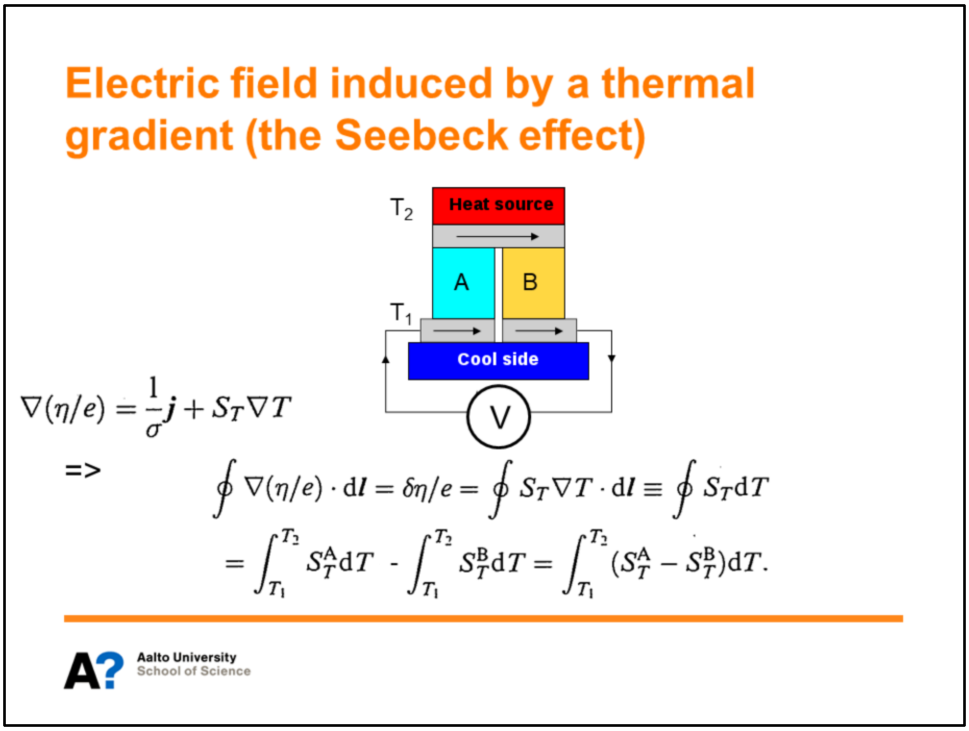
- Electrochemical potential: chemical potential mu: the energy up to which the states are filled, electrostatic potential phi: includes effects from electronic charge imbalance and external potential (electric field).
- Thermopower also known as Seebeck coefficient
- Nabla T can affect electrochem.pot if different T correspond to different mu (due to asymmetric DOS around Fermi-energy, i.e., if velocity above and below EF is different).
- Similarly for Peltier
- Revisit Drawing 4.2 highlighting the fluxes.



Electric field induced by a thermal gradient (the Seebeck effect)

$$\nabla(\eta/e) = \frac{1}{\sigma}\boldsymbol{j} + S_T\nabla T$$

=>

$$\oint \nabla(\eta/e)\cdot \mathrm{d}\boldsymbol{l} = \delta\eta/e = \oint S_T\nabla T\cdot \mathrm{d}\boldsymbol{l} \equiv \oint S_T\mathrm{d}T$$

$$= \int_{T_1}^{T_2} S_T^{\mathrm{A}}\mathrm{d}T - \int_{T_1}^{T_2} S_T^{\mathrm{B}}\mathrm{d}T = \int_{T_1}^{T_2}(S_T^{\mathrm{A}} - S_T^{\mathrm{B}})\mathrm{d}T.$$

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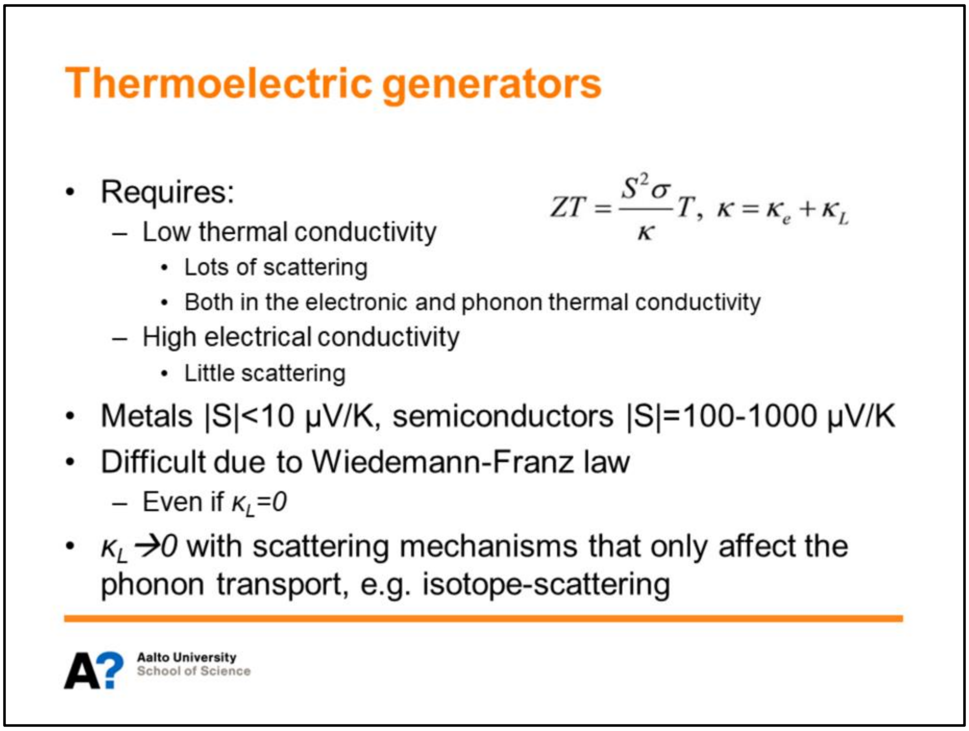
- I think it is better to consider that voltage difference is measured at point 2, electrically not connected but at same temperature.
- j=0, open circuit, builds up potential difference
- Sign error in Elliott.



Thermoelectric generators

- Requires:
  - Low thermal conductivity
    - Lots of scattering
    - Both in the electronic and phonon thermal conductivity
  - High electrical conductivity
    - Little scattering
- Metals |S|<10 μV/K, semiconductors |S|=100-1000 μV/K
- Difficult due to Wiedemann-Franz law
  - Even if $\kappa_L=0$
- $\kappa_L \rightarrow 0$ with scattering mechanisms that only affect the phonon transport, e.g. isotope-scattering

$$ZT = \frac{S^2\sigma}{\kappa}T,\ \kappa = \kappa_e + \kappa_L$$

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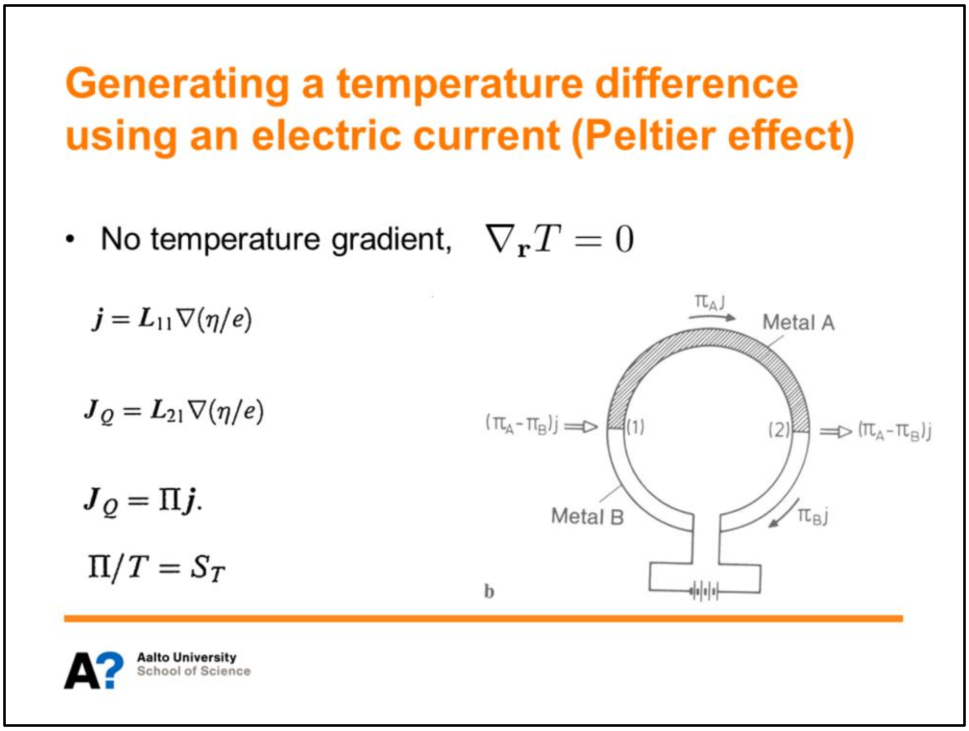
- Take Seebeck ”device” and add load
- Figure of merit ZT, efficiently produce thermoelectric power. Best materials have ZT around 2, which is enough for some niche applications, but not commercially viable for large-scale energy generation.
- Still an active research area, even here in Aalto
- We want only electrons to respond to temperature difference
- Need to have material where Wiedemann-Franz law does not apply, rules out most. Semiconductors are better.



Generating a temperature difference using an electric current (Peltier effect)

- No temperature gradient, $\nabla_{\mathbf{r}} T = 0$

$$\boldsymbol{j} = \boldsymbol{L}_{11}\nabla(\eta/e)$$

$$\boldsymbol{J}_Q = \boldsymbol{L}_{21}\nabla(\eta/e)$$

$$\boldsymbol{J}_Q = \Pi \boldsymbol{j}.$$

$$\Pi/T = S_T$$

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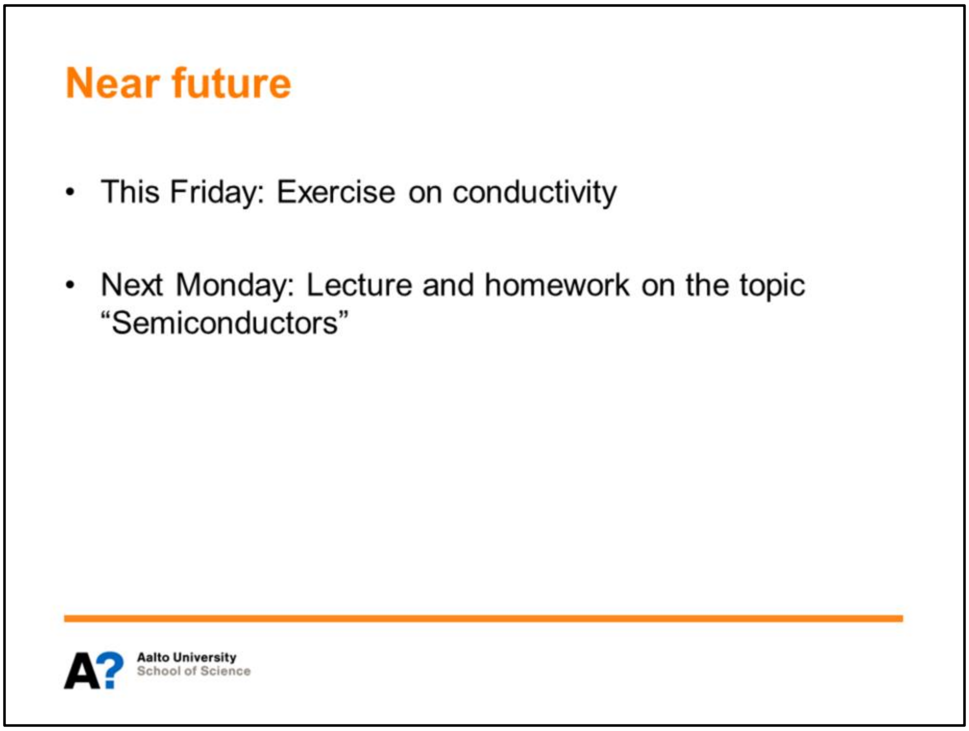
- Peltier coefficient: heat carried per unit charge
- 1. System at fixed temperature, 2. Add current, 3. The heat flux through A and B are different => imbalance, T decrease/increase at point (1)/(2), 4. Remove the heat from (2), or Seebeck effect starts to counteract



Near future

- This Friday: Exercise on conductivity
- Next Monday: Lecture and homework on the topic "Semiconductors"

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