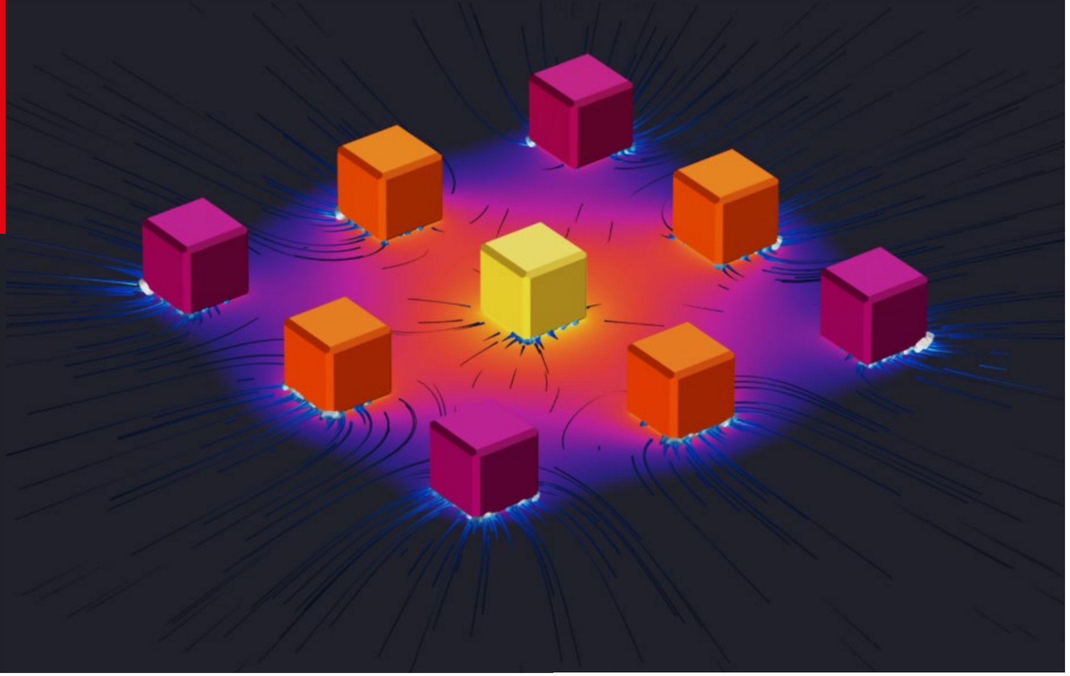
Nanoscale Heat Transfer (and Energy Conversion)

ME469

Instructor: Giulia Tagliabue



École
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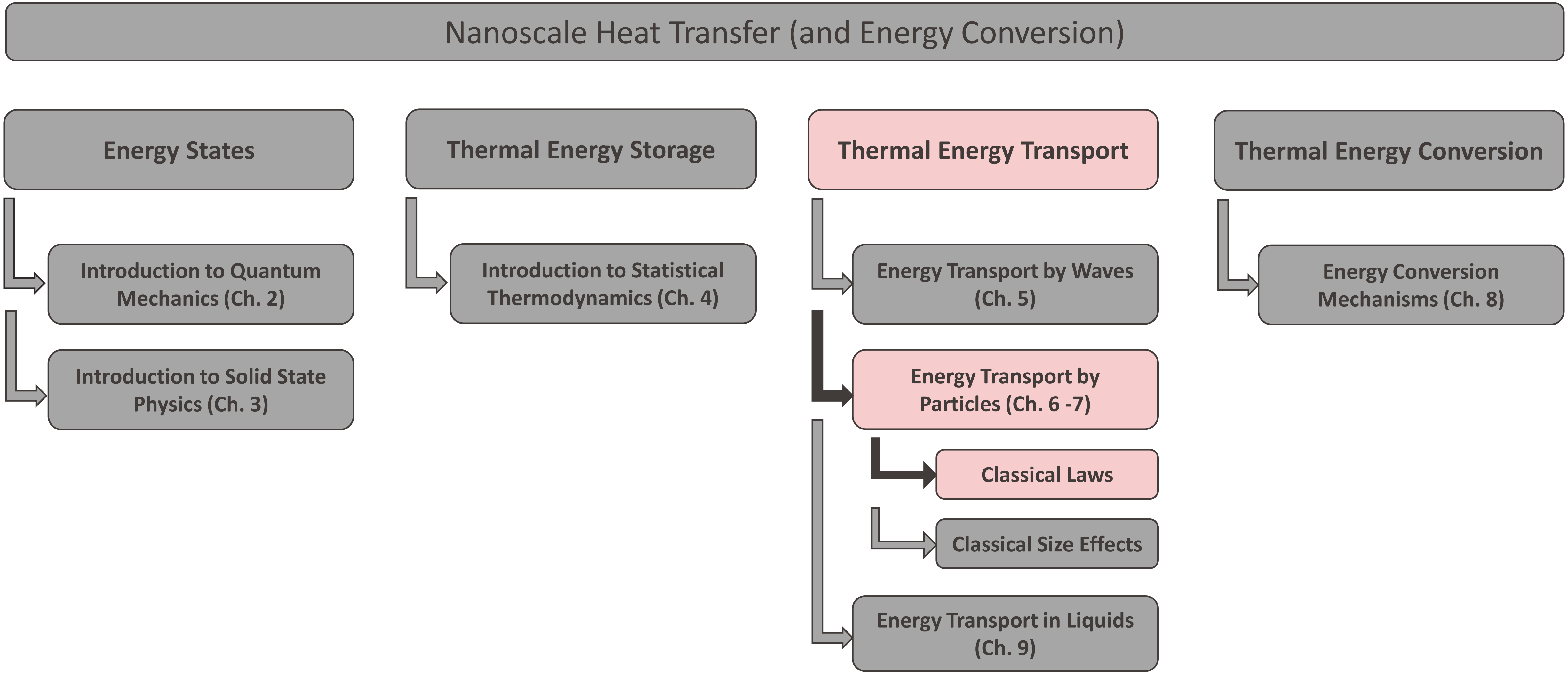
Spring Semester

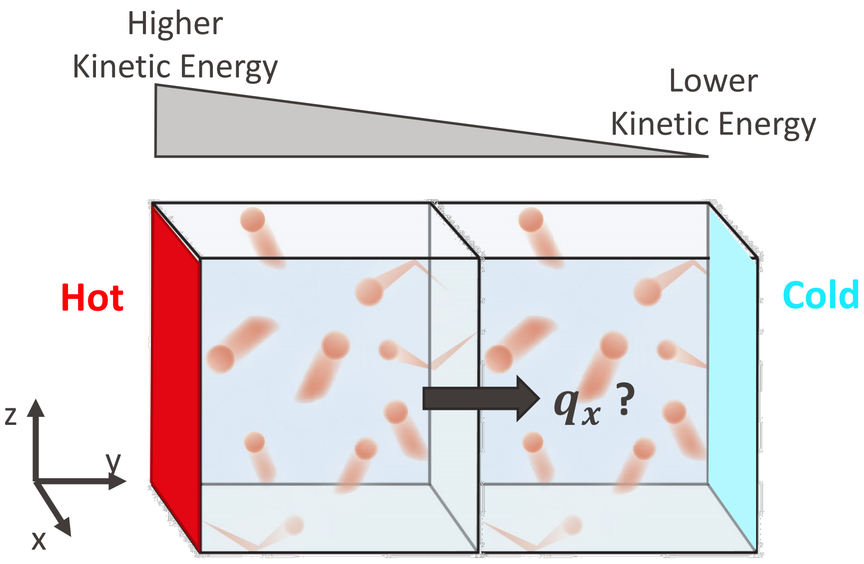
This Week



Nanoscale Heat Transfer (and Energy Conversion)

- 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

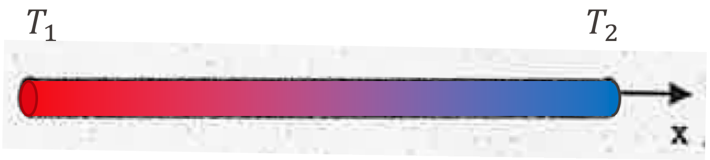
Molecules – Newton’s Stress Law

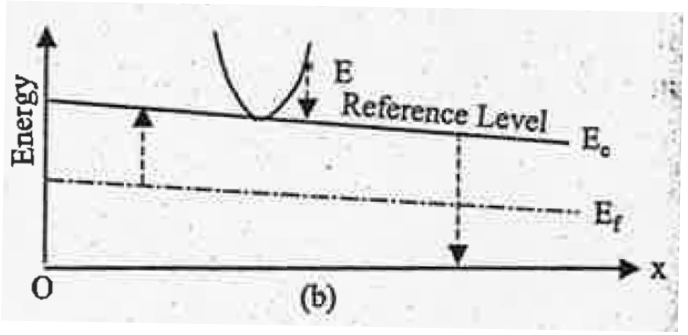
Electrons – Ohm’s Law

In This Lecture

- **Thermoelectric Effects**
    - Seebeck coefficient
    - Peltier coefficient
    - Thomson effects

Electrons – Thermoelectric Effects 1: Seebeck Coefficient





Let's now consider electrons flow in an **conductor subject to both a temperature gradient and an electric field**

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

$$\mathbf{F} = -e\mathscr{E} = e\nabla\varphi_e$$

$$f_0(E, E_f, T) = \frac{1}{\exp\left(\frac{E-E_f}{\kappa_B T}\right) + 1}$$

E_f $= chemical\ potential$ previously μ*

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

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

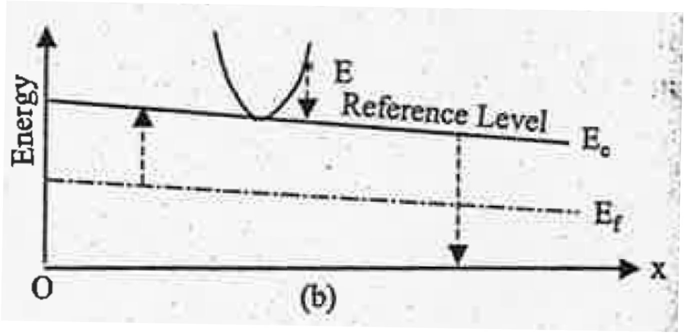
However we now have* that **both** the chemical potential and the temperature change with position along the conductor therefore:

$$\frac{\partial f_0}{\partial x} = \frac{\partial f_0}{\partial E_f}\frac{dE_f}{dx} + \frac{\partial f_0}{\partial T}\frac{dT}{dx} = -\frac{\partial f_0}{\partial E}\frac{dE_f}{dx} - \frac{E-E_f}{T}\frac{\partial f_0}{\partial E}\frac{dT}{dx} = -\frac{\partial f_0}{\partial E}\left[\frac{dE_f}{dx} + \frac{E-E_f}{T}\frac{dT}{dx}\right]$$

$$\frac{\partial f_0}{\partial v_x} = \frac{\partial f_0}{\partial E}\frac{\partial E}{\partial x} = \frac{\partial f_0}{\partial E} m v_x$$

➡ $$f = f_0 + \tau v_x \frac{\partial f_0}{\partial E}\left[\frac{dE_f}{dx} + \frac{E-E_f}{T}\frac{dT}{dx} + e\mathcal{E}\right]$$

Electrons – Current Density



$$f = f_0 + \tau v_x \frac{\partial f_0}{\partial E}\left[\frac{dE_f}{dx} + \frac{E-E_f}{T}\frac{dT}{dx} + e\mathcal{E}\right]$$

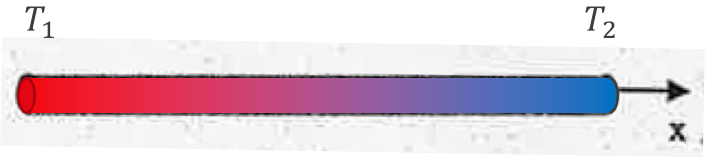
The current density can be thus expressed as:

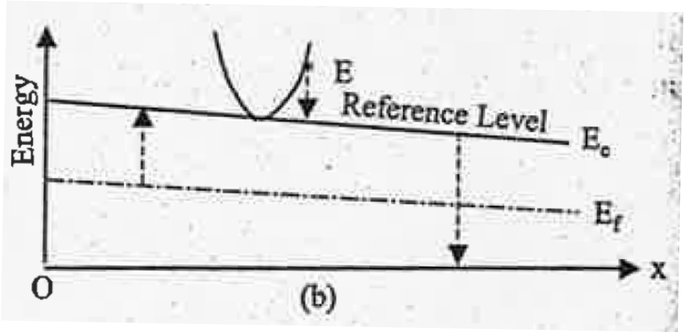
$$J_e = \frac{1}{V}\sum_{k_z=-\infty}^{\infty}\sum_{k_y=-\infty}^{\infty}\sum_{k_z=-\infty}^{\infty}(-e)v_x f$$

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

➡ $$J_e = -\frac{e}{3}\int v^2\tau\left(\frac{dE_f}{dx} + \frac{E-E_f}{T}\frac{dT}{dx} + e\mathscr{E}\right)\frac{\partial f_0}{\partial E}D(E)dE$$

Electrons – Thermoelectric Effects 1: Seebeck Coefficient





We can therefore compute the electrical current as:

$$J_e = -\frac{e}{3}\int v^2\tau\left(\frac{dE_f}{dx} + \frac{E-E_f}{T}\frac{dT}{dx} + e\mathscr{E}\right)\frac{\partial f_0}{\partial E}D(E)dE$$

That we can recast as::

$$J_e = L_{11}\left(\mathscr{E}+\frac{1}{e}\frac{dE_f}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right)$$

➡

$$J_e = L_{11}\left(-\frac{d\Phi}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right)$$

where:

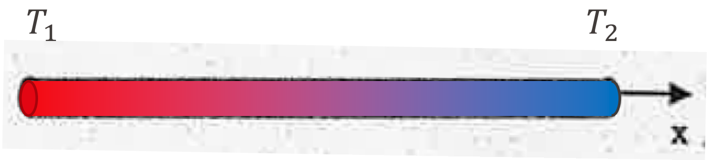
$$\sigma = -\frac{e^2}{3}\int v^2\tau\frac{\partial f_0}{\partial E}D(E)dE = L_{11}$$

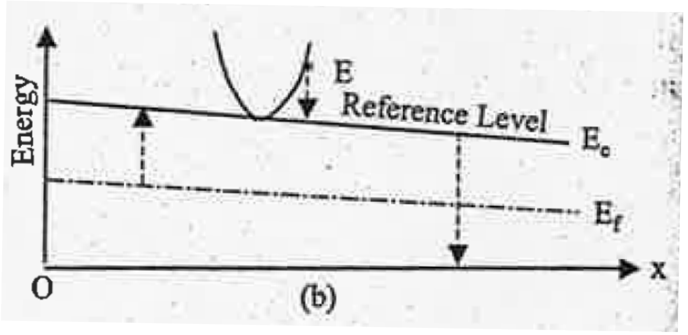
Electrical Conductivity

$$L_{12} = \frac{e}{3T}\int v^2\tau(E-E_f)\frac{\partial f_0}{\partial E}D(E)dE$$

Coupling coefficient between current and temperature gradient

Electrons – Thermoelectric Effects 1: Seebeck Coefficient





At open circuit voltage conditions the current is zero and therefore:

$$\frac{d\Phi}{dx} = -\frac{L_{12}}{L_{11}}\frac{dT}{dx} = -S\frac{dT}{dx}$$

$$S = \frac{-d\Phi/dx}{dT/dx} = \frac{L_{12}}{L_{11}} = -\frac{1}{eT}\frac{\int v^2\tau(E-E_f)\frac{\partial f_0}{\partial E}D(E)dE}{\int v^2\tau\frac{\partial f_0}{\partial E}D(E)dE}$$

Seebeck Coefficient $[V/K]$

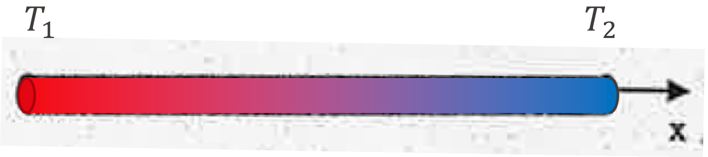
The Seebeck coefficient is a measure of the average heat current carried per electron.

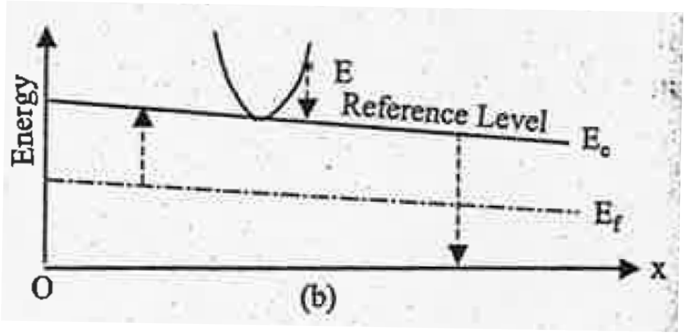
We thus observe that along a conductor subject to a temperature gradient, at open circuit condition:

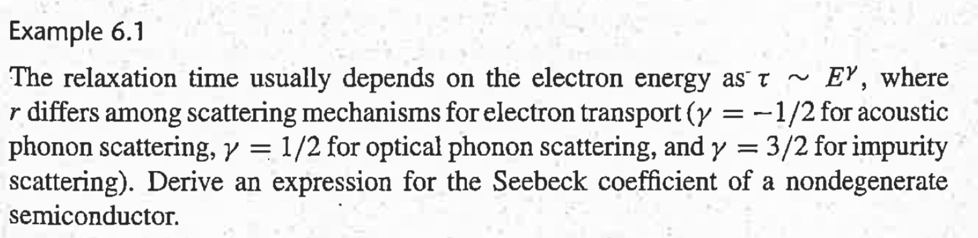
$$-(\Phi_2 - \Phi_1) = S(T_2 - T_1) = -V$$

- Thus in a conductor or semiconductor, a temperature difference generates a voltage difference because electrons from the hot side have higher thermal energy and will diffuse to the cold side.
- Under open-circuit conditions, the charge build-up generate a steady-state voltage equal to the Seebeck coefficient that counteracts further charge diffusion.
- If the material is uniform the generated voltage is independent of the temperature profile and this is the principle used for the thermocouples.

Electrons – Thermoelectric Effects 1: Seebeck Coefficient

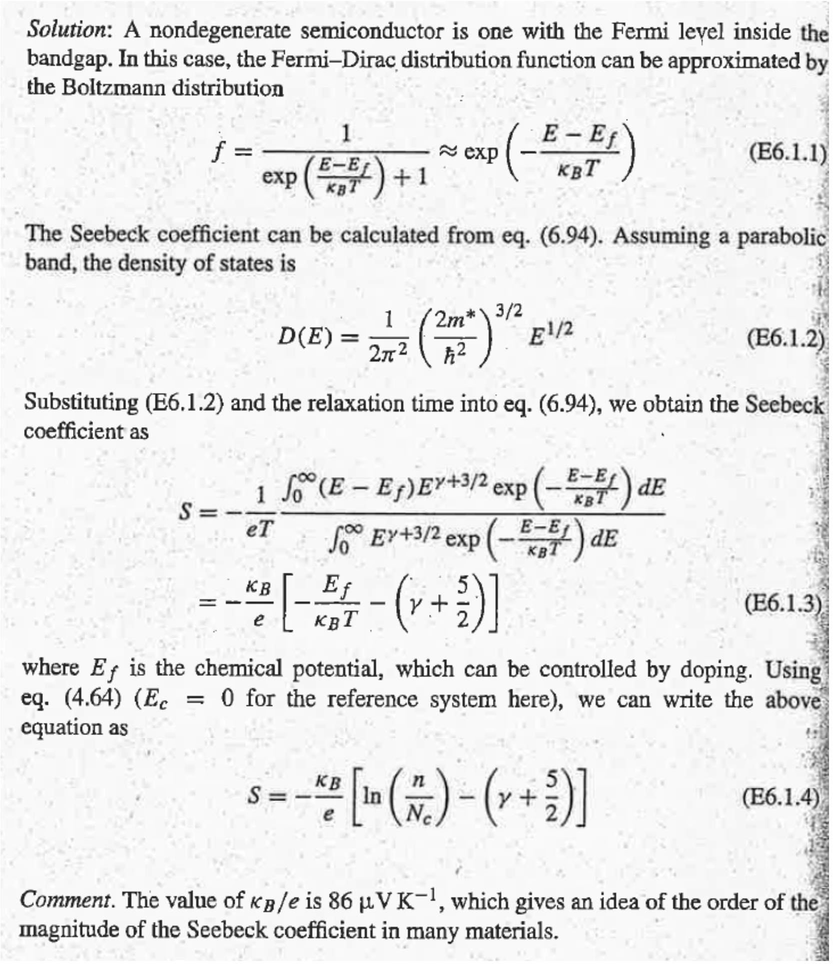






Example 6.1

The relaxation time usually depends on the electron energy as $\tau \sim E^{\gamma}$, where r differs among scattering mechanisms for electron transport ($\gamma = -1/2$ for acoustic phonon scattering, $\gamma = 1/2$ for optical phonon scattering, and $\gamma = 3/2$ for impurity scattering). Derive an expression for the Seebeck coefficient of a nondegenerate semiconductor.



Solution: A nondegenerate semiconductor is one with the Fermi level inside the bandgap. In this case, the Fermi–Dirac distribution function can be approximated by the Boltzmann distribution

$$f = \frac{1}{\exp\left(\frac{E-E_f}{\kappa_B T}\right)+1} \approx \exp\left(-\frac{E-E_f}{\kappa_B T}\right) \qquad \text{(E6.1.1)}$$

The Seebeck coefficient can be calculated from eq. (6.94). Assuming a parabolic band, the density of states is

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2} \qquad \text{(E6.1.2)}$$

Substituting (E6.1.2) and the relaxation time into eq. (6.94), we obtain the Seebeck coefficient as

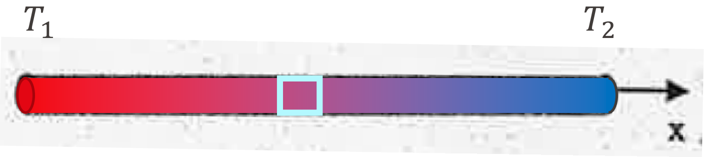
$$\begin{aligned} S &= -\frac{1}{eT}\,\frac{\int_0^\infty (E-E_f)E^{\gamma+3/2}\exp\left(-\frac{E-E_f}{\kappa_B T}\right)dE}{\int_0^\infty E^{\gamma+3/2}\exp\left(-\frac{E-E_f}{\kappa_B T}\right)dE} \\ &= -\frac{\kappa_B}{e}\left[-\frac{E_f}{\kappa_B T} - \left(\gamma + \frac{5}{2}\right)\right] \qquad \text{(E6.1.3)} \end{aligned}$$

where E_f is the chemical potential, which can be controlled by doping. Using eq. (4.64) ($E_c = 0$ for the reference system here), we can write the above equation as

$$S = -\frac{\kappa_B}{e}\left[\ln\left(\frac{n}{N_c}\right) - \left(\gamma + \frac{5}{2}\right)\right] \qquad \text{(E6.1.4)}$$

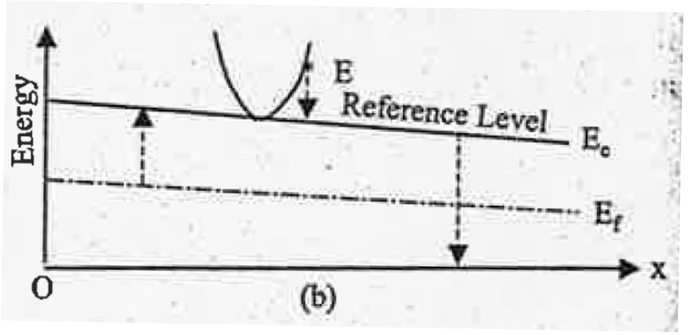
Comment. The value of κ_B/e is 86 μV K^{-1}, which gives an idea of the order of the magnitude of the Seebeck coefficient in many materials.

Electrons – Thermoelectric Effects 2: Peltier Coefficient



We now consider a small control volume within the conductor and we write the first law of thermodynamics accounting for both the flux of heat and particles:

$$dU = dQ + E_f dN$$



$$\underset{\text{Heat flux}}{\underset{\downarrow}{d\mathbf{J}_q}} = \underset{\text{Energy flux}}{\underset{\downarrow}{d\mathbf{J}_E}} - E_f \underset{\text{Particle flux}}{\underset{\downarrow}{d\mathbf{J}_n}}$$

where $J_E = \int E v_x f \, dv_x dv_y dv_z$ $\quad J_n = \int v_x f \, dv_x dv_y dv_z$

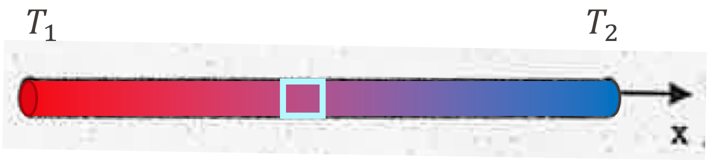
$$J_q = \int (E - E_f) v_x f \, dv_x dv_y dv_z$$

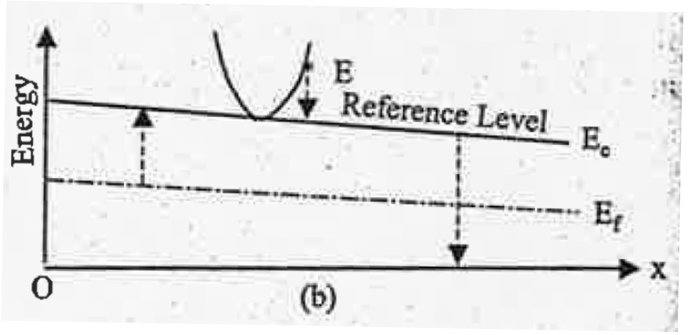
Substituting f

$$J_q = \underbrace{L_{21}\left(\mathscr{E} + \frac{1}{e}\frac{dE_f}{dx}\right)}_{\text{Convection of electrons under an electrochemical potential}} + \underbrace{L_{22}\left(-\frac{dT}{dx}\right)}_{\text{Diffusion of electrons under a temperature gradient}}$$

where $L_{21} = \frac{e}{3}\int (E - E_f) v^2 \tau \frac{\partial f_0}{\partial E} D(E) dE = T L_{12}$ $\quad L_{22} = -\frac{1}{3T}\int (E - E_f)^2 v^2 \tau \frac{\partial f_0}{\partial E} D(E) dE$

Electrons – Thermoelectric Effects 2: Peltier Coefficient





By eliminating the electrochemical potential between:

$$J_q = L_{21}\left(\mathscr{E} + \frac{1}{e}\frac{dE_f}{dx}\right) + L_{22}\left(-\frac{dT}{dx}\right)$$

and

$$J_e = L_{11}\left(\mathscr{E} + \frac{1}{e}\frac{dE_f}{dx}\right) + L_{12}\left(-\frac{dT}{dx}\right)$$

$$J_q = \frac{L_{21}}{L_{11}}J_e + \left(L_{22} - \frac{L_{12}L_{21}}{L_{11}}\right)\left(-\frac{dT}{dx}\right) = \Pi J_e - k\frac{dT}{dx}$$

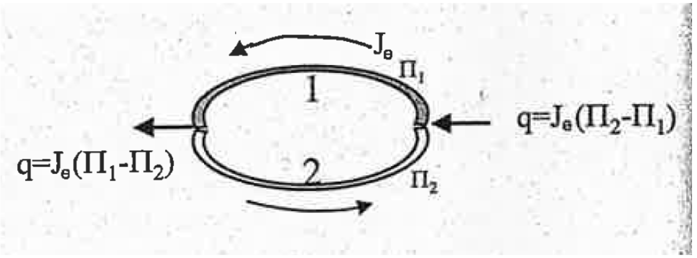
where

$$\Pi = \frac{L_{21}}{L_{11}} = TS$$

Peltier coefficient & Kelvin Relation with *S*

$$k = L_{22} - \frac{L_{12}L_{21}}{L_{11}}$$

Electronic Thermal conductivity



This shows that in addition to normal heat conduction by the electrons, the charge flow carries another heat that is proportional to the current through the Peltier coefficient. When two materials with different Peltier coefficients are joined together and a current flows through the junction, heat must be supplied or rejected based on the difference between the Peltier coefficients:

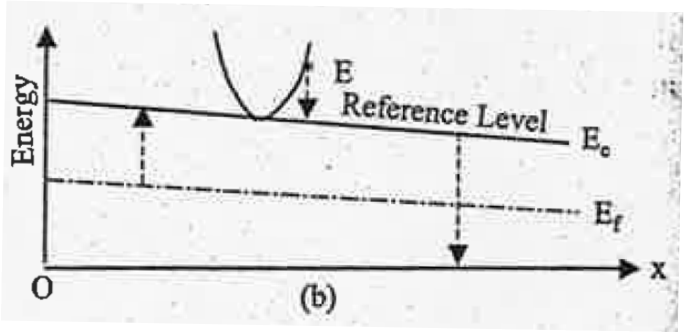
$$q = (\Pi_2 - \Pi_1)J_e$$

$q > 0$ energy is absorbed

$q < 0$ energy is rejected

The heat absorption/release depends on the sign of the current and therefore, contrary to normal heat conduction, it can be reversed by reversing the current flow.
This is the basis of thermoelectric refrigerators and heat pumps.

Electrons – Thermoelectric Effects 3: Thomson Effect



Let's now consider again our conductor subject to an electric field and a temperature gradient and let's look at the energy deposited in a differential volume due to the heat flux variation and the electrochemical potential drop:

$$\dot{q} = -\frac{dJ_q}{dx} + J_e\left(-\frac{d\Phi}{dx}\right) = -\frac{d\Pi}{dx} \bullet J_e + \frac{d}{dx}\left(k\frac{dT}{dx}\right) + J_e\left(-\frac{d\Phi}{dx}\right)$$

$$\Rightarrow \quad \dot{q} = -J_e\frac{d\Pi}{dT}\frac{dT}{dx} + \frac{d}{dx}\left(k\frac{dT}{dx}\right) - SJ_e\left(\frac{dT}{dx}\right) - J_e\frac{d\Phi}{dx}$$

$$\Rightarrow \quad \dot{q} = -\underbrace{\left(T\frac{dS}{dT}\right)J_e\frac{dT}{dx}}_{\textbf{\textit{Thomson Effect}}} + \underbrace{\frac{d}{dx}\left(k\frac{dT}{dx}\right)}_{\textit{Heat conduction}} + \underbrace{\frac{J_e^2}{\sigma}}_{\textit{Joule heating}}$$

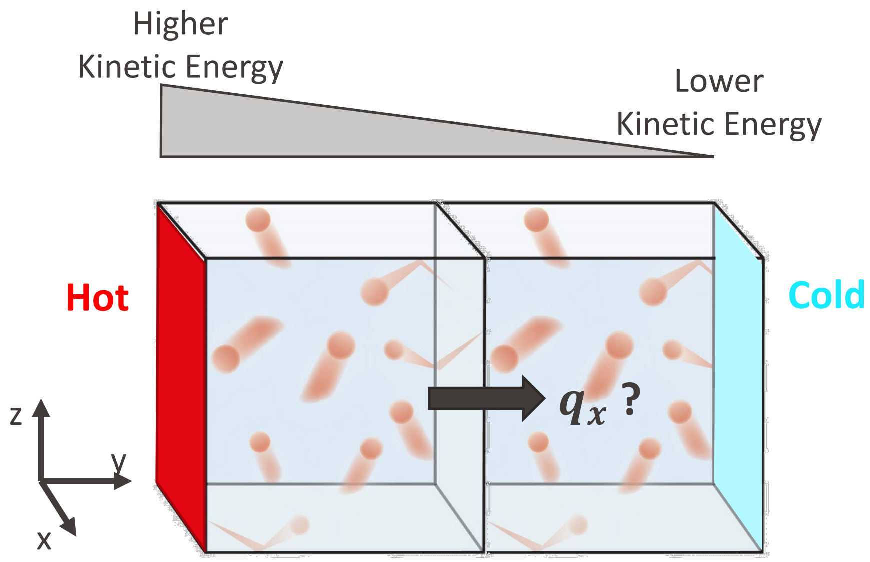
Heat can be absorbed or released depending on the current direction (Thomson Effect).
We define the rate of cooling as:

$$\beta = \dot{q}_c \Big/ \left(J_e\frac{dT}{dx}\right) = T\frac{dS}{dT}$$

Thomson Coefficient & Kelvin relation with *S*

where the negative sign in the first term of eq. (6.105) does not appear because a positive Thomson effect is based on cooling whereas $\dot{q}$ is the heat generation.

Energy Transport



- The transient process must be slow compared to the relaxation time of the carriers.
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- 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

Molecules – Newton’s Stress Law

Electrons – Ohm’s Law & Thermoelectric Effects

Outlook - The Conservation Equations

Previously we have used the Boltzmann equation to calculate the probability distribution function and subsequently we have calculated the average quantities as

$$\langle X \rangle = \frac{\int X f \, d^3\mathbf{v}}{\int f \, d^3\mathbf{v}} = \frac{\int X f \, d^3\mathbf{v}}{n} = \frac{m}{\rho} \int X f \, d^3\mathbf{v}$$

where

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = \frac{\partial v_1}{\partial x_1} + \frac{\partial v_2}{\partial x_2} + \frac{\partial v_3}{\partial x_3} = \frac{\partial v_i}{\partial x_i}$$

We now want to find the equations governing the average value of X. For this reason we rather calculate:

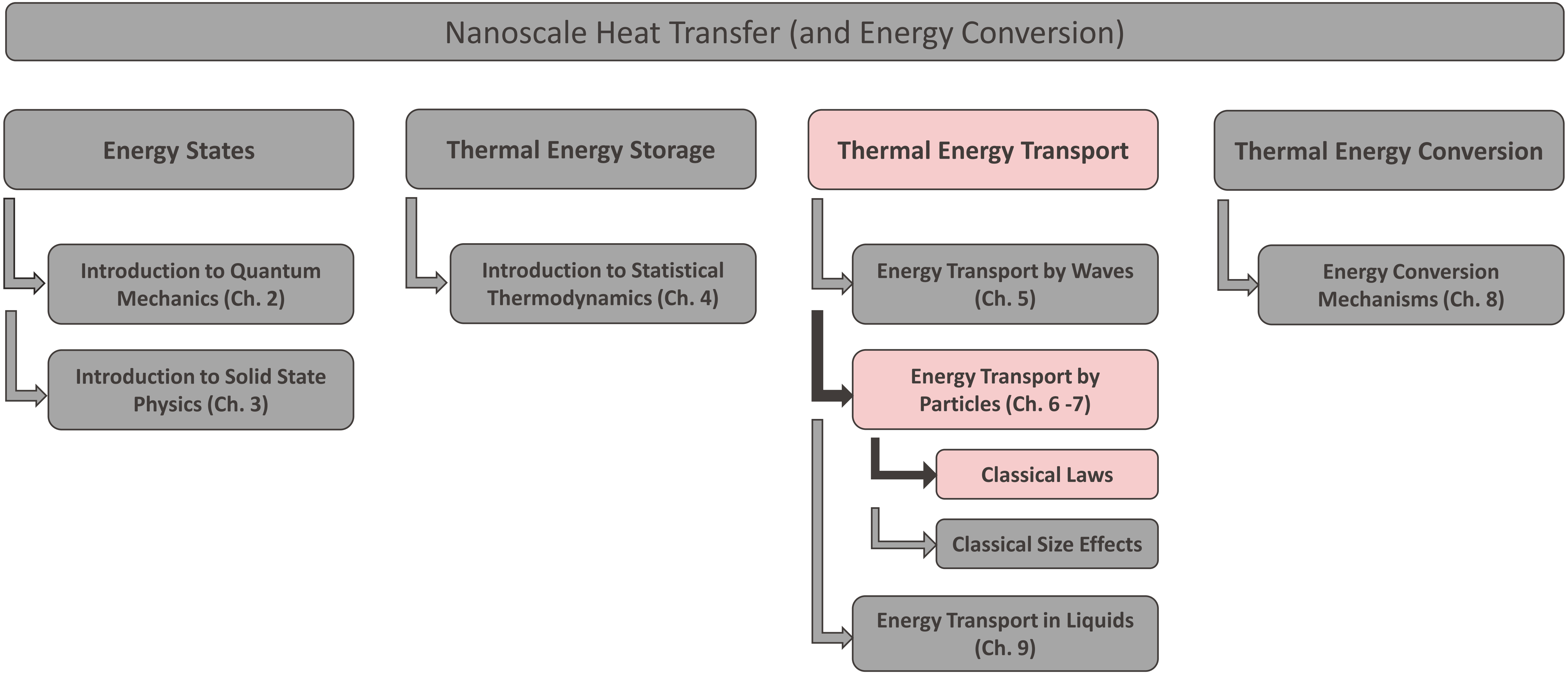
$$\int X \left(\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f \right) d^3\mathbf{v} = \int X \left(\frac{\partial f}{\partial t} \right)_c d^3\mathbf{v}$$

When the quantity X is a conserved quantity such as mass, momentum or energy, then the integral of the collision term (right-hand side) must vanish.

$$\begin{aligned} \text{Mass } X &= m \\ \text{Momentum } \mathbf{X} &= m\mathbf{v} \\ \text{Energy } X &= mv^2/2 + m\psi_{\text{int}} \end{aligned}$$

ψ_{int} is the potential energy per unit mass of a particle.

Next Week



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