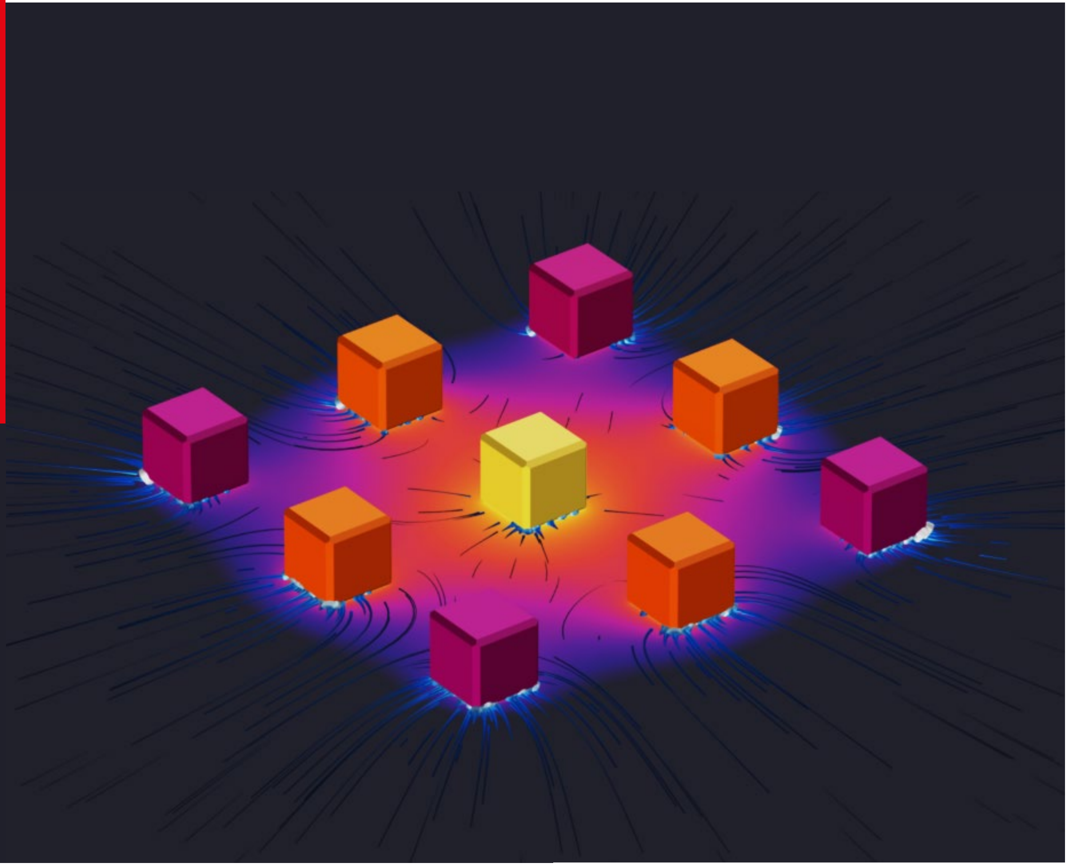
Nanoscale Heat Transfer (and Energy Conversion)

ME469

Instructor: Giulia Tagliabue



École
polytechnique
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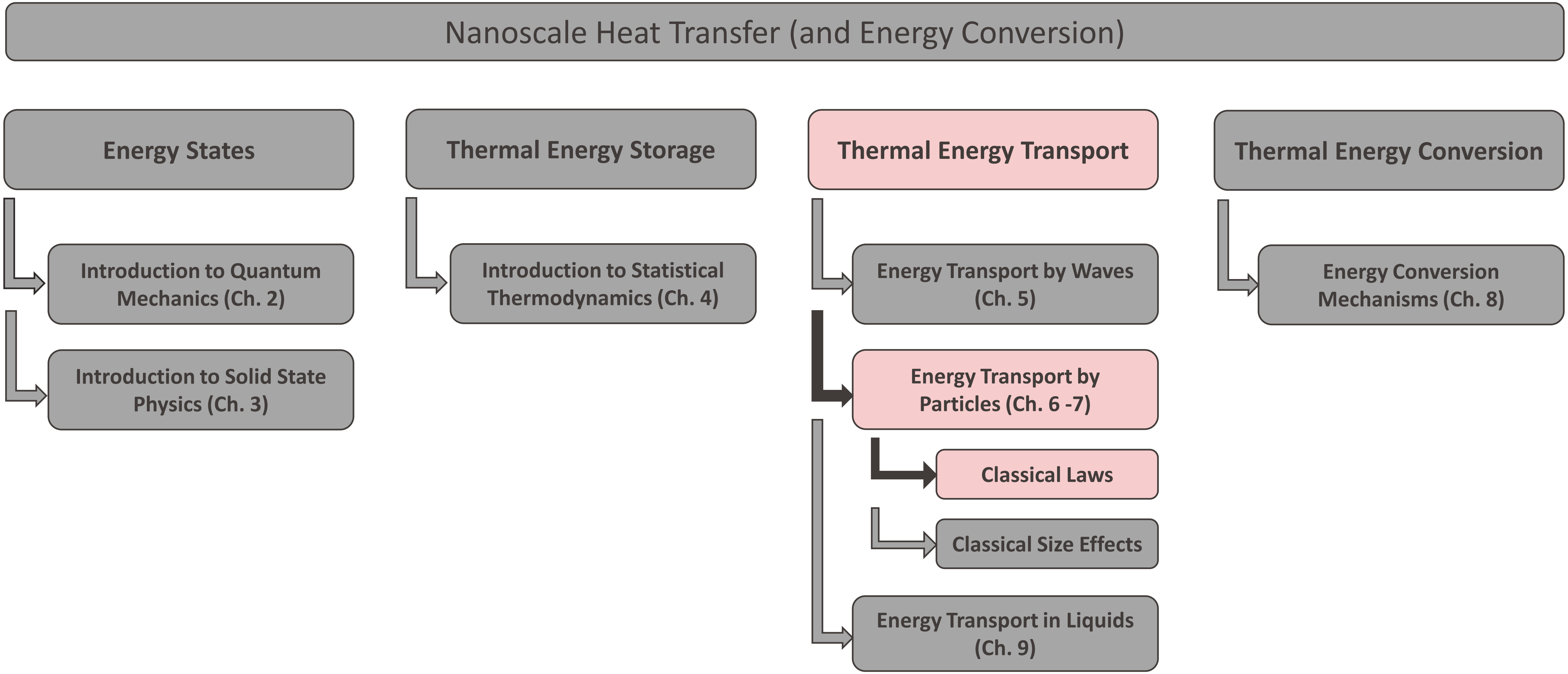
de Lausanne

Spring Semester

This Week



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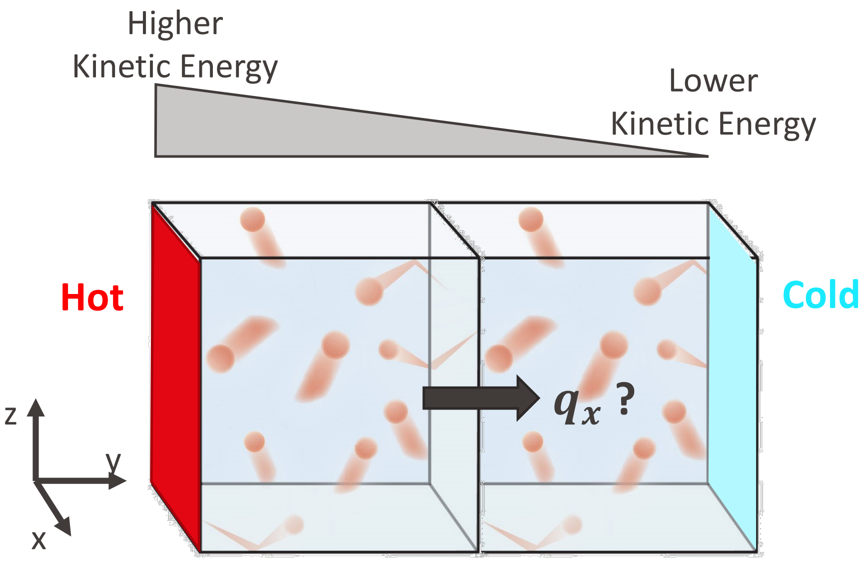
- **Energy States**
  - Introduction to Quantum Mechanics (Ch. 2)
  - Introduction to Solid State Physics (Ch. 3)
- **Thermal Energy Storage**
  - Introduction to Statistical Thermodynamics (Ch. 4)
- **Thermal Energy Transport**
  - Energy Transport by Waves (Ch. 5)
  - Energy Transport by Particles (Ch. 6 -7)
    - Classical Laws
    - Classical Size Effects
  - Energy Transport in Liquids (Ch. 9)
- **Thermal Energy Conversion**
  - Energy Conversion Mechanisms (Ch. 8)

Energy Transport



- The transient process must be slow compared to the relaxation time of the carriers.
- The temperature variation within one mean free path must be small compared to the absolute temperature
- The characteristic length must be much larger than the mean free path of the carrier.

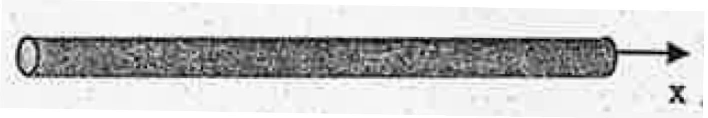
$$f = f_0 - \tau \left(\mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0 \right)$$

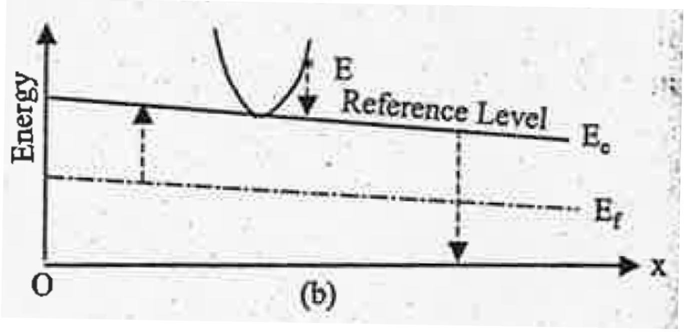
Phonons – Fourier Law and thermal conductivity

In This Lecture

- **Electrons – Ohm’s Law and Wiedemann-Franz Law**

Electrons – Approximated Boltzmann Equation





Let’s finally consider electrons flow in an **isothermal** conductor driven by an external electric field.

$$f = f_0 - \tau\left(\mathbf{v}\bullet\nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m}\bullet\nabla_{\mathbf{v}} f_0\right)$$

where $\mathbf{F} = -e\mathscr{E} = e\nabla\varphi_e$ $\quad f_0(E, E_f, T) = \dfrac{1}{\exp\left(\frac{E-E_f}{\kappa_B T}\right)+1}$ $\quad E = E_c + \dfrac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2)$

$E_f = chemical\ potential$ previously μ*

$$\Rightarrow \quad f = f_0 - \tau\left(v_x\frac{\partial f_0}{\partial x} - \frac{e\mathscr{E}}{m}\frac{\partial f_0}{\partial v_x}\right)$$

Using the above reference system, we express the energy E and the chemical potential E_f with respect to the conduction band. Indeed, with this choice $\partial E/\partial x = 0$.

$$E - E_f = (E - E_c) - (E_f - E_c) = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2) - (E_f - E_c)$$

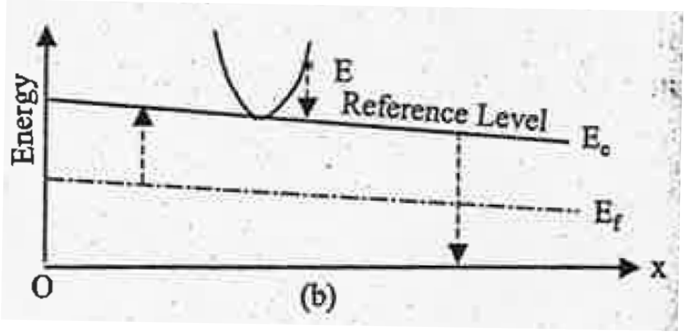
$$\Rightarrow \quad \frac{\partial f_0}{\partial x} = \frac{\partial f_0}{\partial E_f}\frac{dE_f}{dx} = -\frac{\partial f_0}{\partial E}\frac{dE_f}{dx} \quad \Rightarrow \quad f = f_0 + \tau\left(v_x\frac{dE_f}{dx}\frac{\partial f_0}{\partial E} + \frac{e\mathscr{E}}{m}\frac{\partial f_0}{\partial E}\frac{\partial E}{\partial v_x}\right)$$

$$\frac{\partial E}{\partial v_x} = m v_x$$

$$\Rightarrow \quad f = f_0 + \tau v_x\left(\frac{dE_f}{dx} + e\mathscr{E}\right)\frac{\partial f_0}{\partial E}$$

***Note**: remember that the Fermi level is the chemical potential at zero K. Instead the chemical potential depends on the temperature and is related to the charge carrier density L9, slide 14.

Electrons – Electrochemical Potential



$$f = f_0 + \tau v_x \left(\frac{dE_f}{dx} + e\mathscr{E} \right) \frac{\partial f_0}{\partial E}$$

For the external force we observe:

$$F = -\frac{dE}{dx} = -\frac{d(E - E_c + E_c)}{dx} = -\frac{dE_c}{dx} = e\frac{d\varphi_e}{dx}$$

$E = total\ potential$

$\varphi_e = electrostatic\ potential$

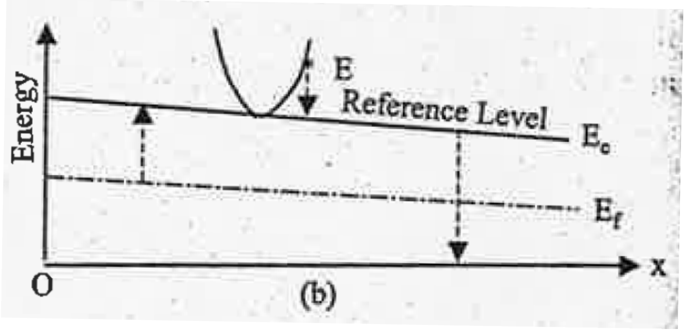
➡ $\varphi_e = -E_c/e$

Yet the total force felt by the electrons will consist of the electrostatic part as well as the diffusion part
The diffusion part is the first term in the parenthesis of the approximated Boltzmann equation:

➡ $\varphi_c = -E_f/e$

We so define the **electrochemical potential**: $\boldsymbol{\Phi = \varphi_e + \varphi_c = -(E_c + E_f)/e}$

Electrons – Current Density



$$f = f_0 + \tau v_x \left(\frac{dE_f}{dx} + e\,\mathscr{E} \right) \frac{\partial f_0}{\partial E}$$

The current density can be thus expressed as:

$$J_e = \frac{1}{V} \sum_{k_z=-\infty}^{\infty} \sum_{k_y=-\infty}^{\infty} \sum_{k_z=-\infty}^{\infty} (-e) v_x f$$

$$= -\frac{2}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e v_x f \, dk_x \, dk_y \, dk_z$$

(two electrons per quantum state)

$$= -\frac{e}{4\pi} \int_{4\pi} \left\{ \int_0^{\infty} v_x^2 \tau \left(\frac{dE_f}{dx} + e\,\mathscr{E} \right) \frac{\partial f_0}{\partial E} D(E) dE \right\} d\Omega$$

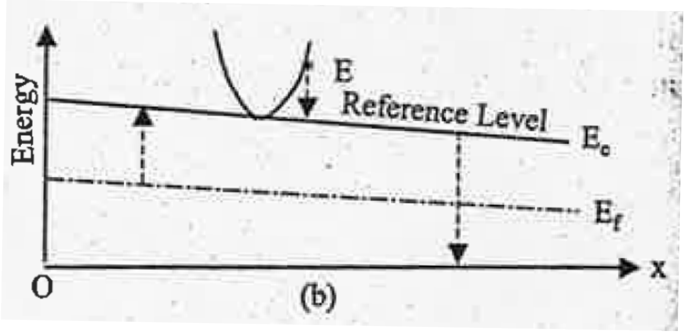
$$= -\frac{e}{3} \left(\frac{dE_f}{dx} + e\,\mathscr{E} \right) \int_0^{\infty} \tau v^2 D(E) \frac{\partial f_0}{\partial E} dE = \frac{e^2}{3} \frac{d\Phi}{dx} \int_0^{\infty} \tau v^2 D(E) \frac{\partial f_0}{\partial E} dE$$

- It is the **electrochemical potential**, and not just the electrostatic one, that is responsible for the current density. In different materials the relative importance of the electrostatic and chemical potential varies.

Electrons – Metals and Ohm’s Law

$$J_e = -\frac{e}{3}\left(\frac{dE_f}{dx} + e\,\mathscr{E}\right)\int_0^\infty \tau v^2 D(E)\frac{\partial f_0}{\partial E}dE = \frac{e^2}{3}\frac{d\Phi}{dx}\int_0^\infty \tau v^2 D(E)\frac{\partial f_0}{\partial E}dE$$

In metal the carrier density n is extremely large and therefore transport does not modify significantly the chemical potential, i.e. $\frac{dE_f}{dx} \sim 0$:



$$J_e = -\frac{e^2}{3}\,\mathscr{E}\int v^2\tau\frac{\partial f_0}{\partial E}D(E)dE = \sigma\,\mathscr{E}$$

Ohm’s Law

We also observe that $\frac{\partial f_0}{\partial E} \sim 0$ everywhere except close to the chemical potential (or Fermi level).
Therefore we can approximate $\frac{\partial f_0}{\partial E} \sim -\,\delta(E - E_f)$ such that the integral becomes:

$$\sigma = \frac{\tau_F D_F e^2 v_F^2}{3}$$

➡ **In metals, only electrons close to the chemical potential (practically coincident with the Fermi level) contribute to the current transport**

$$n = \int_{E_c}^{\mu} D(E)dE \sim \frac{1}{3\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\left(E_f\right)^{3/2}$$

$$E = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E}$$

➡

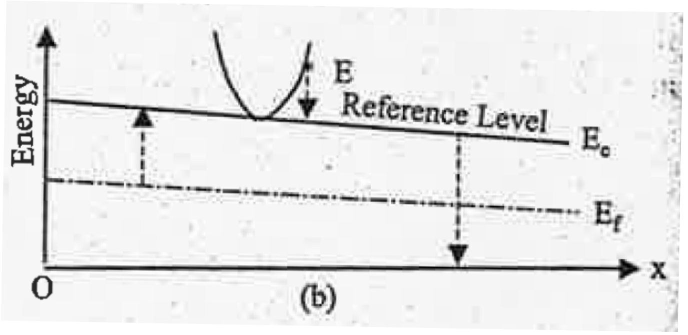
$$n = \frac{2}{3}E_F D_F = \frac{1}{3}mv_F^2 D_F$$

$$E_f = mv_F^2/2.$$

➡

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

Electrons – Semiconductors and the Drift-Diffusion Equation



$$J_e = -\frac{e}{3}\left(\frac{dE_f}{dx} + e\mathscr{E}\right)\int_0^\infty \tau v^2 D(E)\frac{\partial f_0}{\partial E}dE = \frac{e^2}{3}\frac{d\Phi}{dx}\int_0^\infty \tau v^2 D(E)\frac{\partial f_0}{\partial E}dE$$

In semiconductor the carrier concentration changes with the position and the chemical potential is not constant.

$$J_e = \underbrace{-\frac{e}{3}\int v^2\tau\left(e\mathscr{E}\frac{\partial f_0}{\partial E}\right)D(E)dE}_{\textit{Electrostatic (Drift)}} + \underbrace{\frac{e}{3}\int v^2\tau\frac{\partial f_0}{\partial x}D(E)dE}_{\textit{Concentration (Diffusion)}}$$

$$J_e = en\mu_e\mathscr{E} + e\frac{\partial(an)}{\partial x} \approx en\mu_e\mathscr{E} + ea\frac{\partial n}{\partial x}$$

Drift-Diffusion Equation

$$\mu_e = -\frac{\frac{e}{3}\int_0^\infty v^2\tau(\partial f_0/\partial E)D(E)dE}{\int_0^\infty f_0 D(E)dE} = \frac{e\tau_m}{m}$$

Mobility $[m^2/Vs]$

$$a = \frac{\frac{1}{3}\int_0^\infty v^2\tau f_0 D(E)dE}{\int_0^\infty f_0 D(E)dE} \approx \frac{\kappa_B T}{e}\mu_e$$

Diffusivity $[m^2/s]$ - Einstein Relation

τ_m = *momentum relaxation time*

$v_d = \mu_e\mathscr{E}$ =drift velocity

$\sigma = en\mu_e$

Electrons – Thermal Conductivity and Wiedemann-Franz Law

Assuming no current flow one can estimate the thermal conductivity for the electrons:

$$J_x = \int\int\int v_x E_x f\, dv_x dv_y dv_z = k\frac{dT}{dx}$$

$$E = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E}$$

➡ $$k_e = \frac{1}{3}C_e v_F^2 \tau_E$$

$\tau_E = energy\ relaxation\ time$

$C_e = volumetric\ specific\ heat$

Interestingly most metals obey the Wiedemann-Franz law:

L=Lorentz number

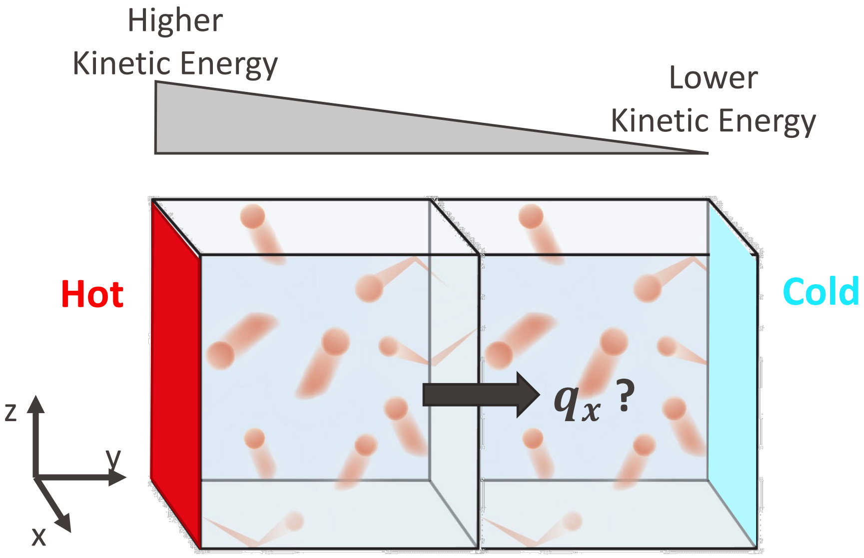
$$L = \frac{k_e}{\sigma T} = \frac{m C_e v_F^2}{3nTe^2} = \frac{\pi^2}{3}\left(\frac{\kappa_B}{e}\right)^2 = 2.45 \times 10^{-8}\,(\mathrm{W\,\Omega\,K^{-2}})$$

Where from L9, sl. 18 we recalled :

$$C_e(T) = \frac{1}{2}\pi^2 n_e \kappa_B \frac{T}{T_f} \propto T$$

In semiconductors the Lorentz number should be calculated because the relationship between n and the fermi level depends on doping. Nonetheless, the Lorentz number remain of the same order of magnitude.

Energy Transport



- The transient process must be slow compared to the relaxation time of the carriers.
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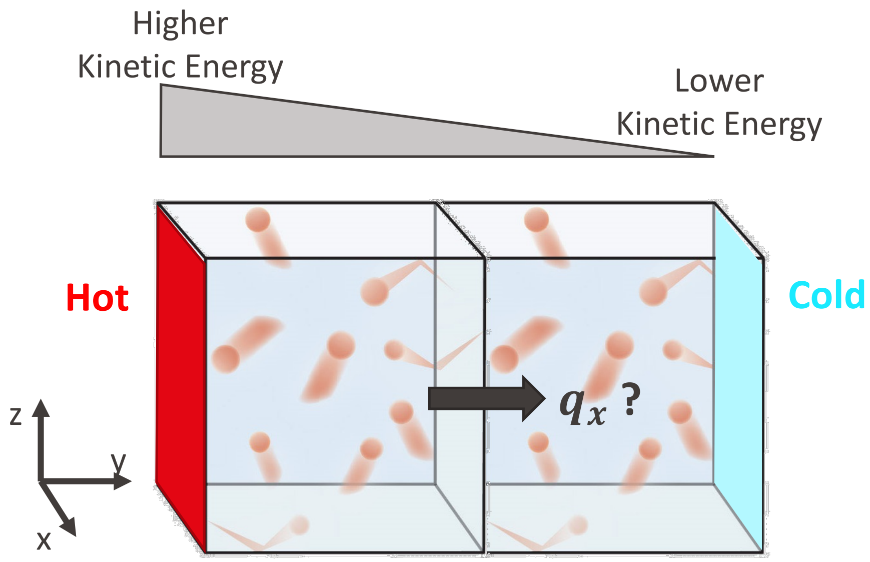
$$f = f_0 - \tau \left(\mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0 \right)$$

Phonons – Fourier Law and thermal conductivity

Molecules – Newton’s Stress Law

Electrons – Ohm’s Law

Next Week



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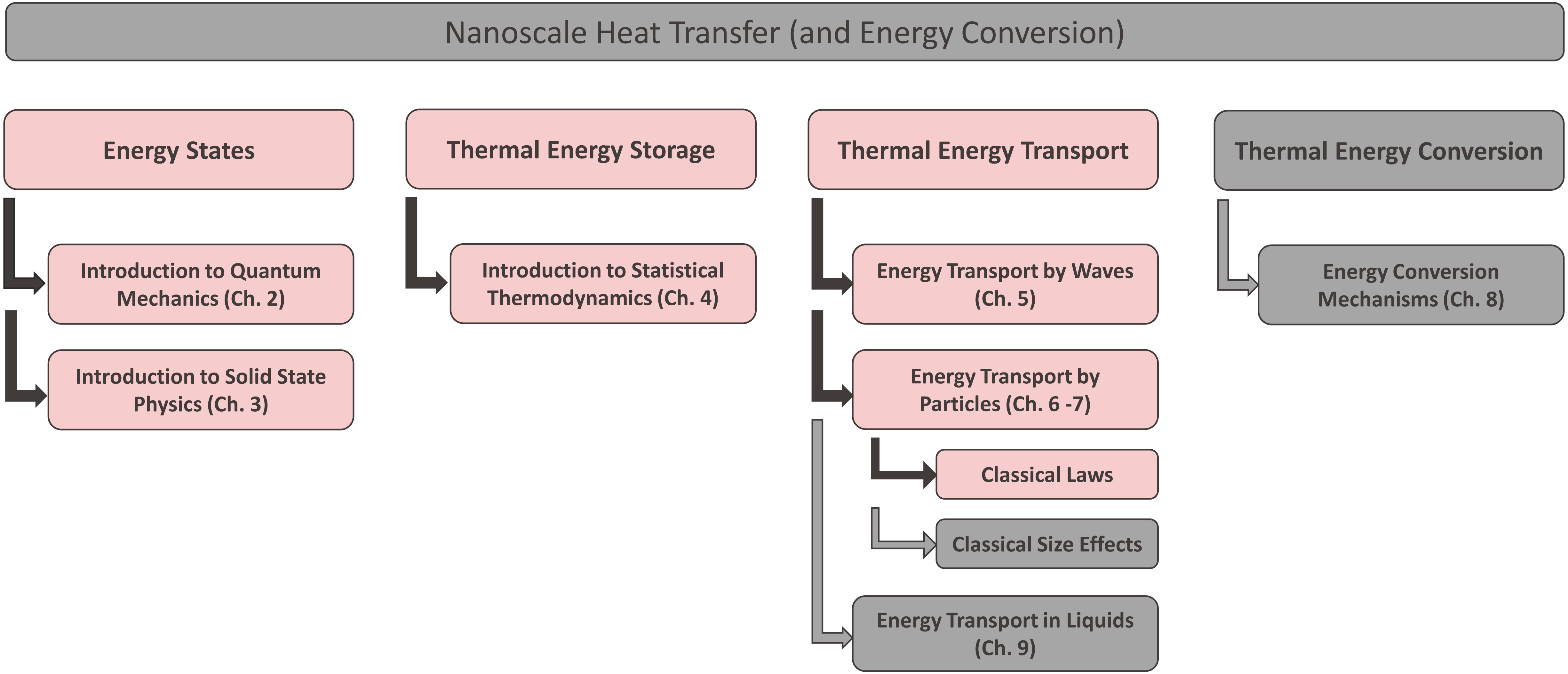
$$f = f_0 - \tau\left(\mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0\right)$$

Electrons – Thermoelectric Effects (Seebeck, Peltier, Thomson)

Content of the Exam



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Thermal Energy Storage

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Thermal Energy Transport

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- **Energy Transport by Particles (Ch. 6 -7)**
  - **Classical Laws**
  - **Classical Size Effects**
- **Energy Transport in Liquids (Ch. 9)**

Thermal Energy Conversion

- **Energy Conversion Mechanisms (Ch. 8)**

Rules of the Mid-Term Exam

- Mid-term Exam will cover the **course content up to Week 8**.
- The Mid-term Exam will consist of exercises similar to the homeworks. A couple of theory questions could be asked as well.
- At the exam, you can bring the lecture slides but NOT the homework sets
- Bring a calculator and your camipro

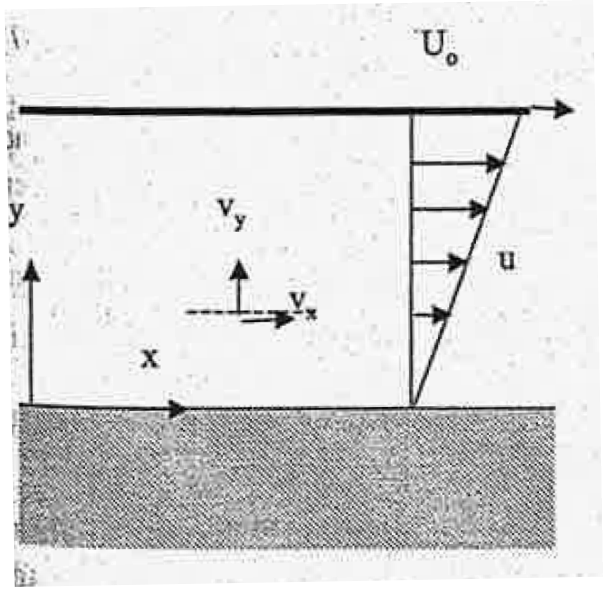
Supplementary

Molecules – Approximated Boltzmann Equation

We recall that the Boltzmann equation is valid only under assumption of molecular chaos, i.e. dilute gas.

The approximated Boltzmann equation to start from is:

$$f = f_0 - \tau \left(\mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0 \right)$$



The statistical distribution for molecules is the Maxwell distribution. However, when a net velocity is imposed due to flow, we need to use the displaced Maxwell distribution. Considering the shear flow in the figure we have:

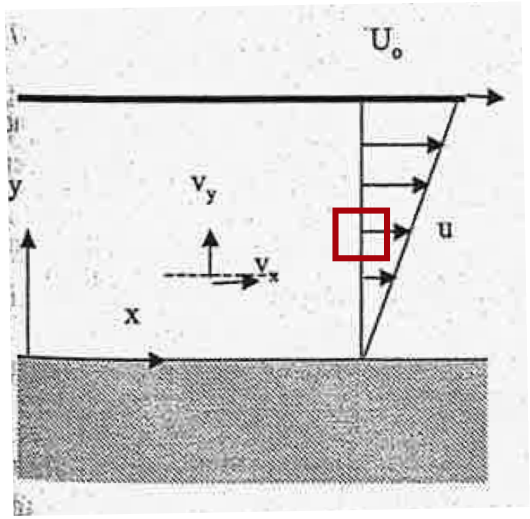
$$P(v_x, v_y, v_z) = \left(\frac{m}{2\pi \kappa_B T} \right)^{3/2} e^{-m[(v_x - u)^2 + v_y^2 + v_z^2]/2\kappa_B T}$$

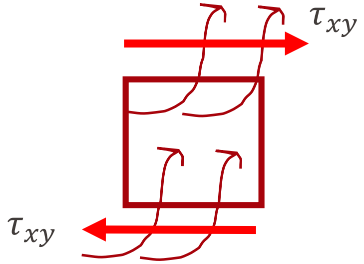
➡ $$f_0(v_x, v_y, v_z) = nP(v_z, v_y, v_z) = n \left(\frac{m}{2\pi \kappa_B T} \right)^{3/2} e^{-m[(v_x - u)^2 + v_y^2 + v_z^2]/2\kappa_B T}$$

And ultimately we get:

$$f = f_0 - \tau v_y \frac{\partial f_0}{\partial y} = f_0 - \tau v_y \frac{\partial f_0}{\partial u} \frac{\partial u}{\partial y}$$

Molecules – Newton’s Shear Stress Law in Gases





The shear stress τ_{xy} along the x-direction of a plane perpendicular to the x-axis is due to the momentum exchange across that plane:

$$\tau_{xy} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overbrace{v_y\underbrace{[mv_x]}_{\textit{Momentum of one particle along x-direction}}f}^{\textit{Rate of momentum change along x-direction due to the flow of the molecule across the y-plane}}\, dv_x\, dv_y\, dv_z = -\frac{\partial u}{\partial y}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \tau v_y^2 m v_x \frac{\partial f_0}{\partial u} dv_x\, dv_y\, dv_z$$

Therefore we get:

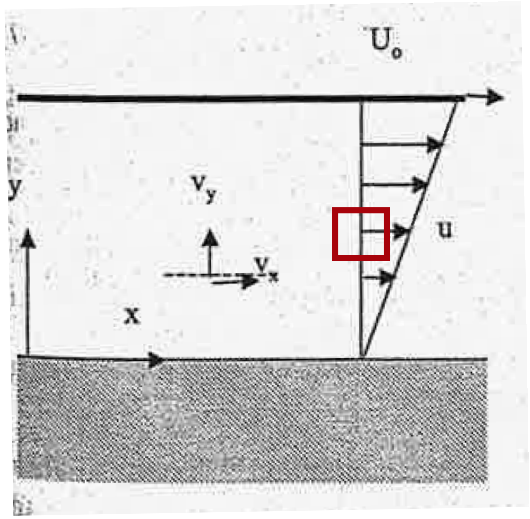
$$\tau_{xy} = \mu\frac{\partial u}{\partial y}$$

Newton’s Shear Stress Law

$$\mu = -\int\int\int \tau v_y^2\,(mv_x)\frac{\partial f_0}{\partial u} dv_x\, dv_y\, dv_z$$

Dynamic Viscosity

Molecules – Dynamic Viscosity

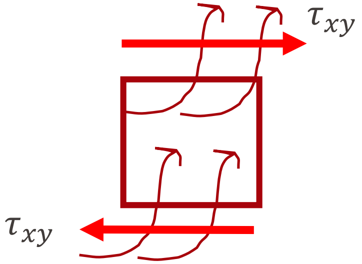


$$\mu = -\int\int\int \tau v_y^2 (m v_x) \frac{\partial f_0}{\partial u} dv_x\, dv_y\, dv_z$$

Dynamic Viscosity

If the relaxation time is a constant and we set $v_x' = v_x - u$ we get:

$$\mu = m^2 \tau n \left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} \int_{-\infty}^{\infty} e^{-mv_z^2/(2\kappa_B T)} dv_z \times \int_{-\infty}^{\infty} v_y^2 e^{-mv_y^2/(2\kappa_B T)} dv_y \int_{-\infty}^{\infty} \frac{v_x'^2}{\kappa_B T} e^{-mv_x'^2/(2\kappa_B T)} dv_x'$$



Recalling: $\Lambda = \frac{m}{\pi\sqrt{2}\rho d^2}$ $\quad \tau = \Lambda/\langle v\rangle \quad \langle v\rangle = [8\kappa_B T/(\pi m)]^{1/2}$

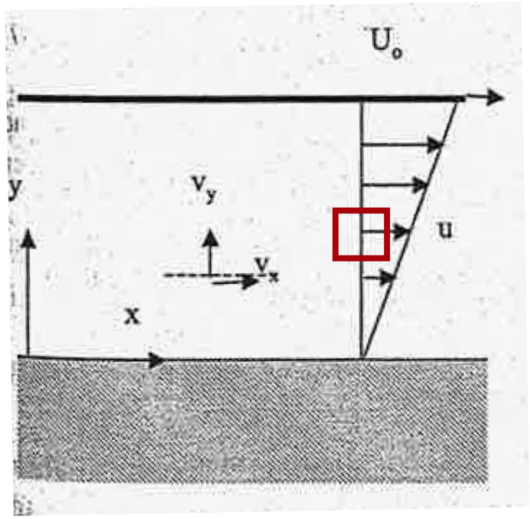
We obtain:

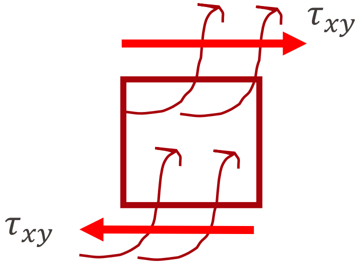
$$\mu = n\tau\kappa_B T = \frac{1}{4d^2}\sqrt{\frac{m\kappa_B T}{\pi}}$$

By solving the Boltzmann equation in integral form we would have obtained the more accurate result:

$$\mu = \frac{5}{16d^2}\sqrt{\frac{m\kappa_B T}{\pi}}$$

Molecules – Thermal Conductivity





Similarly, the energy of the carriers instead of the momentum, we can calculate the heat flux and as a consequence the thermal conductivity as:

$$E = \frac{1}{2}mv^2 = \frac{m}{2}((v_x - u)^2 + v_y^2 + v_z^2)$$

$$f = f_0 - \tau v_y \frac{\partial f_0}{\partial y} = f_0 - \tau v_y \frac{\partial f_0}{\partial u}\frac{\partial u}{\partial y}$$

$$f_0(v_x, v_y, v_z) = nP(v_z, v_y, v_z) = n\left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} e^{-m[(v_x-u)^2+v_y^2+v_z^2]/2\kappa_B T}$$

$$J_x = \int\int\int v_x E_x f\, dv_x dv_y dv_z = k\frac{dT}{dx}$$

$$k = \frac{5}{2}\left(\frac{k_B}{m}\right) n\tau\kappa_B T = \frac{5}{2}\left(\frac{\kappa_B}{m}\right)\mu$$

By solving the Boltzmann equation in integral form we would have obtained the more accurate result:

$$k = \frac{15}{4}\left(\frac{\kappa_B}{m}\right)\mu$$