C. The Boltzmann Transport Equation

- A semi-classical, but general otherwise, approach to Transport Properties
- Works for $\vec{\mathcal{E}}$, $\vec{B}$, $\vec{\nabla} T$, $\vec{\nabla} n(\vec{r})$ and all kinds of collisions
- Under a "driving force", $f_{\text{non-equilibrium}} \neq f^{o}(\varepsilon)$

$f^{o}(\varepsilon)$ here is formally $f^{o} = \dfrac{1}{e^{(\varepsilon - E_F)/kT} + 1} = \dfrac{1}{e^{(\varepsilon(\vec{k}) - E_F)/kT} + 1} = f^{o}(\varepsilon) = f^{o}(\vec{k})$

If picking up the tail, then

$$f^{o} = e^{-(\varepsilon - E_F)/kT} = e^{-(\varepsilon(\vec{k}) - E_F)/kT} = e^{-(\frac{1}{2}m^{*}v^{2} - E_F)/kT}$$

$$= f^{o}(\varepsilon) = f^{o}(\vec{k}) = f^{o}(\vec{v})$$

In Equilibrium, $f^{o}(\vec{k}) = f^{o}(\varepsilon(\vec{k})) = \dfrac{1}{e^{(\varepsilon(\vec{k}) - E_F)/kT} + 1}$

When system is out of equilibrium, introduce $f(\vec{r}, \vec{k}, t)$

Aside: Recall phase space (x, p) or (x, k). We are generalizing $f^0(\vec{k})$ (no $\vec{r}$-dependence because temp. T is the same everywhere at equilibrium) to phase space. More generally, a band index "n" $f_n(\vec{r}, \vec{k}, t)$ should be included. But we consider only one band (e.g. CB for electrons).

In thermal equilibrium (1 band):

$$\underset{\substack{\#\text{ electrons}\\ \text{in CB}\\ \text{(for example)}}}{N} = \overset{\text{spin}}{2} \cdot \frac{V}{(2\pi)^3} \int d^3k \; f^0(\vec{k})$$

$$= \underbrace{\iint d^3r}_{\text{gives } V} \, d^3k \left(2 \cdot \frac{V}{(2\pi)^3} f^0(\vec{k}) \right)$$

$\left[\frac{N}{V} = n = \text{electron \# density} \right]$

[recall: $d^3k \to 4\pi k^2 dk$ plus $\varepsilon = \frac{\hbar^2 k^2}{2m^*}$, then

$$\int \frac{2V}{(2\pi)^3} (\cdots)\, d^3k$$
$$\downarrow$$
$$\int g(\varepsilon) (\cdots)\, d\varepsilon \;]$$

Driving Forces $\rightarrow$ $f(\vec{r}, \vec{k}, t)$

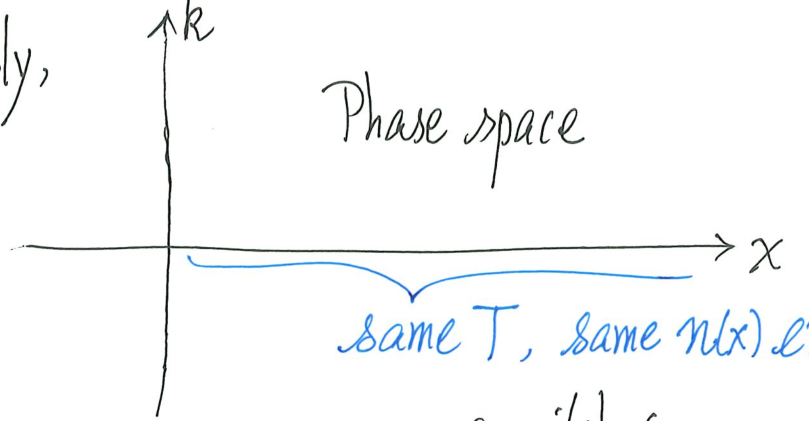
all currents should be due to the out-of-equilibrium $f(\vec{r}, \vec{k}, t)$

<u>Meaning</u>

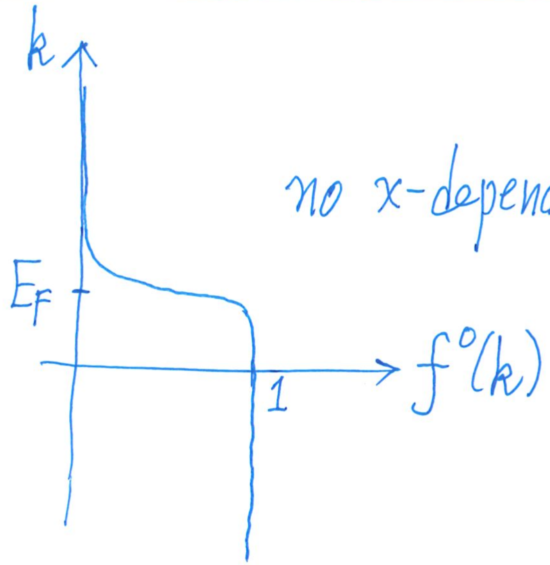
$$\boxed{2 \cdot \frac{1}{(2\pi)^3} f(\vec{r}, \vec{k}, t)\, d^3r\, d^3k = dn(\vec{r}, \vec{k}, t)}$$

= # electrons in volume element d^3r at $\vec{r}$ <u>AND</u> in the reciprocal space volume element d^3k at $\vec{k}$ at time t

Previously,

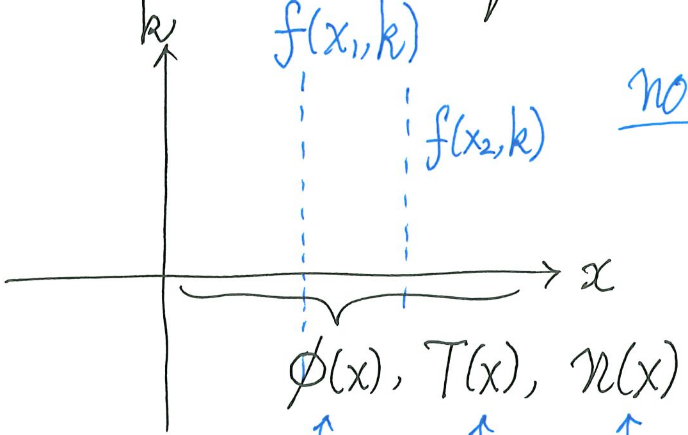


<u>equilibrium</u>



no x-dependence

But driven out of equilibrium in presence of driving forces...



<u>no reason</u> to expect $f(x_1,k) = f(x_2,k)$

$\phi(x)$ ← electric potential ($\vec{\mathcal{E}}$) (electrical conduction)

$T(x)$ ← $\vec{\nabla} T$ (thermal conduction)

$n(x)$ ← $\vec{\nabla} n$ (diffusion)

$\therefore$ Need $\underbrace{\text{an equation}}_{\boxed{\text{Boltzmann Equation}}}$ for $f(\vec{r}, \vec{k}, t)$ to <u>include the effects</u> of

(i) external forces (driving forces)

and (ii) scatterings

How to use $f(\vec{r},\vec{k},t)$, if we have solved it?

- Physical quantities (responses) can be expressed in terms of $f(\vec{r},\vec{k},t)$

e.g. $\vec{J}_e(\vec{r},t)$ = electrical current density (the $\vec{J}(\vec{r},t)$ in EM Theory)

$$\boxed{\vec{J}_e(\vec{r},t) = (-e)\int_{1^{st}\,B.Z.} d^3k\,\frac{2}{(2\pi)^3}\, f(\vec{r},\vec{k},t)\cdot \underbrace{\vec{v}(\vec{k})}_{\text{velocity of electron at } \vec{k}}}$$

$\left(\frac{1}{\hbar}\vec{\nabla}_{\vec{k}}\underbrace{E(\vec{k})}_{\text{band structure}}\right)$

Note: If $f = f^0(\vec{k})$, $\vec{J}_e = 0$ (due to symmetry of $E(\vec{k})$)

e.g. energy current density

$$\vec{J}_U(\vec{r},t) = \int_{1^{st}\,B.Z.} d^3k\,\frac{2}{(2\pi)^3}\, f(\vec{r},\vec{k},t)\cdot \overbrace{E(\vec{k})\,\vec{v}(\vec{k})}^{\text{energy moves}}$$

Setting up the Boltzmann Equation

Ideas: Both external forces and scattering cause electrons to change in $\vec{r}$ and in $\vec{k}$ $\Rightarrow$ $f(\vec{r},\vec{k},t)$ changes with time in general

Steady state: when external forces and scattering work together to maintain an out-of-equilibrium $f(\vec{r},\vec{k})$

Key idea

$$\boxed{\frac{\partial f(\vec{r},\vec{k},t)}{\partial t} = \left(\frac{\partial f(\vec{r},\vec{k},t)}{\partial t}\right)_{\text{field}} + \left(\frac{\partial f(\vec{r},\vec{k},t)}{\partial t}\right)_{\text{scattering}}}$$

How does f change?

due to fields ($\vec{\mathcal{E}}, \vec{B}, -\vec{\nabla}T, -\vec{\nabla}n$)

due to scatterings (phonons, impurities, defects, ...)

This is the Boltzmann Equation (primitive form)

$$\left(\frac{\partial f(\vec{r},\vec{k},t)}{\partial t}\right)_{field} \text{ term} \qquad \left(\frac{\partial f}{\partial t}\right)_{field} = \lim_{\Delta t\to 0}\left(\frac{f(\vec{r},\vec{k},t+\Delta t)-f(\vec{r},\vec{k},t)}{\Delta t}\right)_{field}$$

Key idea: If an electron has $\vec{r}$ and $\vec{k}$ at time $t+\Delta t$, then at an earlier time t, its position was $(\vec{r} - \underbrace{\vec{v}(\vec{k})\Delta t}_{\text{moved this much in } \Delta t \text{ to reach } \vec{r}})$ and its wavevector was $(\vec{k} - \underbrace{\dot{\vec{k}}\Delta t}_{\text{moved this much in } \Delta t \text{ to reach } \vec{k}})$

$$\therefore f(\vec{r},\vec{k},t+\Delta t) = f(\vec{r}-\vec{v}(\vec{k})\Delta t,\ \vec{k}-\dot{\vec{k}}\Delta t,\ t)$$

$$= f(\vec{r},\vec{k},t) - \vec{v}(\vec{k})\cdot \underbrace{\vec{\nabla}_{\vec{r}}}_{\text{gradient in } \vec{r}} f\,\Delta t - \dot{\vec{k}}\cdot \underbrace{\vec{\nabla}_{\vec{k}}}_{\text{gradient in } \vec{k}} f\,\Delta t \qquad (\text{order } \Delta t)$$

$$= f(\vec{r},\vec{k},t) - \vec{v}(\vec{k})\cdot\vec{\nabla}_r f\,\Delta t - \frac{\vec{F}_{ext}}{\hbar}\cdot\vec{\nabla}_{\vec{k}} f\,\Delta t \qquad \left(\because \hbar\frac{d\vec{k}}{dt} = \vec{F}_{ext}\right)$$

$$\Rightarrow \boxed{\left(\frac{\partial f(\vec{r},\vec{k},t)}{\partial t}\right)_{field} = -\vec{v}(\vec{k})\cdot\vec{\nabla}_r f - \frac{\vec{F}_{ext}}{\hbar}\cdot\vec{\nabla}_{\vec{k}} f}$$

Up to now, Boltzmann Equation becomes

$$\frac{\partial f(\vec{r},\vec{k},t)}{\partial t} = -\vec{v}(\vec{k})\cdot\vec{\nabla}_{\vec{r}} f - \frac{\vec{F}_{ext}}{\hbar}\cdot\vec{\nabla}_{\vec{k}} f + \left(\frac{\partial f}{\partial t}\right)_{scattering}$$

- If nothing is there to cause spatially non-uniform distribution, then $f(\vec{k},t)$ only and $\vec{\nabla}_{\vec{r}} f$ term vanishes (e.g. no $-\vec{\nabla} n(\vec{r})$, or $\underbrace{-\vec{\nabla}\mu(\vec{r})}_{\text{gradient of chemical potential}}$)

Next, we handle $\left(\frac{\partial f}{\partial t}\right)_{scattering}$

$\left(\frac{\partial f(\vec{r},\vec{k},t)}{\partial t}\right)_{scattering}$ term under the Relaxation Time Approximation

- Recall: $f(\vec{r},\vec{k},t)$ relaxes back to $f^0(\vec{k})$ by scattering processes

$$\boxed{\left(\frac{\partial f}{\partial t}\right)_{scattering} \cong -\frac{\left(f(\vec{r},\vec{k},t) - f^0(\vec{k})\right)}{\tau(\vec{k})}}$$

This is the Relaxation Time Approximation

- $\tau(\vec{k})$ (or $\tau(\vec{v})$, $\tau(\varepsilon)$, $\tau(\vec{p})$) is relaxation time for an electron in Bloch state $\vec{k}$
- In principle, $\tau(\vec{k})$ (or $1/\tau(\vec{k})$) can be calculated quantum mechanically (time-dependent perturbation theory) for given scattering process
- $\tau(\vec{k})$ depends on $\vec{k}$ (or energy ε, or velocity $\vec{v}$) in general
- $\tau(\vec{k}) \approx \tau$ for simplicity and $\tau(\vec{k})$ can be treated empirically

Boltzmann Equation within relaxation time approximation

$$\boxed{\left(\frac{\partial f}{\partial t}\right) = -\vec{v}(\vec{k})\cdot\vec{\nabla}_{\vec{r}} f - \frac{\vec{F}_{ext}}{\hbar}\cdot\vec{\nabla}_{\vec{k}} f - \frac{\left(f - f^{0}(\vec{k})\right)}{\tau(\vec{k})}}$$

- Still very general
- Starting point for studying transport properties
- Good for $\vec{\mathcal{E}}$, $\vec{B}$, $-\vec{\nabla}T$, $-\vec{\nabla}\mu(\vec{r})$, $\cdots$; and various processes
- Can solve for $f(\vec{r},\vec{k},t)$, thus transient response (time before steady state)
- For studying Steady State properties, set $\left(\frac{\partial f}{\partial t}\right) = 0$, solve for $f(\vec{r},\vec{k})$
- $\underbrace{\vec{\mathcal{E}},\ \vec{B} \text{ go into } \vec{F}_{ext};\ \vec{\nabla}T,\ \vec{\nabla}\mu(\vec{r}) \text{ go into } \vec{\nabla}_{\vec{r}} f}_{\text{can solve } f(\vec{r},\vec{k}) \text{ to any order of forces (linear and nonlinear response)}}$
- Readily generalized to study out-of-equilibrium phonon distributions

Linear Response: a humble strategy with a big idea

Idea: $\vec{F}_{ext} = -e\vec{\mathcal{E}}$, solve steady state $f \cong \underbrace{f^0}_{\vec{J}_e = 0} + \underbrace{\delta f}_{\text{gives } \vec{J}_e \neq 0}$

and aim at $\underbrace{\delta f \text{ to } \mathcal{E}^1}_{1^{st} \text{ order in } \mathcal{E}}$

1^{st} order in $\mathcal{E}$ (not-so-strong $\mathcal{E}$) and ignore $\sim \mathcal{E}^2, \sim \mathcal{E}^3$ terms

$\vec{J}_e \sim \delta f \sim \vec{\mathcal{E}}$, so $\vec{J}_e = \sigma \vec{\mathcal{E}}$

- σ does not depend on $\vec{\mathcal{E}}$ ($\because \vec{\mathcal{E}}^1$ explicitly taken out)
- σ can be expressed in terms of quantities evaluated at equilibrium!

$\therefore$ $\boxed{\text{In linear response, we aim at finding } f(\vec{r}, \vec{k}) \text{ to } 1^{st} \text{ order in the driving (external) forces.}}$

Stimulations		Response Functions
$\vec{\mathcal{E}}$	electric field	conductivity
plus $\vec{B}$	magnetic field	Magnetoresistance, Hall coefficient
$-\vec{\nabla}T$	temperature gradient	thermal conductivity
$-\vec{\nabla}\mu$	gradient of chemical potential	thermal power, Peltier coefficient
	⋮	⋮

Scattering Processes for achieving Steady State

- electron-phonon, impurities (ionized, un-ionized), defects
  sample boundary   low-temp

All can be treated under one roof! (The Boltzmann Equation)

Remarks

(i) $(\vec{r}, \vec{p})$ phase space (instead of $(\vec{r}, \vec{k})$) useful in Solid States, then $f(\vec{r}, \vec{p}, t)$

$$\frac{\partial f}{\partial t} = -\vec{v} \cdot \vec{\nabla}_{\vec{r}} f - \vec{F} \cdot \vec{\nabla}_{\vec{p}} f - \frac{(f - f^0)}{\tau}$$

(ii) There is a quantum version of Boltzmann's approach based on Wigner Functions

(iii) Statistical Dynamics : How systems approach equilibrium (beyond equilibrium statistical mechanics)