Transport Theory

Vijay B. Shenoy

(shenoy@physics.iisc.ernet.in)

Centre for Condensed Matter Theory
Indian Institute of Science

Overview

- **Motivation – Why do this?**
- **Mathematical and Physical Preliminaries**
- **Linear Response Theory**
- **Boltzmann Transport Theory**
- **Quantum Theory of Transport**

What is Transport Theory ?

- **Are we thinking of this?**

What is Transport Theory (in Materials)?

- Material – Atoms arranged in a particular way
- "Stimulus" takes material *away* from thermal equilibrium
- Material "responds" – possibly by transferring energy, charge, spin, momentum etc from one spatial part to another
- Transport theory: Attempt to construct a theory that relates "material response" to the "stimulus"
- ...
- Ok..., so why bother?

Why Bother (Taxpayer Viewpoint)?

- *ALL* **materials are used for their "response" to "stimulus"**
- **Eg. Wool (sweater), Silicon (computer chip), Copper (wire), Carbon (writing) etc...**
- **Key** *materials question*: **What atoms and how should I arrange them to get a desired response to a particular type of stimulus**
- **...**
- **Transport theory lays key foundation of** *theoretical materials design*
- **...**
- **Blah, blah, blah...**

Why Bother (Physicist's Viewpoint)?

- **The way a material responds to stimulus is a "caricature" of its "state"**
- **Transport measurements probe "excitations" above a "ground state"**
- **Characteristic "signatures" for transport are "universal" can can be used to classify materials (metals, insulators etc.)**
- **...**
- **Ok, convinced? So what do we need to study transport theory?**

Prerequisites

- **A working knowledge of Fourier transforms**
- **Basic quantum mechanics**
- **Equilibrium (quantum) statistical mechanics**
- **Band theory of solids**
- **Some material phenomenology – transport phenomenology in metals, mainly**
- **...**
- **Our focus:** *Electronic* **transport**

Fourier Transforms

- **Function $f(\boldsymbol{r}, t)$ is a function of space and time**
- **Its Fourier transform $\hat{f}(\boldsymbol{k}, \omega)$ is defined as**

$$\hat{f}(\boldsymbol{k}, \omega) = \int \mathrm{d}^3\boldsymbol{r} \int \mathrm{d}t \, f(\boldsymbol{r}, t) \, e^{-i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)}$$

- **We will write $\hat{f}(\boldsymbol{k}, \omega)$ as $f(\boldsymbol{k}, \omega)$ (without the hat!)**
- **Inverse Fourier transform**

$$f(\boldsymbol{r}, t) = \frac{1}{(2\pi)^3} \int \mathrm{d}^3\boldsymbol{k} \frac{1}{2\pi} \int \mathrm{d}\omega \, f(\boldsymbol{k}, \omega) \, e^{i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)}$$

Some Useful Results

- **FT of delta function is 1**
- **Step function** $\theta(t) = \begin{cases} 1 & t \geq 0 \\ 0 & t < 0 \end{cases}$
- **FT of step function** $\theta(t)$ **is** $\dfrac{i}{\omega + i\eta}$**,** η **is a vanishingly small positive number**
- **Similarly FT of** $\theta(-t)$ **is** $\dfrac{-i}{\omega - i\eta}$
- **The strangest of them all**

$$\frac{1}{\omega \pm i\eta} = P\left(\frac{1}{\omega}\right) \mp i\pi\delta(\omega)$$

Transport Theory: Introduction

- **Example: A capacitor with a dielectric layer**
- **Stimulus: Voltage applied** V
- **Response: Charge stored** Q
- **In general, we expect the response to be a complicated function of the stimulus**
- **Make life simple (although unreal in many systems), consider only cases where response is** $linear$ **function of the stimulus**
- **Focus on** $Linear$ **transport theory – part of the general** $Linear\ Response\ Theory$
- **What is the most general form of linear response?**

General Linear Response

- **Stimulus may vary in space and time** $V(\boldsymbol{r}, t)$
- **Response also varies in space and time** $Q(\boldsymbol{r}, t)$
- **What is the most general** *linear* **response?**
- **The most general linear response is** *non-local* **in** *both* **space and time**

$$Q(\boldsymbol{r}, t) = \int \mathrm{d}^3\boldsymbol{r} \int \mathrm{d}t' \chi(\boldsymbol{r}, t|\boldsymbol{r}', t') V(\boldsymbol{r}', t')$$

- **The response function** $\chi(\boldsymbol{r}, t|\boldsymbol{r}', t')$ **is a** *property of our system (material)* **– notice the** *nonlocality* **of response**
- **In "nice" systems ("time-invariant and transilationally invariant")** $\chi(\boldsymbol{r}, t|\boldsymbol{r}', t') = \chi(\boldsymbol{r} - \boldsymbol{r}', t - t')$

Linear Response

- **Keep aside spatial dependence: $\chi = \chi(t - t')$, response to spatially homogeneous, time varying stimulus**
- **In Fourier language $Q(\omega) = \chi(\omega)V(\omega)$ – another way to see it – "independent" linear response for different frequencies of stimulus!**
- **What can we say about $\chi(\omega)$ (or $\chi(t - t')$) on general grounds?**
- **Clearly phase of the response may differ from that of stimulus – consequence: response function is complex in general $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$**
- **Looks like linear response is characterised by two real valued functions $\chi'(\omega)$ and $\chi''(\omega)$**

Causal Response

- **We know that the future does not affect the present ("usually") – response must be causal**
- **Another way to say this** $\chi(t-t') = 0$ **if** $t - t' < 0$ **or equivalently** $\theta(-(t-t'))\chi(t-t') = 0$
- **What is the consequence of this?**
- **Maxim of linear response theory: "when in doubt Fourier transform!"**
- **After a bit of algebra (Exercise: Do the algebra)**

$$\begin{aligned} \int \mathrm{d}\omega' \frac{1}{\omega - (\omega' - i\eta)} \chi(\omega') &= 0 \\ \Longrightarrow \quad \mathcal{P}\!\!\int \mathrm{d}\omega' \frac{\chi'(\omega') + i\chi''(\omega')}{\omega - \omega'} &= i\pi\chi'(\omega) - \pi\chi''(\omega) \end{aligned}$$

Kramers-Krönig Relations

- *Real and imaginary parts of response function are not independent of each other*, **in fact one of the completely determines the other:**

$$\chi'(\omega) = \frac{1}{\pi} \fint \mathrm{d}\omega' \frac{\chi''(\omega')}{\omega - \omega'}, \qquad \chi''(\omega) = \frac{1}{\pi} \fint \mathrm{d}\omega' \frac{\chi'(\omega')}{\omega' - \omega}$$

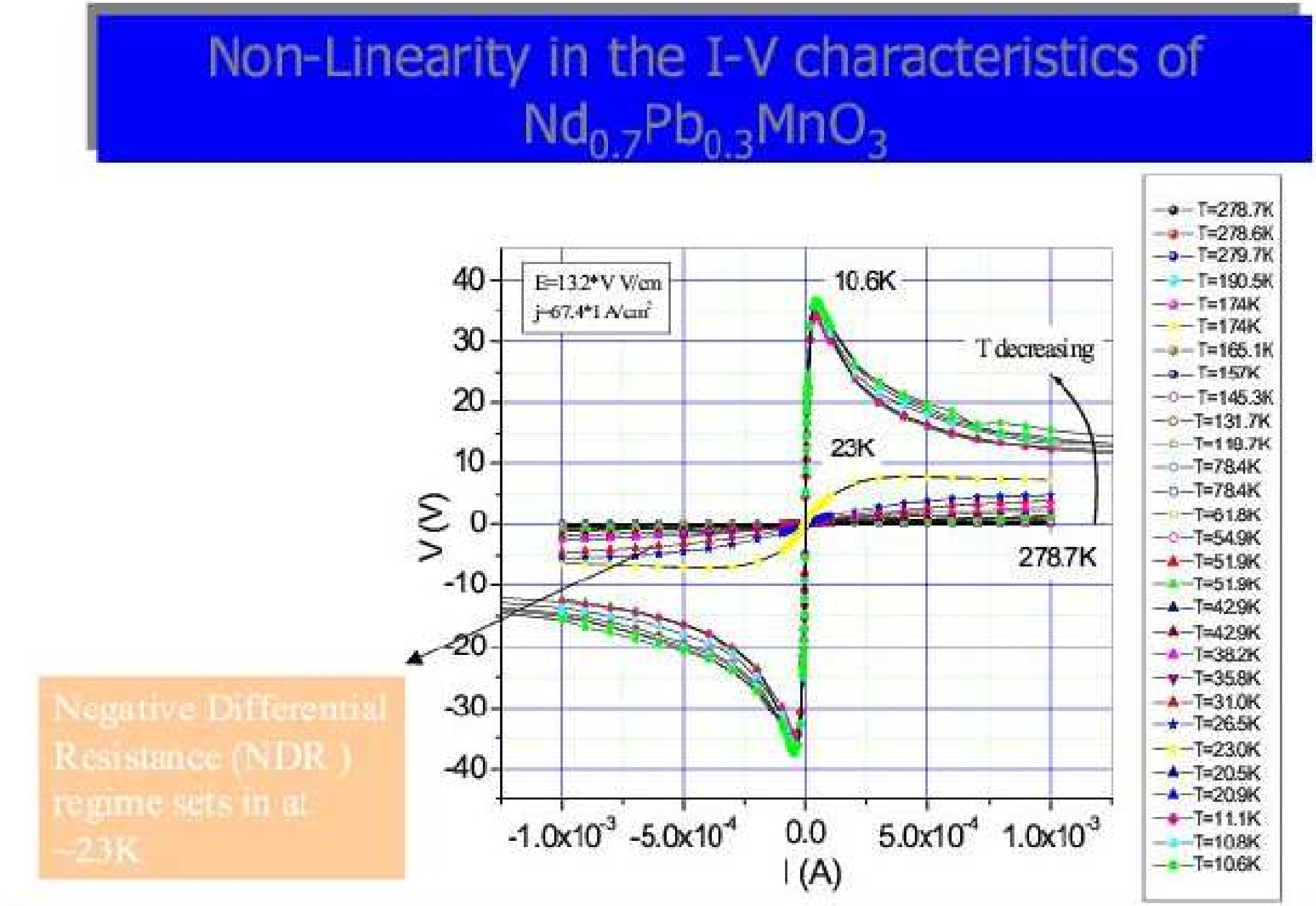
- **Important experimental consequences: example, one can obtain conductivity information from reflectance measurements!**

Its nice when response *is* linear...

But nature has many nonlinear responses...

(Slap!)

Nonlinear Response



Non-Linearity in the I-V characteristics of $Nd_{0.7}Pb_{0.3}MnO_3$

Negative Differential Resistance (NDR) regime sets in at ~23K

(Jain, Raychaudhuri (2003))

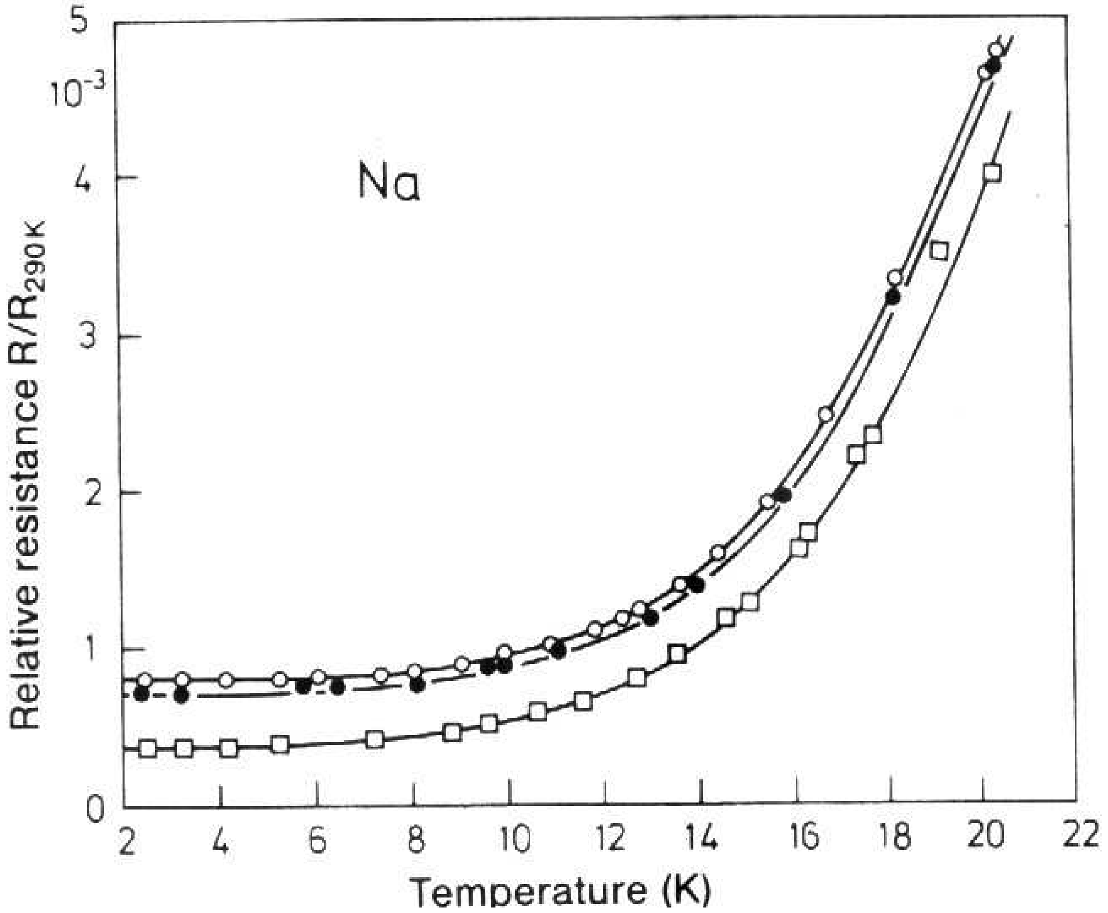
What now?

- **We posited response to be linear**
- **Reduced the problem to obtaining (say) the real part of the response based on very general causality arguments!**
- **...**
- **How do we calculate $\chi(\omega)$?**
- **This is a major chunk of what we will do – obtain response functions**

What we plan to do...

- **Goal: Study transport in** $metals$
- **Focus on zero frequency electrical response ("DC" response)**
- **Review: Drudé theory**
- **Review: Bloch theory and semiclassical approximation**
- **Boltzmann transport theory**
- **...**
- **But before all this, lets see what we need to explain**

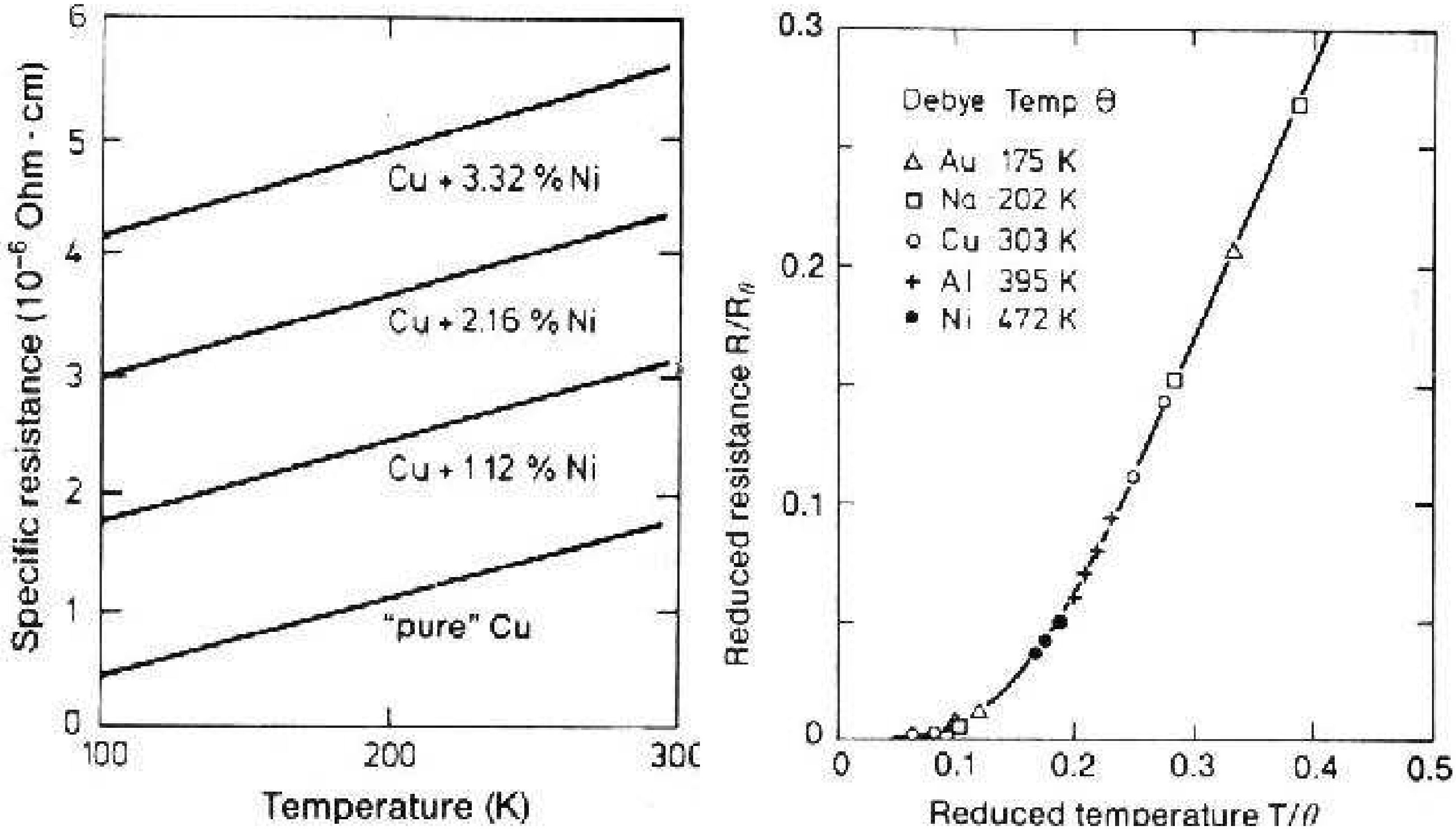
Resistivity in Metals



(Ibach and Lüth)

- **Almost constant at “low” temperatures...all way to linear at high temperatures**

Resistivity in Metals...There's More!



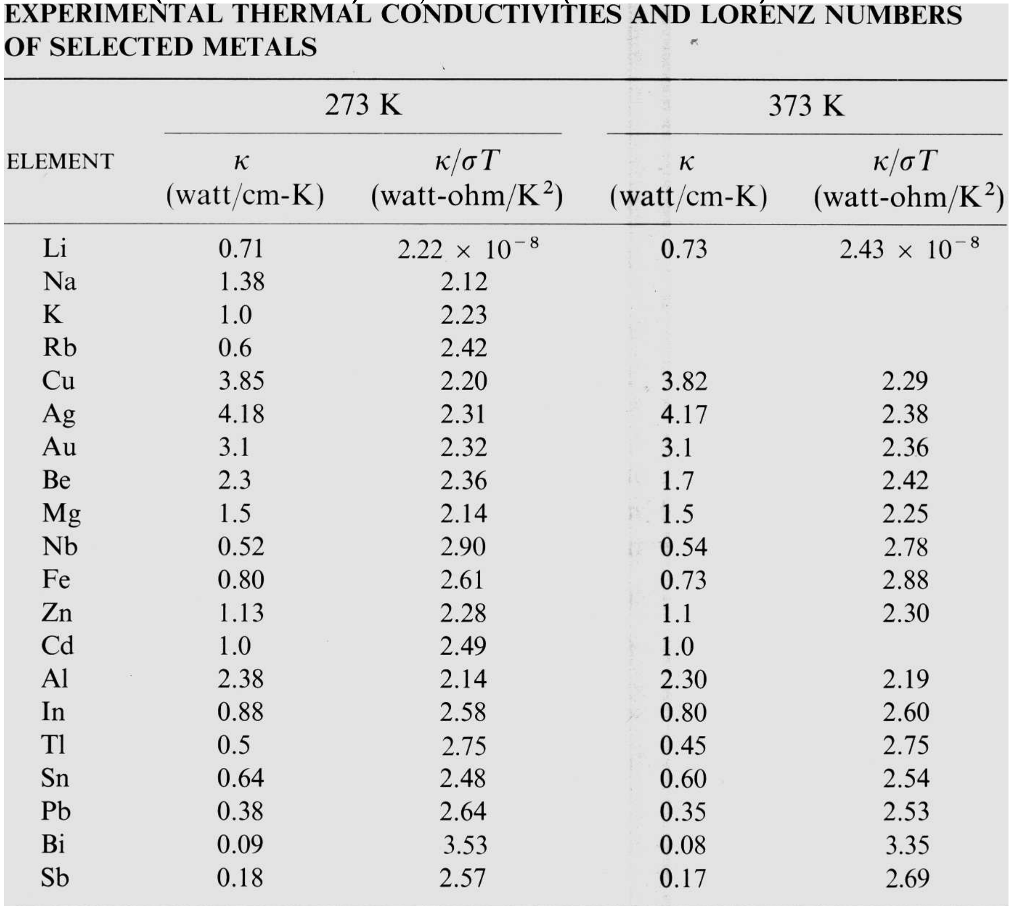
(Ibach and Lüth)

- **Increases with impurity content**
- **Has some "universal" features**

Transport in Metals

- **Wiedemann-Franz Law: Ratio of thermal (κ) to electrical conductivities (σ) depends linearly on T**

$\kappa/\sigma = (Const)T, \qquad (Const) \approx 2.3 \times 10^{-8}$**watt-ohm/K**^{2}



EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENZ NUMBERS OF SELECTED METALS

ELEMENT	273 K		373 K	
	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K^2)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K^2)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-8}
Na	1.38	2.12		
K	1.0	2.23		
Rb	0.6	2.42		
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Be	2.3	2.36	1.7	2.42
Mg	1.5	2.14	1.5	2.25
Nb	0.52	2.90	0.54	2.78
Fe	0.80	2.61	0.73	2.88
Zn	1.13	2.28	1.1	2.30
Cd	1.0	2.49	1.0	
Al	2.38	2.14	2.30	2.19
In	0.88	2.58	0.80	2.60
Tl	0.5	2.75	0.45	2.75
Sn	0.64	2.48	0.60	2.54
Pb	0.38	2.64	0.35	2.53
Bi	0.09	3.53	0.08	3.35
Sb	0.18	2.57	0.17	2.69

(Ashcroft-Mermin)

Magneto-transport! Levitating!

- **Hall effect**
- **Nernst effect**
- **Righi-Leduc effect**
- **Ettingshausen effect**
- **...**
- **Things are getting to be quite “effective”**
- **Goal: Build a “reasonable” theoretical framework to “explain”/”calculate” all this**

Drudé Theory – Review

- **Electrons: a classical gas**
- **Collision time τ, gives the equation of motion**

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = -\frac{\boldsymbol{p}}{\tau} + \boldsymbol{F}$$

$\boldsymbol{p}$ – momentum, $\boldsymbol{F}$ – "external" force

- **Gives the "standard result" for conductivity**

$$\sigma = \frac{ne^2\tau}{m}$$

(all symbols have usual meanings)

- **All is, however, *not* well with Drudé theory!**

Bloch Theory

- **We do need quantum mechanics to understand metals (all materials, in fact)**
- **In the periodic potential of the ions, wave functions are $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})$ ($u_{\boldsymbol{k}}$ is a lattice periodic function), $\boldsymbol{k}$ is a vector in the 1st Brillouin zone**
- **The Hamiltonian expressed in Bloch language $H = \sum_{\boldsymbol{k}\sigma} \varepsilon(\boldsymbol{k}) |\boldsymbol{k}\rangle\langle\boldsymbol{k}|$ (one band), $\varepsilon(\boldsymbol{k})$ is the band dispersion (set aside spin throughout these lectures!)**
- **"Average velocity" in a Bloch state $\boldsymbol{v}(\boldsymbol{k}) = \dfrac{1}{\hbar}\dfrac{\partial \varepsilon}{\partial \boldsymbol{k}}$**
- **Occupancy of a Bloch state $f^0(\boldsymbol{k}) = \dfrac{1}{e^{\beta(\varepsilon(\boldsymbol{k})-\mu)} + 1}$, $\beta = 1/(k_B T)$, μ – chemical potential**

So, what is a metal?

- **Chemical potential μ determined from electron concentration**
- **Try to construct a surface in the reciprocal space such that $\varepsilon(\boldsymbol{k}) = \mu$**
- **If such a surface exists (at $T = 0$) we say that the material is a *metal***
- **A metal has a *Fermi surface***
- **Ok, so how do we calculate conductivity?**
- **Need to understand “how electron moves” under the action of “external forces”**

Semi-classical Electron Dynamics

- **Key idea: External forces (F; electric/magnetic fields) cause transition of electronic states**
- **Rate of transitions $\hbar \frac{\mathrm{d}\boldsymbol{k}}{\mathrm{d}t} = \boldsymbol{F}$ – Quantum version of "Newton's law"**
- **By simple algebra, we see the "acceleration" $\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \boldsymbol{M}^{-1}\boldsymbol{F}$, $\boldsymbol{M}^{-1} = \frac{1}{\hbar^2}\frac{\partial^2\varepsilon}{\partial\boldsymbol{k}\partial\boldsymbol{k}}$**
- **Electron becomes a "new particle" in a periodic potential! Properties determined by value of M at the chemical potential**
- **But, what about conductivity? If you think about this, you will find a very surprising result! (Essentially infinite!)**

Conductivity in Metals

- **What makes for *finite* conductivity in metals?**
- **Answer: “Collisions”**
- **Electrons may scatter from impurities/defects, electron-electron interactions, electron-phonon interaction etc...**
- **How do we model this? Brute force approach of solving the full Schrödinger equation is highly impractical!**
- **Key idea: The electron gets a “life-time” – i.e., an electron placed in a Bloch state $\boldsymbol{k}$ evolves according to $\psi(t) \sim \psi_{\boldsymbol{k}} e^{-i\varepsilon(\boldsymbol{k})t - \frac{t}{\tau_{\boldsymbol{k}}}}$; “lifetime” is $\tau_{\boldsymbol{k}}$!**
- **Conductivity could plausibly be related to $\tau_{\boldsymbol{k}}$; how?**

Boltzmann Theory

- **Nonequilibrium distribution function $f(\boldsymbol{r}, \boldsymbol{k}, t)$:**
  - **"Occupancy" of state $\boldsymbol{k}$ at position $\boldsymbol{r}$ and time t**
  - **$\boldsymbol{r}$ in $f(\boldsymbol{r}, \boldsymbol{k}, t)$ represents a suitable "coarse grained" length scale (much greater than the atomic scale) such that "each" $\boldsymbol{r}$ represents a thermodynamic system**
- **Idea 1: The (possibly nonequilibrium) state of a system is described by a** *distribution function* $f(\boldsymbol{r}, \boldsymbol{k}, t)$
- **Idea 2: In equilibrium, $f(\boldsymbol{r}, \boldsymbol{k}, t) = f^0(\boldsymbol{k})$! External forces act to drive the distribution function** *away* **from equilibrium!**
- **Idea 3: Collisions act to** *"restore"* **equilibrium – try to bring f back to f^0**

Time Evolution of $f(\boldsymbol{r}, \boldsymbol{k}, t)$

- **Suppose we know f at time $t = 0$, what will it be at a later time t if we know all the "forces" acting on the system?**
- **Use semi-classical dynamics: An electron at $\boldsymbol{r}$ in state $\boldsymbol{k}$ at time t was at $\boldsymbol{r} - \boldsymbol{v}\Delta t$ in the state $\boldsymbol{k} - \frac{\boldsymbol{F}}{\hbar}\Delta t$ at time $t - \Delta t$**
- **Thus, we get the Boltzmann transport equation**

$$
\begin{aligned}
f(\boldsymbol{r}, \boldsymbol{k}, t) = f(\boldsymbol{r} - \boldsymbol{v}\Delta t, \boldsymbol{k} - \frac{\boldsymbol{F}}{\hbar}\Delta t, t - \Delta t) \quad &+ \quad \left.\frac{\partial f}{\partial t}\right|_{coll.} \Delta t \\
\Longrightarrow \frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \frac{\boldsymbol{F}}{\hbar} \cdot \frac{\partial f}{\partial \boldsymbol{k}} \quad &= \quad \left.\frac{\partial f}{\partial t}\right|_{coll.}
\end{aligned}
$$

- **If we specify the forces and the collision term, we have an initial value problem to determine $f(\boldsymbol{r}, \boldsymbol{k}, t)$**

Boltzmann Theory

- **So what if we know $f(\boldsymbol{r},\boldsymbol{k},t)$?**
- **$f(\boldsymbol{r},\boldsymbol{k},t)$ is determined by the "external forces" $\boldsymbol{F}$ – the stimulus (and, of course, the collisions which we treat as part of our system)**
- **If we know $f(\boldsymbol{r},\boldsymbol{k},t)$ we can calculate the responses, eg.,**

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{k}\,(-e\boldsymbol{v})\,(f(\boldsymbol{r},\boldsymbol{k},t) - f^0(\boldsymbol{k}))$$

- **Intuitively we know that $f(\boldsymbol{r},\boldsymbol{k},t) - f^0(\boldsymbol{r},\boldsymbol{k},t) \sim \boldsymbol{F}$, so we see that we can calculate linear response functions!**

Approximations etc.

- **We know the forces $\boldsymbol{F}$, eg., $\boldsymbol{F} = -e(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$**
- **What do we do about $\left.\frac{\partial f}{\partial t}\right|_{coll.}$?**
- **Some very smart folks have suggested that we can set**

$$\left.\frac{\partial f}{\partial t}\right|_{coll.} = -\frac{f - f^0}{\tau_{\boldsymbol{k}}}$$

– the famous “relaxation time appoximation”...

- **In general, $\tau_{\boldsymbol{k}}$ is not same as the electron lifetime (more later)...this is really a “phenomenological approach” – it embodies experience gained by looking at experiments**

Electrical Conductivity

- **BTE becomes**

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \frac{\boldsymbol{F}}{\hbar} \cdot \frac{\partial f}{\partial \boldsymbol{k}} = -\frac{f - f^0}{\tau_{\boldsymbol{k}}}$$

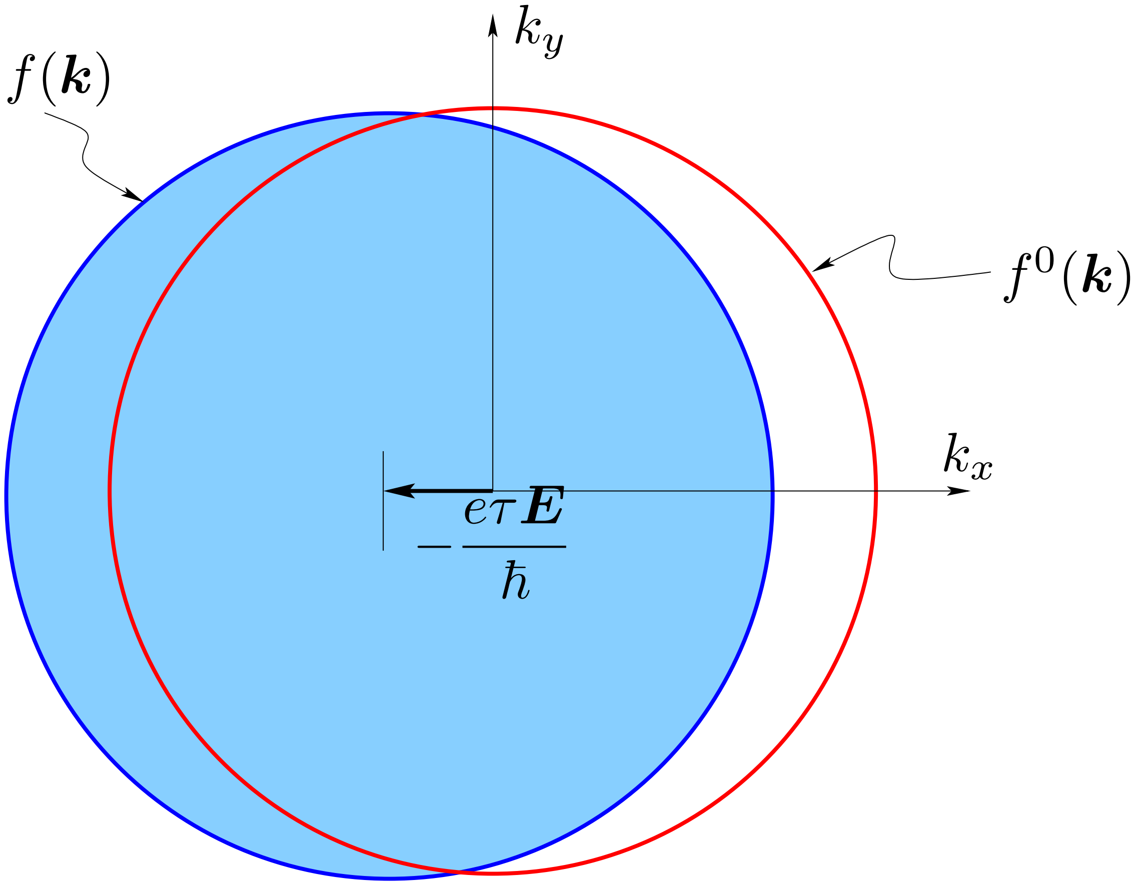
- **Homogeneous DC electric field** $\boldsymbol{F} = -e\boldsymbol{E}$
- **We look for the** *steady homogeneous* **response**

$$\frac{\boldsymbol{F}}{\hbar} \cdot \frac{\partial f}{\partial \boldsymbol{k}} = -\frac{f - f^0}{\tau_{\boldsymbol{k}}} \implies f = f^0 - \frac{\tau_{\boldsymbol{k}}\boldsymbol{F}}{\hbar} \cdot \frac{\partial f}{\partial \boldsymbol{k}}$$

- **Approximate solution (Exercise: Work this out)**

$$f(\boldsymbol{k}) \approx f^0 + \frac{e\tau_{\boldsymbol{k}}\boldsymbol{E}}{\hbar} \cdot \frac{\partial f^0}{\partial \boldsymbol{k}} \approx f^0\left(\boldsymbol{k} + \frac{e\tau_{\boldsymbol{k}}\boldsymbol{E}}{\hbar}\right)$$

Solution of BTE



- **Fermi surface “shifts”** (**Exercise:** *estimate* **order of magnitude of shift**)

Conductivity from BTE

- **Current**

$$\boldsymbol{j} = \frac{1}{(2\pi)^3} \int \mathrm{d}^3\boldsymbol{k} \, (-e\boldsymbol{v}) \, \frac{e\tau_{\boldsymbol{k}} \boldsymbol{E}}{\hbar} \cdot \frac{\partial f^0}{\partial \boldsymbol{k}}$$

- **Conductivity tensor**

$$\boldsymbol{\sigma} = -\frac{1}{(2\pi)^3} \frac{e^2}{\hbar} \int \mathrm{d}^3\boldsymbol{k} \; \tau_{\boldsymbol{k}} \; \boldsymbol{v} \; \frac{\partial f^0}{\partial \boldsymbol{k}}$$

- **Further, with spherical Fermi-surface (free electron like), $\tau_{\boldsymbol{k}}$ roughly independent of $\boldsymbol{k}$ (Exercise: Show this)**

$$\boldsymbol{\sigma} = \frac{ne^2\tau}{m} \mathbf{1}$$

This looks strikingly close to the Drudé result, but the physics could not be more different!

What about experiments?

- **Well, we now have an expression for conductivity; we should compare with experiments?**
- **What determines the T dependence of conductivity? Yes, it** *is essentially* **the T dependence of τ (***only in metals***)**
- **But we do not yet have τ!!**
- **Need a way to calculate τ...**
- **...**
- **Revisit the idea of electron-lifetime...how do we calculate life time of an electron?**

Lifetime due to Impurity Scattering

- **Impurity potential V_I, causes transitions from one Bloch state to another**
- **Rate of transition from $\boldsymbol{k} \to \boldsymbol{k}'$**

$$W_{\boldsymbol{k}\to\boldsymbol{k}'} = \frac{2\pi}{\hbar} |\langle \boldsymbol{k}' | V_I | \boldsymbol{k} \rangle|^2 \delta(\varepsilon(\boldsymbol{k}') - \varepsilon(\boldsymbol{k}))$$

- **Total rate of transition, or inverse lifetime**

$$\frac{1}{\tau^I_{\boldsymbol{k}}} = \frac{1}{(2\pi)^3} \int \mathrm{d}^3\boldsymbol{k}' \, W_{\boldsymbol{k}\to\boldsymbol{k}'}$$

- **Can we use $\tau^I_{\boldsymbol{k}}$ as the τ in the Boltzmann equation?**
- **Ok in order of magnitude, but not alright! Why?**

How to calculate τ?

- **Look back at the collision term, can write it more elaborately as**

$$\begin{aligned}\left.\frac{\partial f}{\partial t}\right|_{coll.} &= \frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{k}'\, W_{\boldsymbol{k}\to\boldsymbol{k}'}\,\big(f(\boldsymbol{k})(1-f(\boldsymbol{k}')) - f(\boldsymbol{k}')(1-f(\boldsymbol{k} \\ &= \frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{k}'\, W_{\boldsymbol{k}\to\boldsymbol{k}'}\,\big(f(\boldsymbol{k}) - f(\boldsymbol{k}')\big)\end{aligned}$$

Note that $\boldsymbol{k}$ and $\boldsymbol{k}'$ are of the same energy

- **Take $\tau_{\boldsymbol{k}}$ to depend only on $\varepsilon(\boldsymbol{k})$**
- **Now,** $(f(\boldsymbol{k}) - f(\boldsymbol{k}')) \approx -\frac{\tau e}{\hbar}\frac{\partial f^0}{\partial \varepsilon}\big(\boldsymbol{v}(\boldsymbol{k}) - \boldsymbol{v}(\boldsymbol{k}')\big)\cdot \boldsymbol{E}$

Calculation of τ cont'd

- **Putting it all together**

$$
\begin{aligned}
-\frac{e}{\hbar}\frac{\partial f^0}{\partial \varepsilon}\boldsymbol{v}(\boldsymbol{k})\cdot\boldsymbol{E} &= -\frac{1}{(2\pi)^3}\frac{\tau e}{\hbar}\frac{\partial f^0}{\partial \varepsilon}\int \mathrm{d}^3\boldsymbol{k}'\, W_{\boldsymbol{k}\to\boldsymbol{k}'}\left(\boldsymbol{v}(\boldsymbol{k})-\boldsymbol{v}(\boldsymbol{k}')\right)\cdot \\
\Longrightarrow \frac{1}{\tau} &= \frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{k}'\, W_{\boldsymbol{k}\to\boldsymbol{k}'}\left(1-\frac{\boldsymbol{v}(\boldsymbol{k}')\cdot\hat{\boldsymbol{E}}}{\boldsymbol{v}(\boldsymbol{k})\cdot\hat{\boldsymbol{E}}}\right) \\
\Longrightarrow \frac{1}{\tau} &= \frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{k}'\, W_{\boldsymbol{k}\to\boldsymbol{k}'}\left(1-\cos\left(\widehat{\boldsymbol{k},\boldsymbol{k}'}\right)\right)
\end{aligned}
$$

- **Note τ is *different* from the "quasiparticle" life time!**
- **Key physical idea: Forward scattering *does not* affect electrical conductivity!**

T dependence of τ

- We now need to obtain T dependence of τ
- T dependence strongly depends on the mechanism of scattering
- Common scattering mechanisms
  - Impurity scattering
  - e–e scattering
  - e–phonon scatting
- More than one scattering mechanism may be operative; one has an effective τ (given by the Matthiesen’s rule)

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}$$

τ from Impurity Scattering

- Essentially independent of temperature
- Completely determines the residual resistivity (resistivity at $T = 0$)
- $\frac{1}{\tau}$ directly proportional to concentration of impurities (Matthiesen's rule!)
- Well in agreement with experiment!

τ from e–e Scattering

- **One might suspect that the effects of e–e interactions are quite strong...this is not actually so, thank to Pauli**
- **e–e scattering requires conservation of *both* energy and momentum**
- **"Phase space" restrictions severely limit e–e scattering**
- **Simple arguments can show** $\frac{1}{\tau} \sim \left(\frac{k_B T}{\mu}\right)^2$
- **Also called as "Fermi liquid" effects**
- **Can be seen in experiments on very pure samples at low temperatures**
- **At higher temperatures other mechanisms dominate**

τ from e–Phonon Scattering

- **There is a characteristic energy scale for phonons – T_D, the Debye temperature**
- **Below the Debye temperature, the quantum nature of phonons become important**
- **Natural to expect different T dependence above and below T_D**
- **e–phonon scattering is, in fact, *not* elastic in general**
- **Study two regimes separately : $T \gg T_D$ and $T \ll T_D$**

τ from e–Phonon Scattering $(T \gg T_D)$

- **Scattering processes are definitely inelastic**
- **Electron can change state $\boldsymbol{k}$ to $\boldsymbol{k}'$ by absorption or emission of phonon**
- **The matrix element of transition rate in a phonon emission with momentum $\boldsymbol{q}$**

$$\begin{aligned} W_{\boldsymbol{k}\to\boldsymbol{k}-\boldsymbol{q}} &\sim |M_{\boldsymbol{q}}\langle \boldsymbol{k}-\boldsymbol{q}, n_{\boldsymbol{q}}+1|a^\dagger_{\boldsymbol{q}}|\boldsymbol{k}, n_{\boldsymbol{q}}\rangle|^2 \\ &\sim |\langle n_{\boldsymbol{q}}+1|a^\dagger_{\boldsymbol{q}}|n_{\boldsymbol{q}}\rangle|^2 \sim \langle n_{\boldsymbol{q}}\rangle \sim k_B T \end{aligned}$$

- $\frac{1}{\tau}$ **varies linearly with temperature!**

τ from e–Phonon Scattering $(T \ll T_D)$

- **Scattering process is approximately elastic since only very long wavelength phonons (acoustic) are present**
- **Using expression for τ**

$$\frac{1}{\tau} \sim \int_{|\boldsymbol{q}|<\frac{k_B T}{c}} \mathrm{d}^3\boldsymbol{q} W_{\boldsymbol{k}\rightarrow\boldsymbol{k}-\boldsymbol{q}} \underbrace{\left(1 - \cos(\widehat{\boldsymbol{k}, \boldsymbol{k}-\boldsymbol{q}})\right)}_{|\boldsymbol{q}|^2} \sim \left(\frac{T}{T_D}\right)^5$$

Bloch-Gruneisen Law!

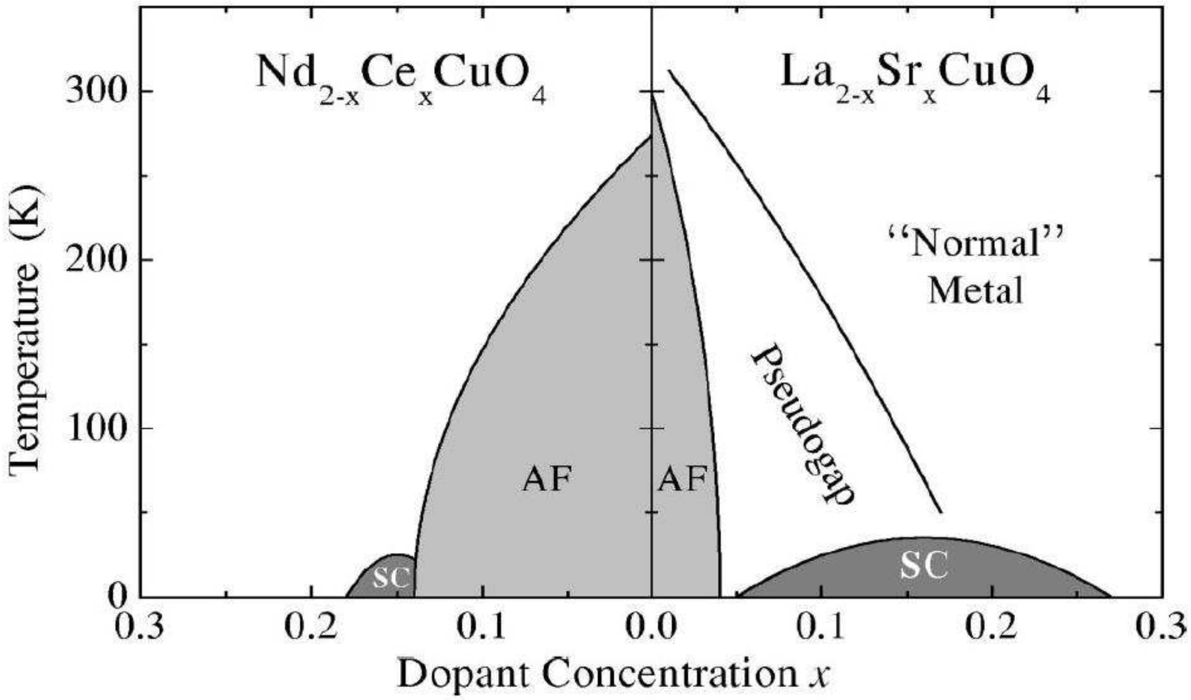
- **Phonons give a resistivity of T at $T \gg T_D$ and T^5 for $T \ll T_D$**
- **The key energy scale in the system is T_D – "universal" features are not surprising**

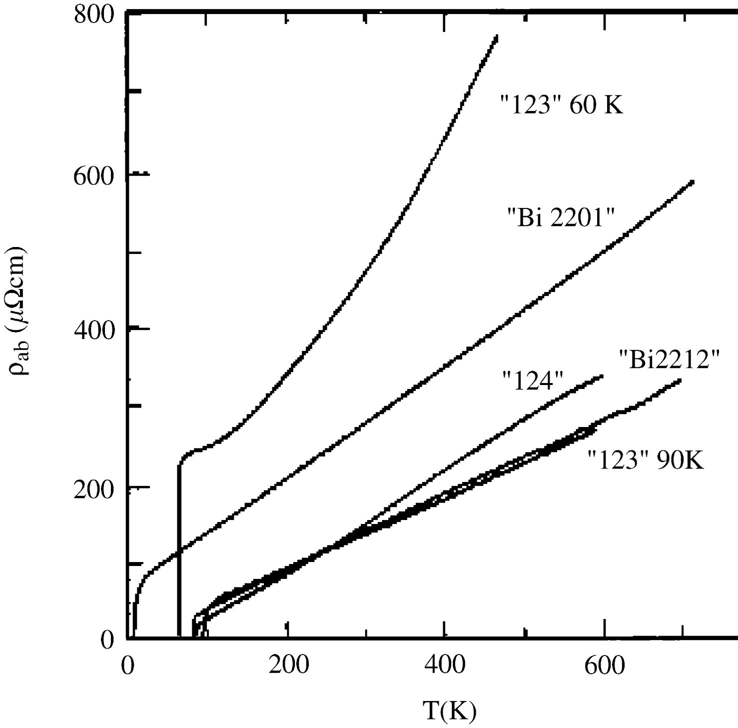
Experiments, Finally!

- Our arguments show
  - Impurity resistivity does not depend on temperature and is approximately linear with concentration of impurities
  - At very low temperatures an in pure enough samples, we will see a T^2 behaviour in resistivity
  - This is followed by a T^5 at low T ($T \gg T_D$) going over to T ($T \gg T_D$), and this behaviour with appropriate rescale should be universal
- All of these are verified experimentally in nice metals!

High T_c Surprise

- **Resistivity in high T_c normal state**





- **Looking for a research problem?**

What next?

- **We now have a handle on resistivity...how about thermal conductivity?**
- **We need also to explain Widemann-Franz!**
- **Plan: Study thermo-galvanic transport in general**
- **Include Seebeck effect, Peltier effect etc**
- **...**
- **How do we study thermal conductivity?**
- **...**
- **Back to Boltzmann**

Thermogalvanic Transport

- **Stimuli: Both $\boldsymbol{E}$ and $\boldsymbol{\nabla}T$, Response : $\boldsymbol{j}$ and $\boldsymbol{j}_Q$**
- **Cannot ignore spatial dependence of f!**
- **Steady state satisfies**

$$\boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} - \frac{e\boldsymbol{E}}{\hbar} \cdot \frac{\partial f}{\partial \boldsymbol{k}} = -\frac{f - f^0}{\tau}$$

- **Approximate solution (Exercise: Work this out)**

$$f - f^0 \quad = \quad \tau \frac{\partial f^0}{\partial \varepsilon} \left(\frac{(\varepsilon - \mu)}{T} \boldsymbol{\nabla} T + e\boldsymbol{E} \right) \cdot \boldsymbol{v}$$

- **Heat current $\boldsymbol{j}_Q$ is given by (Question: Why $(\varepsilon - \mu)$?)**

$$\boldsymbol{j}_Q = \frac{1}{(2\pi)^3} \int \mathrm{d}^3\boldsymbol{k}\, (\varepsilon - \mu) \boldsymbol{v} \left(f(\boldsymbol{k}) - f^0(\boldsymbol{k}) \right)$$

Thermogalvanic Transport

- **Transport relations can be expressed in compact from**

$$\begin{aligned} \boldsymbol{j} &= e^2 \boldsymbol{A}_0 \boldsymbol{E} + \frac{e}{T} \boldsymbol{A}_1 (-\boldsymbol{\nabla} T) \\ \boldsymbol{j}_Q &= e \boldsymbol{A}_1 \boldsymbol{E} + \frac{1}{T} \boldsymbol{A}_2 (-\boldsymbol{\nabla} T) \end{aligned}$$

where matrices $\boldsymbol{A}_\alpha = -\frac{1}{(2\pi)^3} \int \mathrm{d}^3\boldsymbol{k} (\varepsilon - \mu)^\alpha \, \tau \, \boldsymbol{v}\boldsymbol{v} \, \frac{\partial f^0}{\partial \varepsilon}$

- **For nearly free electrons**

$$\begin{pmatrix} \boldsymbol{j} \\ \boldsymbol{j}_Q \end{pmatrix} = \frac{n\tau}{m} \begin{pmatrix} e^2 & \frac{1}{2} e k_B \frac{k_B T}{\mu} \\ \frac{1}{2} e k_B T \frac{k_B T}{\mu} & \frac{1}{3} k_B^2 T \end{pmatrix} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla} T \end{pmatrix}$$

Thermogalvanic Transport

- **Experimentally more useful result**

$$\begin{aligned}\boldsymbol{E} &= \rho\boldsymbol{j} + Q\boldsymbol{\nabla}T\\ \boldsymbol{j}_Q &= \Pi\boldsymbol{j} - \kappa\boldsymbol{\nabla}T\end{aligned}$$

- **Thermoelectric properties**
  - $\rho = \frac{m}{ne^2\tau}$ **– Resistivity** $\sim 10^{-8}$ **ohm m**
  - $Q = \frac{1}{2}\frac{k_B}{e}\frac{k_BT}{\mu}$ **– Thermoelectric power** $\sim 10^{-8}T$**V/K (check factors!)**
  - $\Pi = QT$ **– Peltier coefficient**
  - $\kappa = \frac{\pi^2}{3}\frac{n\tau k_B^2T}{m}$ **– Electronic thermal conductivity** ~ 100 **watt/(m^2 K)**

Widemann-Franz!

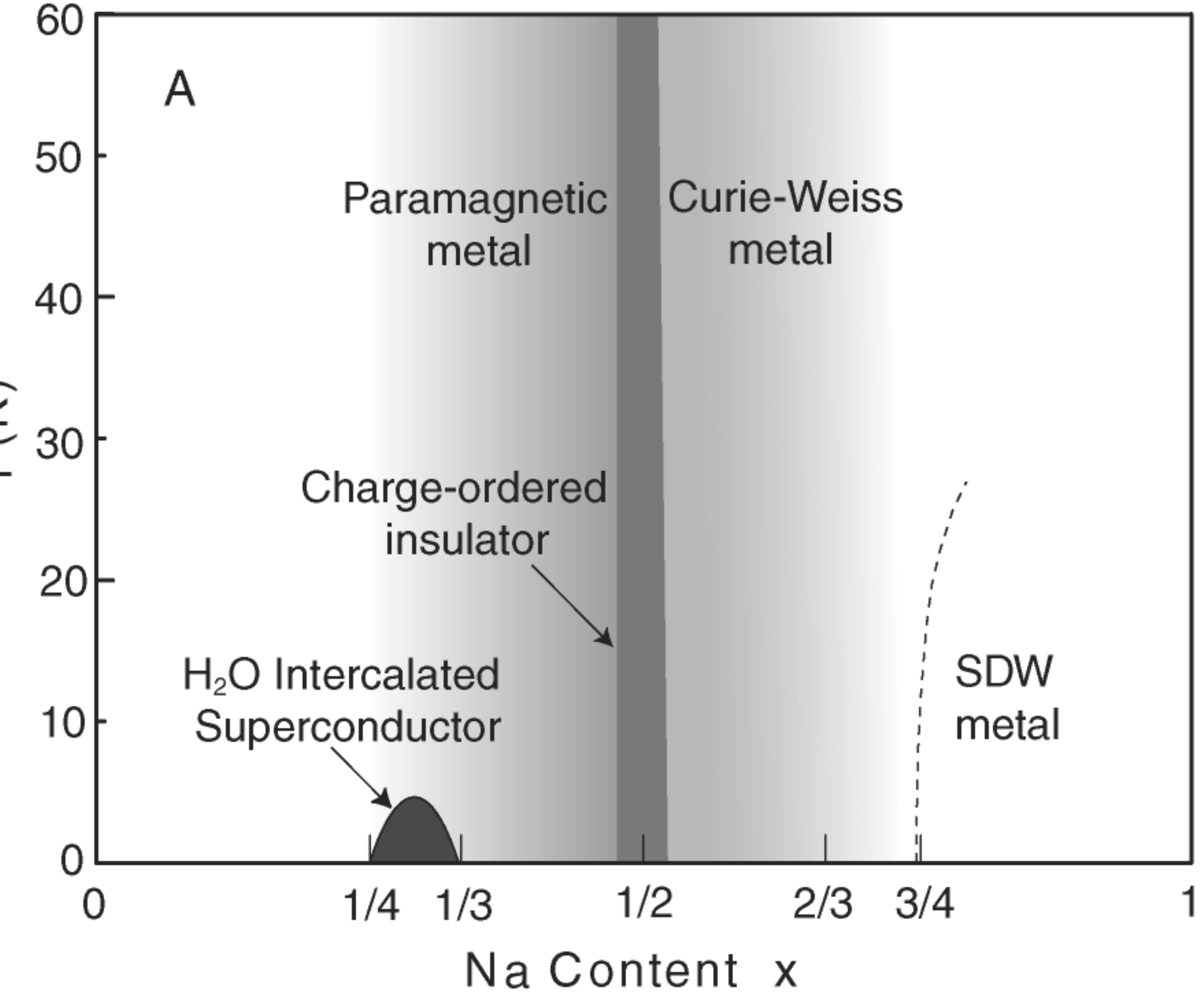
- **We see the "Lorenz number"**

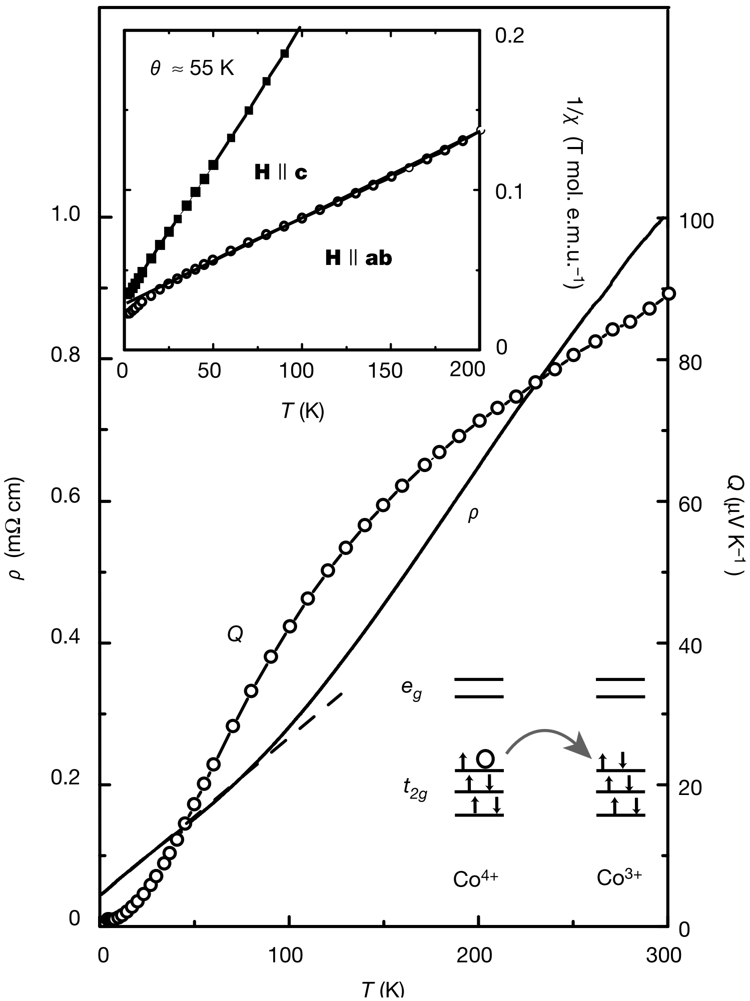
$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$$

– amazingly close to experiments (makes you wonder if something is wrong!)

- **Actually, Widemann-Franz law is valid strictly only when collisions are elastic...**
- **Reason: Roughly,** *inelastic forward scattering cannot degrade an electrical current*, **but it** *does* **degrade the thermal current (due to transfer of energy to phonons)**
- **Not expected to hold at** $T \geq T_D$

Amazing Cobaltate Na_xCoO_2





- **High thermoelectric power!!**
- **Another research problem!**

Magneto-Transport

- **Transport maxim: When you think you understand everything, apply magnetic field!**
- **Think of the Hall effect; the Hall coefficient is strictly not a linear response fucntion... We will not worry about such technicalities; take that the magnetic field B is applied and the response functions depend parametrically on B – in our original notation $\chi = \chi(\omega, \boldsymbol{B})$.**
- **Let us start with an isothermal system and understand how electrical transport is affected by a magnetic field – Hall effect**
- **But before that we will investigate semi-classical dynamics in presence of a magnetic field**

Semiclassical Dynamics in a Magnetic Field

- **In a magnetic field B, the an electron state changes according to $\hbar\dot{\boldsymbol{k}} = -e\boldsymbol{v} \times \boldsymbol{B}$**
- **Clearly, the k-states "visited" by the electron must be of same energy**
- **For a state at the Fermi surface, this could lead to two types of orbits depending on the nature of the Fermi surface:**
  - **Closed surfaces: The electron executes motion in a closed orbit in k space and a closed orbit in real space...it has a characteristic time scale for this given by the** *cyclotron frequency* $\omega_c = \frac{eB}{m^*}$**, ($m*$ – cyclotron mass)**
  - **Open surfaces: story is a bit more complicted...we will not get into this**

BTE with Magnetic Field

- **We will work with closed Fermi surfaces in the** *weak magnetic field* **regime** $\tau\omega_c \ll 1$**...an electron undergoes many collisions before it can complete one orbit**
- **Boltzmann equation becomes**

$$-e(\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{B})\cdot\frac{\partial f}{\partial \boldsymbol{k}} = -\frac{f-f^0}{\tau}$$

- **With a bit of (not-so-interesting) algebra** $(bB\cdot\boldsymbol{E}) = 0$

$$f - f^0 = \frac{e\tau}{1+(\omega_c\tau)^2}\Big(\boldsymbol{E}+(\omega_c\tau)\hat{\boldsymbol{B}}\times\boldsymbol{E}\Big)\cdot\boldsymbol{v}\frac{\partial f^0}{\partial\varepsilon}$$

And we attain the “Hall of fame”!

- **Setting $B = Be_z$, we get “in plane” response**

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \frac{\sigma_0}{(1+(\omega_c\tau)^2)} \begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

$\sigma_0 = \frac{ne^2\tau}{m}$

- **In the Hall experiment, $j_y = 0$, thus**

$$\begin{aligned} j_x &= \sigma_0 E_x \\ E_y &= -\omega_c\tau E_x \Longrightarrow R_H = \frac{E_y}{j_x B} = -\frac{1}{ne} \end{aligned}$$

- **Our model predicts a vanishing magnetoresistance!**

Magnetoresistance

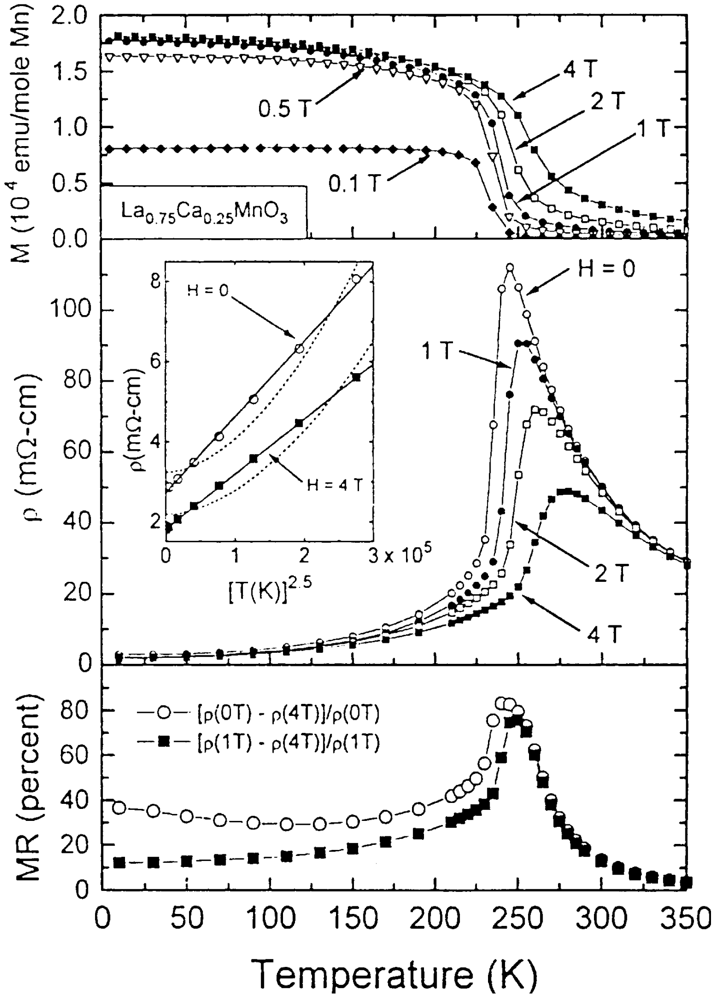
- **There is weak magnetoresistance present even in nice metals $\Delta\rho \sim \rho(0)B^2$ (this form arises from time reversal symmetry)**
- **For nice metals there is something called the Koehler’s rule**

$$\frac{\rho(B,T)-\rho(0,T)}{\rho(0,T)} = \mathcal{F}\left(\frac{\rho_{ref}B}{\rho(0,T)}\right)$$

The key idea is that magnetoresistance is determined by the ratio of two length scales – the mean free path and the “Larmour radius”

- **For metals with open orbits etc. magnetoresponse can be quite complicated!**
- **Research problem: Magnetoresponse of high T normal**

Manganites: Colossal Responses



- **Colossal magnetoresistance in LCMO!**

Magneto-Thermo-Galvano Transport

- **In general we can have both an electric field and temperature gradient driving currents in presence of a magnetic field**
- **The general "linear" response is of the form**

$$\begin{aligned} \boldsymbol{E} &= \rho \boldsymbol{j} + R_H \boldsymbol{B} \times \boldsymbol{j} + Q \boldsymbol{\nabla} T + N \boldsymbol{B} \times \boldsymbol{\nabla} T \\ \boldsymbol{j}_Q &= \Pi \boldsymbol{j} + K \boldsymbol{B} \times \boldsymbol{j} - \kappa \boldsymbol{\nabla} T + L \boldsymbol{B} \times \boldsymbol{\nabla} T \end{aligned}$$

- **Leads to many interesting "weak" effects**
- **Magnetic field in the z-direction in the discussion**

Nernst Effect

- **A temperature gradient $\frac{\partial T}{\partial x}$ is applied along the x-direction**
- $j_x = j_y = 0$ **and** $\dfrac{\partial T}{\partial y} = 0$
- **One finds an electric field in the y direction!**

$$N = \frac{E_y}{B \frac{\partial T}{\partial x}}$$

- **There is a lot of excitement with the Nernst effect in high-T_c...the pseudogap "phase" shows a large anomalous Nernst effect in a certain temperature range**

Righi-Leduc Effect

- **A temperature gradient is applied** $\frac{\partial T}{\partial x}$ **along the** x**-direction**
- $j_x = j_y = 0$ **and** $(j_Q)_y = 0$
- **A temperature gradient** $\frac{\partial T}{\partial y}$ *develops*
- **Response determined by**

$$\frac{\frac{\partial T}{\partial y}}{B\frac{\partial T}{\partial x}} = \frac{L}{\kappa}$$

Ettingshausen Effect

- **Current j_x flows, $\frac{\partial T}{\partial x} = 0$ along the x-direction**
- $j_y = 0$ **and** $(j_Q)_y = 0$
- **A temperature gradient $\frac{\partial T}{\partial y}$** *develops*
- **Response determined by Ettingshausen coefficient**

$$\frac{\frac{\partial T}{\partial y}}{B j_x} = \frac{K}{\kappa}$$

K **is related to the Nernst coefficient** $K = NT$

Thank You, Boltzmann!

- **This is how far we will go with Boltzmann theory...**
- **Of course, one can do many more things...its left to you to discover**
- **...**
- **Key ideas I : Distribution function, semiclassical equation of motion, collision term,...**
- **Key ideas II : Relaxation time, "quasi-Bloch-electrons" life-time, transportation life-time**
- **Boltzmann theory deals with "expectation value of operators", and does not worry about "quantum fluctuations" – it of course takes into account** *thermal* **fluctuations, but "cold shoulders" quantum fluctuations**
- **Our next task is to develop a fully quantum theory of**

Quantum Transport Theory

- There are many approaches...
- Our focus: Green-Kubo theory
- What we will see
  - Theory of the response function (Green-Kubo relations)
  - Fluctuation-dissipation theorem
  - Onsager's principle
- Our development will be "formal" and "real calculations" in this framework require (possibly) "advanced" techniques such as Feynman diagrams

The System

- **Our system: A (possibly many-particle) system with Hamiltonian** H_0
- **Eigenstates** $H_0|n\rangle = E_n|n\rangle$
- **Time evolution: Schrödinger** $i\frac{\partial|\psi\rangle}{\partial t} = H_0|\psi\rangle$ **(**$\hbar$ **set to 1)**
- **Also write as:** $|\psi(t)\rangle = e^{-iH_0t}|\psi(0)\rangle$
- **In presence of a perturbation (stimulus), Hamiltonian becomes** $H = H_0 + V$
- **One can study the time evolution in different "pictures" : Schrödinger picture, Heisenberg picture, Dirac ("interaction") picture**

Dirac (“interaction”) picture

- **State evolve according to** $|\psi_I(t)\rangle = e^{iH_0t}e^{-iHt}|\psi(0)\rangle$
- **Operators evolve according to** $A_I(t) = e^{iH_0t}Ae^{-OH_0t}$
- **Time evolution:** $i\dfrac{\partial|\psi_I\rangle}{\partial t} = V_I|\psi_I\rangle$
- **Expectation value of operator** A**:** $\langle A(t)\rangle = \langle\psi_I(t)|A_I(t)|\psi_I(t)\rangle$
- **Interaction picture** *reduces* **to the Heisenberg picture when there is no stimulus!**
- **...**
- **Ok, how does one describe the thermodynamic (possibly nonequilibrium) state of a quantum system?**

The Density Matrix

- **The "thermodynamic state" of a system can be described by the following statement – the system is in the state $|\alpha\rangle$ with a probability p_α**
- **States $|\alpha\rangle$ *may not* be the energy eigenstates**
- **p_α is the *statistical weight or probability* that the system is in the state $|\alpha\rangle$; clearly $\sum_\alpha p_\alpha = 1$**
- **Define a Hermitian operator $\rho = \sum_\alpha p_\alpha |\alpha\rangle\langle\alpha|$ – the density matrix! This operator describes the "thermodynamic (possibly nonequilibrium) state" of the system**
- **The *thermodynamic average* of an observable $\boldsymbol{A} = \mathrm{tr}\rho A = \sum_\alpha p_\alpha \langle\alpha|A|\alpha\rangle$**

What about Equilibrium?

- **Well, "clearly" the equilibrium density matrix**
  $\rho_0 = \sum_n \frac{e^{-\beta E_n}}{Z} |n\rangle\langle n|$, **partition function** $Z = \sum_n e^{-\beta E_n}$
- **Exercise: Work out expressions for internal energy, entropy, etc**
- **So far –*fixed particle number* (canonical ensemble)**
- **Treat $|n\rangle$ to count states with different particle number – state $|n\rangle$ has N_n particles, and move over to the grand canonical ensemble by introducing a chemical potential μ**
- $\rho_0 = \sum_n \frac{e^{-\beta(E_n - \mu N_n)}}{Z} |n\rangle\langle n|$, $Z = \sum_n e^{-\beta(E_n - \mu N_n)}$
- **Question: How does one get Fermi distribution out of this?**

Evolution of the Density Matrix

- **Suppose I know the density matrix at some instant of time... what will it be at a later instance?**
- **Now** $\rho(t_0) = \sum_\alpha p_\alpha |\alpha\rangle\langle\alpha|$**...if there system where in the state** $|\alpha\rangle$**, it will evolve to** $|\alpha(t)\rangle = e^{-iH(t-t_0)}|\alpha\rangle$**...This means** $\rho(t) = \sum_\alpha p_\alpha |\alpha(t)\rangle\langle\alpha(t)|$**, or**

$$\rho(t) = e^{-iH(t-t_0)}\rho(t_0)e^{iH(t-t_0)} \Longrightarrow i\frac{\partial\rho}{\partial t} + [\rho, H] = 0 \quad !!!!$$

This is the "quantum Louisville equation"!

- **In thermal equilibrium (no perturbations),** ρ_0 **is stationary!** **Question: Why?** **– all this fits very well with our earlier understanding**

Evolution of the Density Matrix

- **Time evolution in the interaction representation**

$$i\frac{\partial\rho_I}{\partial t} + [\rho_I, V_I] = 0$$

- **Perturbation was "slowly" switched on in the distant past** $t_0 \to -\infty$
- $\rho_I = \rho_0 + \Delta\rho_I$**, the piece of interest is** $\Delta\rho_I$
- **Clearly,** $\Delta\rho_I(-\infty) = 0$**, and we have**

$$\Delta\rho_I(t) = i\int_{-\infty}^{t} dt'[\rho_0, V_I(t')]$$

We know the evolution of the density matrix to $linear$ **order in the perturbation...we can therefore calculate the linear response**

Linear Response

- **The "stimulus"** $V(t) = f(t)B$ **where** B **is some operator (e.g. for an AC electric potential** $V(t) = -e\phi(t)\mathcal{N}$ **where** $\mathcal{N}$ **is the number density operator,** $\phi(t)$ **is a time dependent potential**
- Any **response (observable)** A **of interest can now be calculated**

$$\begin{aligned}\langle \Delta A \rangle(t) &= \mathrm{tr}(\Delta\rho_I(t) A_I(t)) \\ &= i\int_{-\infty}^{t} \mathrm{d}t' \mathrm{tr}([\rho_0, B_I(t')]A_I(t)) f(t') \\ &= \int_{-\infty}^{\infty} \mathrm{d}t' \underbrace{-i\theta(t-t')\langle[A(t), B(t')]\rangle_0}_{\chi_{AB}(t-t')} f(t')!\end{aligned}$$

Note that we have dropped all the I**'s in the last eqn.**

Linear Response

- **Completely solved** *any* **linear response problem –** *in principle!*
- $\chi_{AB}(t-t') = -i\theta(t-t')\langle[A(t),B(t')]\rangle_0$ **is called Green-Kubo relation**
- **Key physical idea: Linear response to stimulus is determined by an** *equilibrium correlation function* **(indicated by subscript 0)**
- **Causality is automatic!**
- **In systems with strong interaction/correlations, response calculation using Green-Kubo relation is a difficult task**

Fluctuation Dissipation Theorem

- **The imaginary part of χ is related to the** *dissipation*
- **Going back to the motivating "capacitor" example, the dielectric response function will** $\epsilon(t-t') \sim -i\theta(t-t')\langle[\mathcal{N}(t),\mathcal{N}(t')]\rangle_0$
- **The "leakage current loss" will be determined by the imaginary part of** $\epsilon(\omega)$
- **One can then go on to show that the imaginary part of $\chi(\omega)$ is directly proportional to the autocorrelator of the density operator (i.e., FT of $\langle\{\mathcal{N}(t),\mathcal{N}(t')\rangle\}_0$) Exercise: Do this, not really difficult**
- **The autocorrelator is a measure of the** *fluctuations in equilibrium*
- **The key physical idea embodied in the Fluctuation Dissipation Theorem:** *Fluctuations in equilibrium (how they correlated in time) completely govern the dissipation when the system is slightly disturbed*

Whats more?

- **Lots!**
- **Semiconductors/Ionic solids**
- **Phonon Transport**
- **Disordered systems**
- **Correlated systems**
- **Nanosystems – Landauer ideas**
- **...**