

Physics 474 – Applied Solid State Physics - Course Notes

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Introduction:

Notes written while following Dr. Alannah Hallas's PHYS 474 UBC lecture notes. If any errors are found in the notes, feel free to email me at tobias.faehndrich@gmail.com. Overleaf formatting was copied from Rio W.

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1 Introduction

This lecture talked about the course structure, grading and basic questions about solid state physics and why it is important.

2 Heat Capacity Models I — Boltzmann and Einstein

Chapter 2 covers the Specific Heat of Solids

Recall:

- Heat capacity of material is how much energy (heat) you need to add to change the temp (by 1K).

$$C = \frac{d \langle E \rangle}{dT} \quad (2.1)$$

- Solids are incompressible so $C_v \simeq C_p$
- “specific heat” and “heat capacity” are used interchangeably
- strictly we are speaking about molar heat capacity (per mol of material) with units of $[J/\text{mol} \cdot K]$
-

$$1 \text{ mol} = N_A = 6.022 \times 10^{23}$$

Why do we care?

- gives us info about thermally excited states and so we can look for phase transitions
- largest factor in specific heat is atomic vibrations

Heat capacity of an ideal monoatomic gas at constant volume (3-D)

- Equipartition theorem: each quadratic degree of freedom in the energy contributes $\frac{1}{2}k_B T$ to $\langle E \rangle$
- Ideal Gas only has kinetic energy with x, y, and z components so we get

$$\langle E \rangle = \frac{3}{2}k_B T \quad (2.2)$$

per atom

$$\langle E \rangle = \frac{3}{2}RT \quad (2.3)$$

per mol

$$C = \frac{d \langle E \rangle}{dT} = \frac{3}{2}R \quad (2.4)$$

- Note that:

$$R = N_A \cdot k_B = 8.314 J/\text{mol} K$$

Experimental observations from 1820-1910

- Dulong-Petit Law:

$$C = 3k_B \quad (2.5)$$

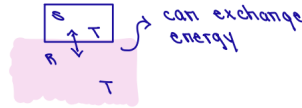
per atom (or $C = 3R$ per mol)

- Boltzmann made classical statistical model that explained the Dulong-Petit result
 - It treated each atom as a **simple harmonic oscillator**
 - each of which were held in place in each direction by a spring vibrating at a frequency, ω .

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{k\hat{x}^2}{2} \quad (2.6)$$

where $\omega = \sqrt{\frac{k}{m}}$ which you will show on HW1 that it gives $C = 3R$

- But this still does not explain diamond or any solid significantly below room temperature
- Thermodynamics refresher
 - The probability of finding a system, S, that is in thermal equilibrium with a reservoir, R, at some temperature, T, in a given energy state, E_i ,



is given by

$$\mathbb{P}(E_i) \propto e^{-\beta E_i}$$

where $\beta = \frac{1}{k_B T}$ with units of $\left[\frac{1}{\text{energy}} \right]$

Note that the exponential term is the Boltzmann distribution

- We can use the **partition function (Z)** to normalize our probabilities.
i.e. so that we get $\sum_i \mathbb{P}(E_i) = 1$

$$\mathbb{P}(E_i) = \frac{e^{-\beta E_i}}{e^{-\beta E_1} + e^{-\beta E_2} + \dots} = \frac{e^{-\beta E_i}}{Z}$$

where $Z = \sum_i e^{-\beta E_i}$

- The **expectation value (or thermal average)** for a given quantity is the sum of the possible values weighted by their normalized probabilities.

$$\langle x \rangle = \sum_i x_i \mathbb{P}(E_i) = \sum_i x_i \left(\frac{e^{-\beta E_i}}{Z} \right) = \frac{1}{Z} \sum_i x_i e^{-\beta E_i}$$

where $Z = \sum_i e^{-\beta E_i}$

- Taking the **derivative of the partition function with respect to β** we uncover a useful trick.

$$\frac{dZ}{d\beta} = \sum_i (-E_i) e^{-\beta E_i}$$

Divide by $-Z$ and we get

$$\frac{-1}{Z} \frac{dZ}{d\beta} = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} = \langle E \rangle$$

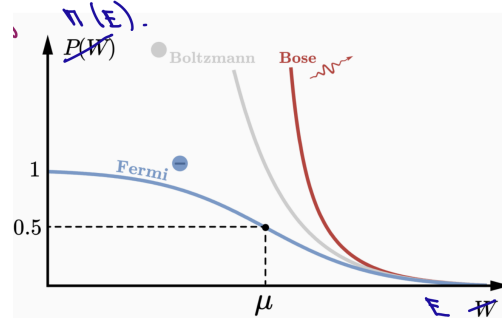
Thus we get the equation that relates the average internal energy to the partition function.

$$\langle E \rangle = \frac{-1}{Z} \frac{dZ}{d\beta}$$

which is useful because we want to calculate $C = \frac{d\langle E \rangle}{dT}$

- **Bose-Einstein and Fermi-Dirac Statistics** to describe the energy distribution of quantum particles
 - * BE: photons, cooperes pairs, He^4 , atomic vibrations (phonons)

- The Bose occupation factor n_B gives the number of bosonic particles occupying a given energy state at a given temperature.
As $T \rightarrow 0$, all particles occupy the ground state.



$$n_B = \frac{1}{e^{(E-\mu)\beta} - 1}$$

- where in the high T limit looks identical to Boltzmann distribution.
- as $T \rightarrow 0$, $\beta \rightarrow \infty$ and only the lowest E state ($E \approx \mu$) is occupied
- and μ is the chemical potential (energy cost to add a particle to the system)
- * FD: electrons, other leptons, He^3
 - The Fermi factor n_F gives the number of fermionic particles occupying a given energy state at a given temperature where each state can only be single occupied due to the Pauli exclusion principle.

$$n_F = \frac{1}{e^{(E-\mu)\beta} + 1}$$

- also looks identical to the Boltzmann distribution in the high T limit

3 Heat Capacity Models II — Einstein Revisited and Debye

Einstein's model for specific heat

- Einstein improved upon Boltzmann's model by treating each atom as a quantum mechanical simple harmonic oscillator, still being held in place in each spatial direction by a spring that vibrates at a frequency, ω .

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

where ω is the frequency of the spring, and n is the quantum number.

- Note that in this model the atoms are still not connected to each other.
- You can follow the steps:

- Find Z
- $\langle E \rangle = \frac{1}{Z} \frac{dZ}{d\beta}$,
- $C = \frac{d\langle E \rangle}{dT}$

and then you get

$$C = 3R(\beta\hbar\omega)^2 \cdot \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

Note that this expression depends on temperature!

- For HW1:

$$\sum_n x^n = \frac{1}{1-x} \quad \text{for } |x| < 1$$

and

$$\sinh(x) = \frac{e^x - e^{-x}}{2}$$

- The **high T limit of Einstein's model** gives the expected **Dulong-Petit** value

$$\text{As } T \rightarrow \infty, \beta \rightarrow 0$$

You can Taylor expand for the exponential term in the denominator

$$C \approx 3R(\beta\hbar\omega)^2 \cdot \frac{(1 + \beta\hbar\omega)^{\sim 0}}{(\beta\hbar\omega)^2}$$

$$\boxed{C = 3R} \quad \text{which is the Dulong Petit value!}$$

- The **low T limit** accounts for the observation that specific heat decreases with T

$$\text{As } T \rightarrow 0, \beta \rightarrow \infty$$

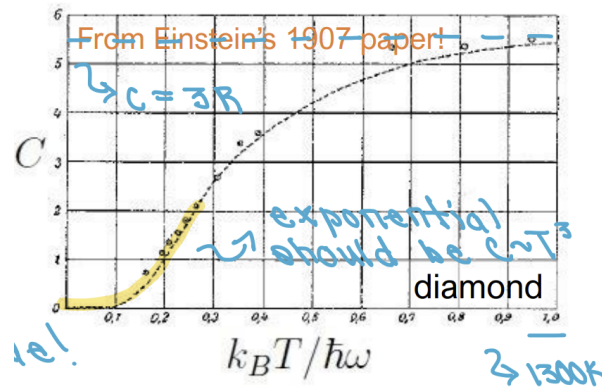
$$C \approx 3R(\beta\hbar\omega)^2 \cdot \left(\frac{1}{e^{\beta\hbar\omega}} \right)$$

Correctly shows that

$$\text{As } T \rightarrow 0, C \rightarrow 0$$

And also the discrepancy for diamond where C increased to 3R above room temp.

But incorrectly suggests an exponential decrease at low T. The data (Einstein's 1907 paper) showed that at low T, $C \sim T^3$.



- Einstein temperature is then defined as

$$T_E = \frac{\hbar\omega}{k_B}$$

where you can think of a materials hardness to be related to the stiffness of the spring holding it in place

$$T_E \propto \omega, \quad \text{and} \quad \omega = \sqrt{\frac{k}{m}}$$

so that the the mass of the atom also determines this temperature.

- You can calculate the typical frequency scale using a typical Einstein temperature using

$$f = \frac{\omega}{2\pi}$$

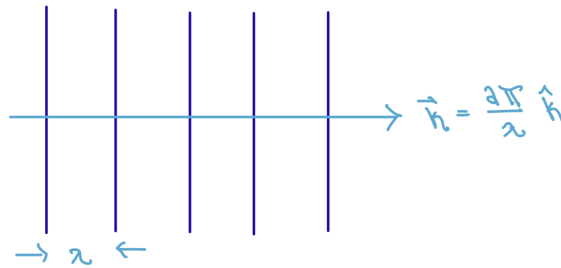
Debye's model for specific heat

- Debye took Einstein's calculation one step further by realizing that **the atomic vibrations in solids are sound waves** and therefore – not only should the energy levels be quantized – but the energy should vary as a function of the wave vector, k .

– Einstein: $\omega = \text{constant}$

– Debye: $\omega(\vec{k}) = v|\vec{k}|$

- How should we think about the wavevector, k ?
e.g. 2D plane wave?



k-space is useful because solids are periodic

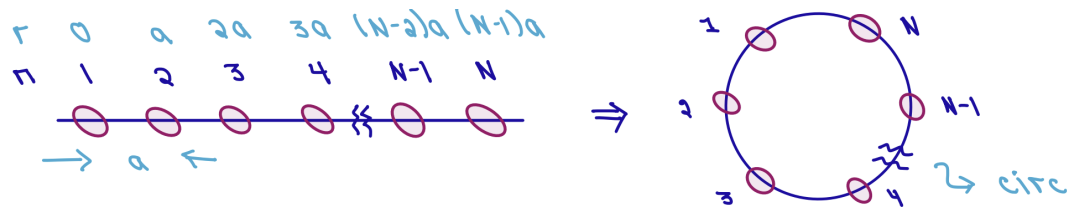
other names:

- momentum space
- reciprocal space
- Q space

Normal space is called "real space"

Periodic (Born-von Karman) boundary conditions (equivalent to particle in a box, but easier)

- Rather than treating our solids as having fixed end points, it is very convenient to apply **periodic boundary conditions**.
- In 1D this means taking a very long chain and attaching the ends together.
- Surfaces account for only a tiny fraction of a material so this is a reasonable thing to do.



$$L = N \cdot a$$

- This imposes a condition on the possible k-values: the values of k are quantized!
- A wave e^{ikr} must have the same value at r and $r + L$:

$$e^{ikr} = e^{ik(r+L)} \Rightarrow e^{ikL} = 1 \Rightarrow k \cdot L = 2\pi n \quad (n = \text{integer})$$

$$k = \frac{2\pi}{L} n$$

k is quantized! and $\Delta n = 1 \Rightarrow \delta k = \frac{2\pi}{L}$ so that $L \gg 1$, then $\delta k \ll 1$.

- In 3D ($v = L^3$) we can use the same trick except the solid gets folded into a hypertorus.

- allowed k states $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$
- Volume of a k-point ($\Delta n_i = 1$): $\delta k = \left(\frac{2\pi}{L}\right)^3$

- Since the number of allowed wave vectors is discrete, we can count them:

$$\#k\text{-points} = \sum_k = \frac{\text{volume of k space}}{\text{volume of k point}} = \frac{\int d\vec{k}}{\left(\frac{2\pi}{L}\right)^3}$$

- We can convert the sum over all k to a 1D integral (assume spherical symmetry).

$$\int_{-\infty}^{\infty} d\mathbf{k} \rightarrow \int_0^{\infty} d\varphi \int_0^{\pi} d\theta \sin(\theta) \cdot \int_0^{\infty} k^2 dk$$

For the 3D. Can check 2D and 1D too.

- Now pulling the pieces together for Debye's model, we can calculate the specific heat by starting with an expression analogous to Einstein's except where ω depends on \mathbf{k} .
 - Einstein:

$$\langle E \rangle = 3\hbar\omega \left[n_B(\beta\hbar\omega) + \frac{1}{2} \right]$$

(from $\langle E \rangle = -\frac{1}{Z} \frac{dZ}{d\beta}$)

- Debye:

$$\langle E \rangle = 3 \sum_{\mathbf{k}} \hbar\omega(\mathbf{k}) \left[n_B(\beta\hbar\omega(\mathbf{k})) + \frac{1}{2} \right]$$

(where $\omega = v|\vec{k}|$)

- We can use the relationship above to then convert our sum to an integral – Then, it is preferable to evaluate this integral with respect to ω instead of k .
 1. Convert $\sum_{\vec{k}}$ to $\int d\vec{k}$
 2. Convert 3D integral to 1D
 3. Change of variable, $k = \frac{\omega}{v}$, $dk = \frac{1}{v} d\omega$
 4. Result:

$$\langle E \rangle = \int_0^{\infty} d\omega \cdot \left[L^3 \cdot \frac{12\pi\omega^2}{(2\pi)^3 v^3} \right] \hbar\omega \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right)$$

Note the velocity term!

4 Heat Capacity Models III — Drude Model

Recall: **The Density of states**

- It is conventional to express integrals of this type in terms of the density of states, $g(\omega)$, which is defined as the number of states per unit frequency interval, i.e.,

$$\langle E \rangle = \int_0^\infty d\omega \, g(\omega) \hbar\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right]$$

where $\beta = \frac{1}{k_B T}$, and k_B is the Boltzmann constant.

$$g(\omega) = L^3 \frac{12\pi\omega^2}{(2\pi)^3 v^3}$$

- The density of states tells us how many new modes (sound waves here) are available at a given temperature / frequency ($\hbar\omega = k_B T$).
- The DOS for the Einstein model would look like a delta function at $\omega = \omega_E$.
- The DOS for the Debye model is a parabola ($g(\omega) \propto \omega^2$), which is a good approximation for low frequencies.
- Solving for the integral for $\langle E \rangle$ (as done in HW #1) gives:

$$\langle E \rangle \propto T\text{-independent} + aT^4$$

where the T-independent term is the zero-point energy, and the aT^4 term is the contribution from the phonons. a being some constant.

- The low T limit accounts for the T^3 law

$$\frac{d\langle E \rangle}{dT} = C \propto aT^3$$

which agrees with experiment.

- The high T limit does not saturate at the Dulong-Petit Law value,

$$C \propto aT^3$$

still at all temperatures, and never saturates to the Dulong-Petit Law value of $3Nk_B$.

- Debye comes up with a solution to this problem, imposing that there should only be as many modes as there are degrees of freedom, i.e. integrate between 0 and ω_{cutoff}

$$3N = N_{\text{atoms}} \cdot 3 = \# \text{ allowed modes}$$

This was built into Einstein's calculation.

$$3N = \int_0^{\omega_{\text{cutoff}}} d\omega \, g(\omega)$$

then evaluate this integral to find the cutoff frequency, ω_{cutoff} .

- This now gives the correct high T limit agreeing with the Dulong-Petit Law:

$$\langle E \rangle = \int_0^{\omega_{\text{cutoff}}} d\omega g(\omega) \hbar\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right] \Rightarrow 3RT \text{ as } T \rightarrow \infty$$

where R is the gas constant, and $3R$ is the Dulong-Petit Law value.

- This cutoff frequency is the Debye frequency, ω_D , and the Debye temperature is defined as:

$$\omega_{\text{cutoff}} = \omega_D = \sqrt[3]{\frac{6\pi^2 N^3}{V^3}} = \sqrt[3]{6\pi^2 n v^3}$$

where n is the number density of atoms ($n = \frac{N}{V}$), and v is the speed of sound in the material.

- T_D is the Debye temperature (also called θ_D)

$$T_D = \frac{\hbar\omega_D}{k_B}$$

- If a material undergoes a phase transition causing its volume to half. What will happen to the Debye temperature? (assume v is constant - is this a good assumption?)

$$- T_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k_B} \sqrt[3]{6\pi^2 n v^3}$$

- n will double, so T_D will increase by a factor of $\sqrt[3]{2}$.

- If the speed of sound is not constant, then the change in T_D will depend on how the speed of sound changes with volume.

- Debye and Einstein are similar, but Debye model is more accurate for low temperatures.
- Note that at intermediate temperatures, the integral in the Debye formulation can only be solved numerically.
- Debye model very successful, but not perfect:
 - Less accurate at intermediate temperatures.
 - Introduction of ω_{cutoff} is somewhat arbitrary.
 - Assumption of $\omega = vk$ becomes questionable for short wavelengths (high frequencies).
 - Metals have an additional T-linear contribution to C that is missed by the Debye model.

4.1 Drude Theory (Chapter 3)

- So far, we've talked about atomic vibrations (effectively, a property of the nucleus). next we are going to talk about the conduction of electricity (a property of the electrons).
- What we already know from real life: some materials conduct electricity and are therefore metals, and others do not. We are going to skip over (for now) what makes a material a metal and jump straight into understanding the properties of the conduction electrons.
- Basic idea: Drude (Drew-duh) extended Boltzmann's kinetic theory of gases (see the ideal gas law) to the motion of electrons in a metal (no atoms, just a gas of electrons).

Assumptions of the Drude model

- The basic assumptions of the Drude model are:
 1. The electrons have some characteristic scattering time, τ (material dependent, average time between collisions). The probability of scattering in a time interval dt is $P = \frac{dt}{\tau}$. (reasonable. note that it assumes nothing about nature of scattering).
 2. After scattering, the electron has zero kinetic energy (i.e. $\vec{p} = 0$). This is questionable, but true on average.
 3. The electrons will respond to externally applied electric and magnetic fields. This is reasonable, electrons are charged.

Equation of motion for the Drude Model

- In order to understand the behaviour of the conduction electrons, we will start by defining the average momentum for an electron, which depends on whether or not it experienced a scattering event.

time dt later:

$$\begin{aligned}\langle \vec{p}(t + dt) \rangle &= \mathbb{P}_{\text{no scatter}} \cdot \vec{p}_{\text{no scatter}} + \mathbb{P}_{\text{scatter}} \cdot \vec{p}_{\text{scatter}} \\ &= \left(1 - \frac{dt}{\tau}\right) \cdot (\vec{p}(t) + \vec{F}dt) + \left(\frac{dt}{\tau}\right) \cdot 0\end{aligned}$$

where $d\vec{p} = \vec{F}dt$ and Lorentz force $\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B})$

$$\langle \vec{p}(t + dt) \rangle = \vec{p}(t) - \frac{\vec{p}(t)dt}{\tau} + \vec{F}dt - \frac{\vec{F}dt^2}{\tau}$$

- For $dt \ll 1$, we can keep only terms that are of first-order in dt :

We get an equation of motion!

$$\boxed{\frac{d\vec{p}}{d\tau} = \vec{F} - \frac{\vec{p}(t)}{\tau}}$$

last term acts like a drag force on the electron.

- What does this give in the absence of any applied field? Does that make sense?

$$\vec{F} = 0 \Rightarrow \frac{d\vec{p}}{d\tau} = -\frac{\vec{p}(t)}{\tau}$$

$$\vec{p}(t) = \vec{p}(0) \cdot e^{-\frac{t}{\tau}}$$

which gives an exponential decay of the momentum of the electron to zero. In the model this makes sense, but in real life this is not the case.

5 Electrical conductivity and the Hall effect

5.1 Electrical conductivity in the Drude model

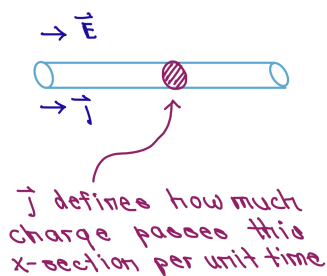
- Next, let's consider when we have a non-zero electrical field (with \mathbf{B} still 0):

$$\vec{E} \neq 0, \quad \vec{B} = 0$$

Equation of motion:

$$\frac{d\vec{p}}{dt} = -e\vec{E} - \frac{\vec{p}(t)}{\tau}$$

- We can now define the conductivity of a metal, σ , which is the constant of proportionality between the current density \vec{j} , and the applied electric field \vec{E} .



where

$$\vec{j} = \text{current density}$$

which is the charge per unit time per unit area

$$\vec{j} = -ne\vec{v}$$

where n is the density of electrons

$$\left[e^- / m^3 \right] \left[C / e^- \right] [m/s] = \frac{C}{m^2 \cdot s}$$

$$\vec{j} = \frac{e^2 n \tau}{m} \vec{E} \Rightarrow \boxed{\sigma = \frac{e^2 n \tau}{m}} \text{ units } [\Omega^{-1} m^{-1}]$$

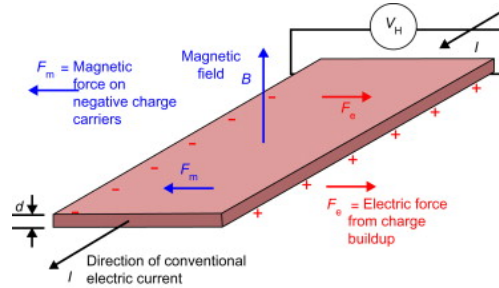
- Thus we can define resistivity ρ as the inverse of conductivity:

$$\boxed{\rho = \frac{1}{\sigma}} \text{ units } [\Omega m]$$

- If the resistivity of a metal is given by $\rho = \frac{1}{\sigma} = \frac{m}{e^2 n \tau}$, then decreasing the collision rate ($\frac{1}{\tau}$), will increase τ and thus lower the resistance.

- Note that increasing or decreasing the size of the sample does not change the resistivity. ρ is *intrinsic* (depends on material properties), while $R = \rho \cdot \frac{L}{A}$ is *extrinsic* (depends on the size and shape of the sample).
- $\sigma \propto \tau \Rightarrow \uparrow \tau$ means fewer collisions per electron (lower collision rate)

5.2 Hall Effect



- Next, we can apply an electric and magnetic field to our metal simultaneously (in perpendicular directions). By convention, we will always apply \mathbf{B} in the z direction.
- Recall – equation of motion:

$$\frac{d\vec{p}}{dt} = -e(\vec{E} + \vec{v} \times \vec{B}) + \frac{\vec{p}(t)}{\tau}$$

- If we again assume steady state, we get:

$$\vec{E} = \left(\frac{m}{ne^2\tau} \right) \vec{j} + \left(\frac{1}{ne} \right) \vec{j} \times \vec{B}$$

where the first term is "longitudinal" and the second term is off diagonal.

- We can define a 3×3 resistivity matrix and we find that the application of a \mathbf{B} field deflects the electrons causing a measurable potential difference in the orthogonal direction – this is the Hall effect.

$\vec{B} \parallel \hat{z}$, \vec{j} can be applied along \hat{x} , \hat{y} , or \hat{z}

$$\rho_{xx} = \rho_{yy} = \rho_{zz} = \frac{m}{ne^2\tau}$$

Hall resistivity:

$$\boxed{\rho_{xy} = -\rho_{yx} = \frac{B}{ne}}$$

- Note that in steady state the current flows in only one spatial direction.
 - In the steady state, once the potential difference is established in the transverse direction, no additional current flows in that direction.

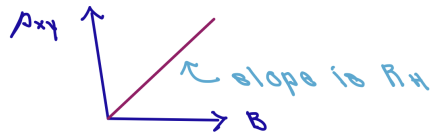
i.e. $|\vec{F}_e| = |\vec{F}_B|$ on the previous diagram

– current only flows in the “applied” direction.

- KEY! Whereas the longitudinal resistivity (ρ_{xx}) depends on both τ and n – so that they cannot be uniquely determined – **the Hall resistivity depends only on n** , so we can determine the number of conduction electrons.
- We can define the Hall coefficient, R_H :

$$R_H = \frac{-1}{ne} = \frac{-\rho_{xy}}{|B|} \quad \text{units } [m^3/C]$$

note: “normal” metals have a negative R_H (NOT a resistance).



- Some metals have a positive Hall coefficient – seeming to imply the existence of a positively charged carrier of electrical current. This is foreshadowing for later in the course when we will get introduced to the concept of holes in semiconductors.
- The Hall coefficient R_H for copper (good metal) is of order $0.1 \text{ mm}^3/C$ and its resistivity at RT is of order $10^{-8} \Omega m$. The order of magnitude of the scattering time, τ .

$$R_H = 0.1 \text{ mm}^3/C = 10^{-10} m^3/C = \frac{-1}{ne}$$

$$\rho = \frac{1}{\sigma} = 10^{-8} \Omega m = \frac{m}{ne^2 \tau}$$

$$\tau = \frac{-mR_H}{e^2 \rho} = \frac{-(10^{-30} \text{ kg})(10^{-10} m^3/C)}{(-10^{-19} C)(10^{-8} \Omega m)} = 10^{-13} s$$

- Average metal $\approx 10^{-14} s$, so this is reasonable. Scattering time is extraordinarily short.