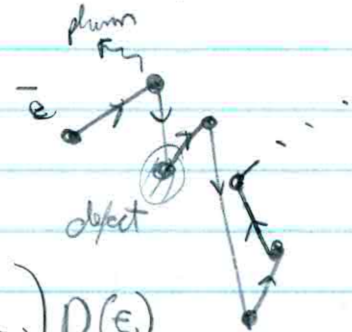
The drift – diffusion eqn:

Lecture #23 : Thermal conductivity and electrical conductivity

▶ The interaction of electrons with defects and phonons leads to a mean relaxation time τ for electrons $\underset{\substack{\uparrow \\ \text{mean} \\ \text{free} \\ \text{path}}}{l} = \bar{v}\, \underset{\substack{\uparrow \\ \text{mean time} \\ \text{between collisions} \\ \text{"relaxation time"}}}{\tau}$. How to relate electrical conductivity to τ?

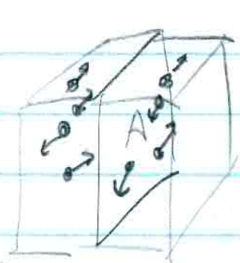


$$\frac{1}{\tau_K} = \frac{2\pi}{\hbar}\left(|V_{e\text{-}ph}|^2 + |V_{e\text{-}defect}|^2 + \dots\right) D(\epsilon_K)$$

- Ballistic versus diffusive behavior.

▶ Same for phonons: But in insulators, phonons carry heat $\Rightarrow$ Heat conductivity is determined by τ!

Diffusion eqn approach: Describe motion of particles at scales $x \gg l$.



$dx = \frac{\bar{v}_x t}{2}$ $\quad \frac{\bar{v}_x t}{2} = dx$

$$N^{\text{Left}\to\text{right}}_{\text{particles}} = A \frac{\bar{v}_x t}{2} \underset{\substack{\downarrow \\ \text{density}}}{n_{x-dx}} \Rightarrow \frac{1}{A}\frac{dN^{\text{Left}\to\text{right}}_{\text{particle}}}{dt} = \underbrace{\sigma^+_x}_{\substack{\text{Flux or current} \\ \text{density}}} = \frac{1}{2}\bar{v}_x n_{x-dx}$$

Similarly, $G_x^- = \frac{1}{2}\bar{v}_x \, n_{x+dx}$

Total current:

$$G_x = G_x^+ - G_x^- = \underbrace{\bar{v}_x \left(\frac{n_{x-dx} - n_{x+dx}}{2dx}\right)}_{-\frac{\partial n(x)}{\partial x}} \underbrace{dx}$$

Take smallest possible value of dx, $dx = \ell_x$ (mean free path)

$$\Rightarrow G_x = -\underbrace{\bar{v}_x}_{=\frac{\bar{v}}{\sqrt{3}}} \underbrace{(\bar{v}_x \tau)}_{\ell} \frac{\partial n}{\partial x} = -\underbrace{\left(\frac{1}{3}\bar{v}^2 \tau\right)}_{D} \frac{\partial n}{\partial x} = -D \frac{\partial n}{\partial x}$$

(assumed $\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 = 3\bar{v}_x^2$)

Define Diffusion constant as $\boxed{D = \frac{1}{3}\bar{v}^2 \tau = \frac{1}{3}\frac{\ell^2}{\tau}}$

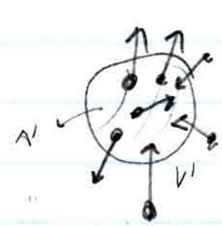
$$\Rightarrow \boxed{\vec{G} = -D \vec{\nabla} n}$$

"Diffusion approximation": $n(\vec{r})$ changes slowly in the scale $x \sim \ell$

Can also write $\vec{G} = n\vec{v} \Rightarrow \boxed{\vec{v} = -D\frac{\vec{\nabla} n}{n}}$

(where $\vec{v}$ is a drift velocity).

Conservation law: # of particles is conserved



$$\frac{\partial}{\partial t}\left(\int_{V'} d^3r \, n(\vec{r})\right) = \int_{A'} dA \left(\text{Flux in} - \text{Flux out}\right) = -\int_{A'} d\vec{A} \cdot \vec{G}$$

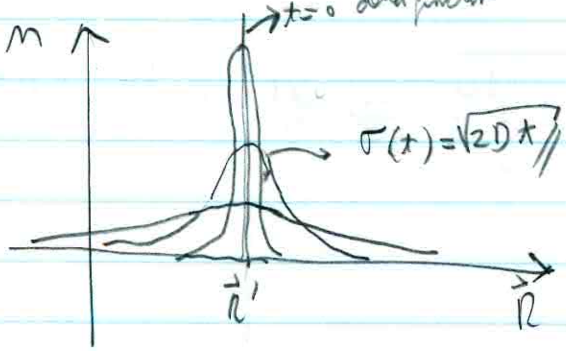
$$\int_{V'} d^3r \frac{\partial n(\vec{r})}{\partial t} = -\int_{V'} d^3r \, \nabla \cdot \vec{G} \Rightarrow \int_{V'} d^3r \left(\frac{\partial n}{\partial t} + \vec{\nabla}\cdot\vec{G}\right) = 0 \quad \forall \, V' \text{ volumes.}$$

$$\Rightarrow \quad \frac{\partial n}{\partial t} = -\vec{\nabla}\cdot\vec{G} = -\vec{\nabla}\cdot\left(-D\vec{\nabla} n\right) = D\nabla^2 n$$

$$\boxed{\frac{\partial n}{\partial t} = D\nabla^2 n}$$

Diffusion eqn.

If at $t=0$, $n(\vec{r}, t=0) = \delta(\vec{r}-\vec{r}\,') \Rightarrow n(\vec{r}, t) = \dfrac{e^{-\frac{|\vec{r}-\vec{r}\,'|^2}{4Dt}}}{(4\pi D t)^{3/2}}$



$$\langle x^2\rangle = \sigma^2 = 2Dt$$

$\Rightarrow \sqrt{\langle x^2\rangle} \propto \sqrt{t}$ "Brownian motion".

(Einstein's Ph.D. thesis)

For any initial condition $n(\vec{r}, t=0)$:

$$n(\vec{r}, t) = \int d^3r'\, n(\vec{r}\,', t=0)\, \underbrace{\frac{e^{-\frac{|\vec{r}-\vec{r}\,'|}{4Dt}}}{(4\pi D t)^{3/2}}}_{\text{"Green's fnc"}}$$

This is the general solution of the Diffusion eqn.

Thermal conductivity (phonon current in insulators)

u = energy density

$$\underbrace{du}_{} = \underbrace{\bar{E}}_{\text{Avg energy of phonons}} \underbrace{dn}_{\text{Avg \# of phonons}} \Rightarrow \frac{\partial u}{\partial t} = D_u \nabla^2 u$$

$$\left(D_u = \frac{1}{3} \bar{v}_{ph}^2 \tau\right)$$

From $C_V = \left(\frac{\partial U}{\partial T}\right)_V = V\left(\frac{\partial u}{\partial T}\right)_V \Rightarrow (dT) = \frac{V\,du}{C_V} \Rightarrow \frac{\partial T}{\partial t} = \frac{V}{C_V}\frac{\partial u}{\partial t} = \frac{V}{C_V} D_u \nabla^2 u$

$$\Rightarrow \boxed{\frac{\partial T}{\partial t} = D \nabla^2 T}$$

Energy flux or current: $\vec{\phi} = u\vec{v} = -D_u \vec{\nabla} u = -K \vec{\nabla} T$

"Thermal conductivity"

Use $dT = \frac{V}{C_V} du \Rightarrow -D_u \frac{C_V}{V} \vec{\nabla} T = -K \vec{\nabla} T$

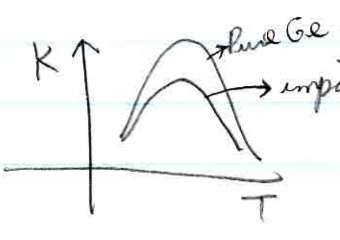
$$\Rightarrow \boxed{K = \frac{D_u C_V}{V}}$$

At low T, expect $l \to \infty \to L \Rightarrow D = \frac{\bar{v} l}{3} \approx \frac{v_{ph}}{3} L = \text{Const}$

size of sample

Low T $\Rightarrow K \propto C_V \propto T^3$ increases with increasing T

High T $\Rightarrow \frac{1}{\tau} \propto \omega^5 \propto T^5 \Rightarrow D = \frac{\bar{v}^2}{3} \tau \propto T^{-5} \Rightarrow K \propto T^{-5} \Rightarrow$ decreases with increasing T.



Electrical conductivity

Electric field produces a drift: $\vec{a} = \frac{d\vec{v}}{dt} = \frac{\vec{F}}{m} = \frac{q}{m}\vec{E}$

$\vec{F}$ is "drift force"

Assuming the electron propagates "ballistically" until it scatters:

$$\langle \vec{v} \rangle = \vec{a}\langle t \rangle = \vec{a}\,\tau = \frac{\vec{F}}{m}\tau$$

Current density: $\vec{J} = q\vec{v}\,n = q\frac{\vec{F}}{m}\tau n = \underbrace{\frac{q^2\tau n}{m}}_{\sigma}\vec{E}$

Def. of electrical conductivity: $\vec{J} = \sigma\vec{E}$

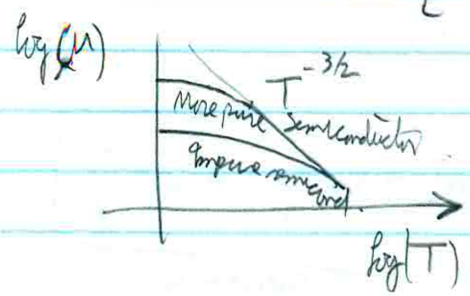
$$\sigma = \frac{q^2\tau}{m} n = q\mu n \Rightarrow \boxed{\mu = \frac{q\tau}{m}}$$

where $\vec{v} = \mu\vec{E}$ is def. of mobility

D and μ are connected by τ: $D = \frac{1}{3}\underbrace{(v)^2}_{\frac{1}{2}m(v)^2 = \frac{3}{2}k_BT}\tau = \frac{1}{3}\cancel{3}\frac{k_BT}{m}\underbrace{\tau}_{\frac{m\mu}{q}} = \frac{k_BT\mu}{q}$ "Einstein's relation"!

High $T \Rightarrow$ e-ph scattering dominates $\frac{1}{\tau} \propto T^{3/2} \Rightarrow \mu \propto \tau \propto T^{-3/2}$

Low $T \Rightarrow$ e-defect dominates $\frac{1}{\tau}$ independent of T (Because when $(ka) \ll 1$ e-defect is independent of k)



Drift + diffusion

Combine both effects:

$$\vec{v} = -D\frac{\vec{\nabla} n}{n} + \frac{\tau}{m}\vec{F}$$

$$n\vec{v} = -D\vec{\nabla} n + \frac{\tau}{m} n\vec{F} \Rightarrow \vec{\nabla}\cdot(n\vec{v}) = -D\nabla^2 n + \frac{\tau}{m}\vec{\nabla}\cdot(n\vec{F})$$

But from particle conservation, the left hand side equals to $-\frac{\partial n}{\partial t}$:

$$\frac{\partial n}{\partial t} = D\nabla^2 n - \frac{\tau}{m}\vec{\nabla}\cdot(n\vec{F})$$

Assume: $\begin{cases} n(\vec{r}) = n_0 e^{+\frac{\mu(\vec{r})}{k_B T}} & \text{"Local" chemical potential} \Rightarrow \vec{\nabla} n = n_0 e^{+\frac{\mu}{k_B T}}\left(+\frac{\vec{\nabla}\mu}{k_B T}\right) \\ \vec{F} = -\vec{\nabla} U & \Rightarrow \frac{\vec{\nabla} n}{n} = +\frac{\vec{\nabla}\mu}{k_B T} \end{cases}$

$$\Rightarrow \vec{v} = -D\left(+\frac{\vec{\nabla}\mu}{k_B T}\right) - \frac{\tau}{m}\vec{\nabla} U = -\underbrace{\left(\frac{k_B T\tau}{m}\right)}_{D}\frac{1}{k_B T}(\vec{\nabla}\mu) - \frac{\tau}{m}\vec{\nabla} U$$

$$\vec{v} = -\frac{\tau}{m}\vec{\nabla}\left(\mu(\vec{r}) + U(\vec{r})\right)$$

Shows why chemical potential is called a potential: Diffusion can be related as motion arising from the gradient of μ, just like drift is motion arising from the gradient of a potential.

From $\frac{\partial n}{\partial t} = -\vec{\nabla}\cdot(n\vec{v})$ we get

$$\Rightarrow \boxed{\frac{\partial \mu}{\partial t}(\vec{r},t) = \frac{\tau}{m}(\vec{\nabla}\mu)\cdot\vec{\nabla}(\mu + U) + \frac{k_B T}{m}\tau\nabla^2(\mu + U)}$$

Drift-diffusion equation

Use $\vec{\nabla}[\phi\vec{A}] = \phi\vec{\nabla}\cdot\vec{A} + (\vec{\nabla}\phi)\cdot\vec{A}$

Describes non-equilibrium behavior of carriers in time

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Relationship between heat conductivity (due to free electrons) and electrical conductivity :

$$\begin{cases} \vec{Q} = n \bar{E} \vec{v} \\ \vec{J} = n q \vec{v} \end{cases}$$

$$K = \frac{D_u C_v}{V} = \underbrace{\frac{1}{3} v_F^2 \tau}_{D_u} \underbrace{\frac{C_v}{V}}$$

Use Sommerfeld relation: $C_v = \frac{\pi^2}{2} \frac{k_B T}{E_F} k_B N = \frac{\pi^2}{2} \frac{k_B T}{\frac{1}{2} m v_F^2} k_B N$

$$K = \frac{1}{3} \cancel{v_F^2} \underbrace{\left(\frac{m\sigma}{e^2 \cancel{n}}\right)}_{\text{From } \sigma = \frac{ne^2\tau}{m}} \frac{\pi^2 k_B^2 T}{m \cancel{v_F^2}} \frac{\cancel{N}}{\cancel{V}} = \frac{\pi^2}{3} \frac{k_B^2 T}{e^2} \sigma \quad //$$

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

Wiedemann-Franz law