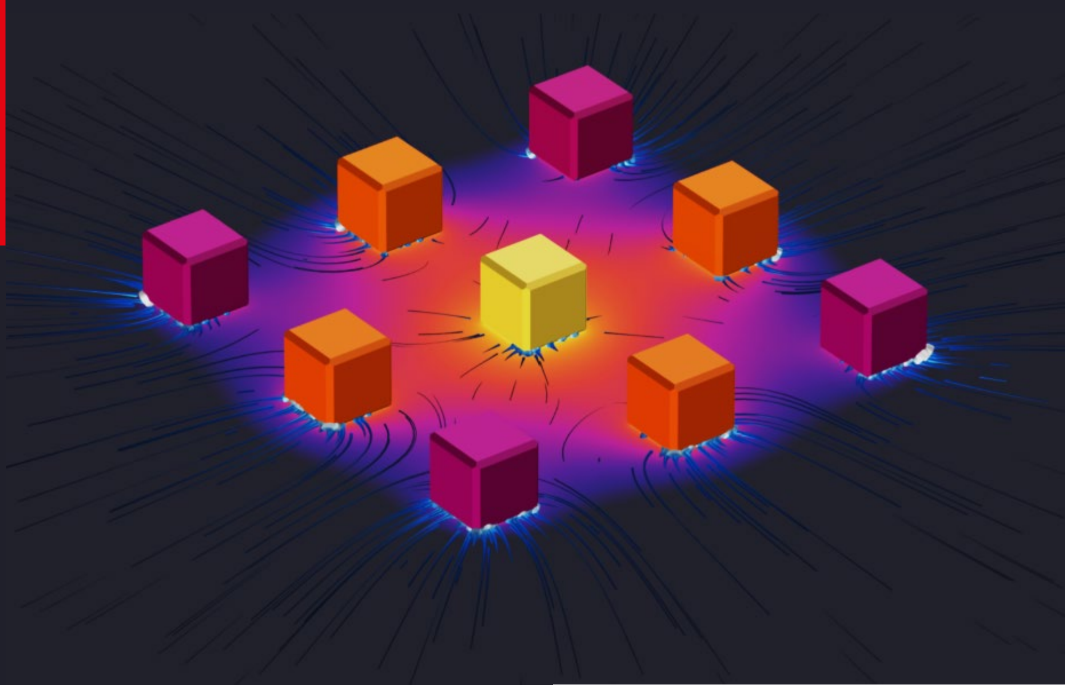
Nanoscale Heat Transfer (and Energy Conversion)

ME469

Instructor: Giulia Tagliabue



École
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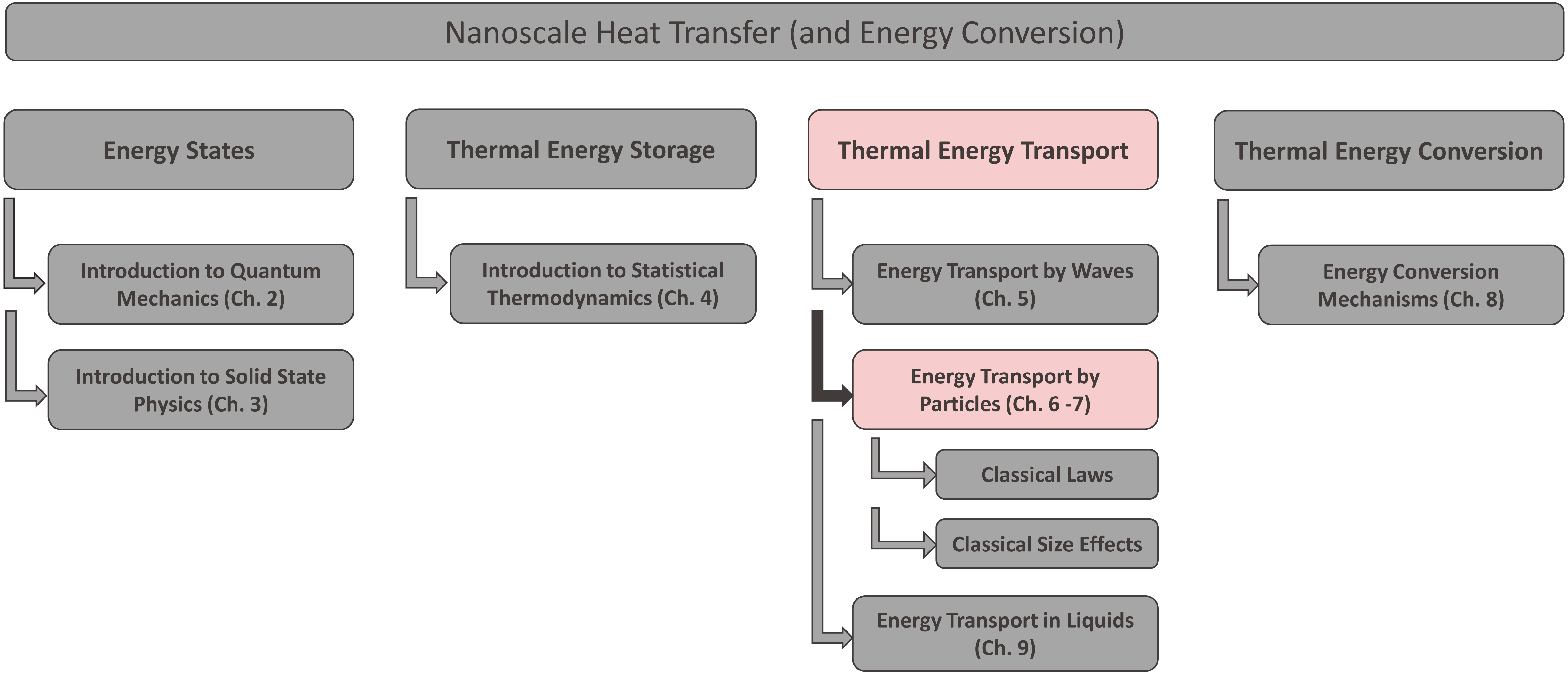
Spring Semester

Last Week



Nanoscale Heat Transfer (and Energy Conversion)

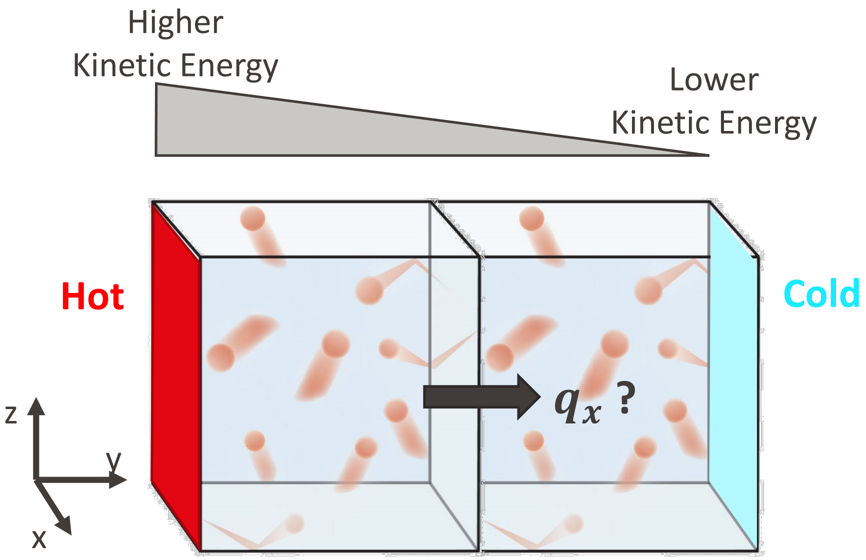
Energy States
- Introduction to Quantum Mechanics (Ch. 2)
- Introduction to Solid State Physics (Ch. 3)

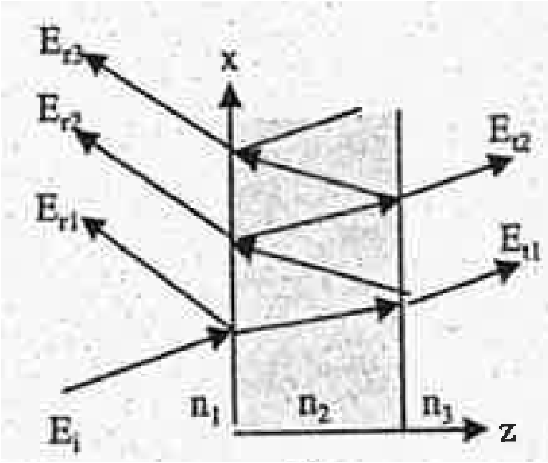
Thermal Energy Storage
- Introduction to Statistical Thermodynamics (Ch. 4)

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)

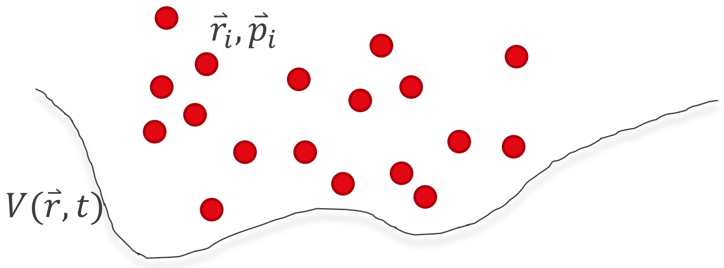
Energy Transport



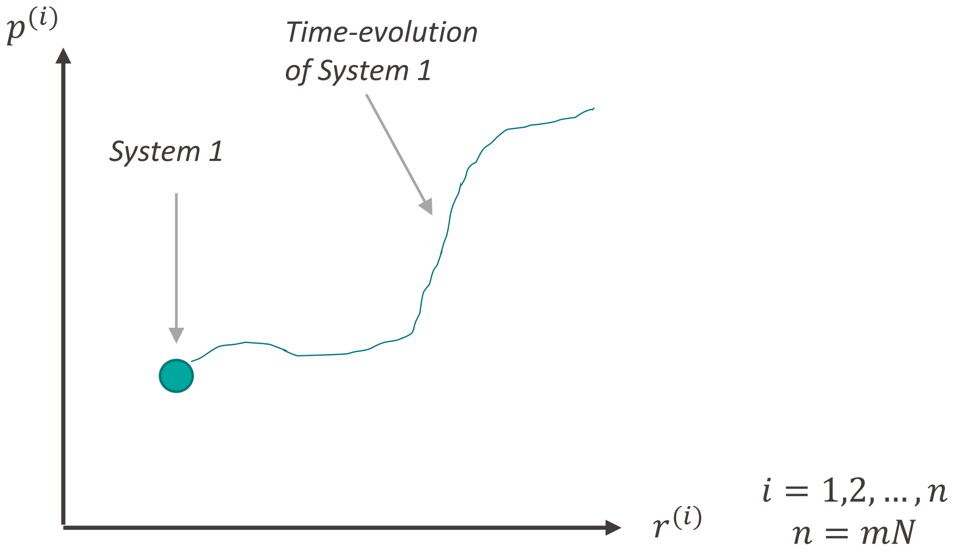


- If the phase of the carriers is important (interference effects), transport is coherent and the wave approach must be used (**ballistic transport**)
- **If the phase of the carriers in unimportant, a particle approach can be used (diffuse transport)**
- In between we have the **partially coherent regime**

The phase-space and the Liouville Equation



Phase Space Representation



In a system with N particles, each particle can be described by a generalized spatial coordinate $\vec{r}$ and a generalized momentum coordinate $\vec{p}$ which depend on the number of degrees of freedom in space, *m*. For example:

- Diatomic molecule: $\vec{r_1} = (\underbrace{x_1, y_1, z_1}_{\textit{position}}, \underset{\downarrow\ \textit{Vibrational coordinate}}{\Delta r_1}, \underbrace{\theta_1, \varphi_1}_{\textit{rotation}})$ and $\vec{p_1} = (mv_{x1}, mv_{y1}, mv_{z1}, \mathrm{md}\Delta r_1/dt, I_{\theta 1}, I_{\varphi 1})$

The total number of degrees of freedom for the system is $2n = 2mN$ and the $2n$-dimensional space is called the **phase-space**.

A given system is represented by a point in the phase-space and its time evolution corresponds to a unique trajectory*.

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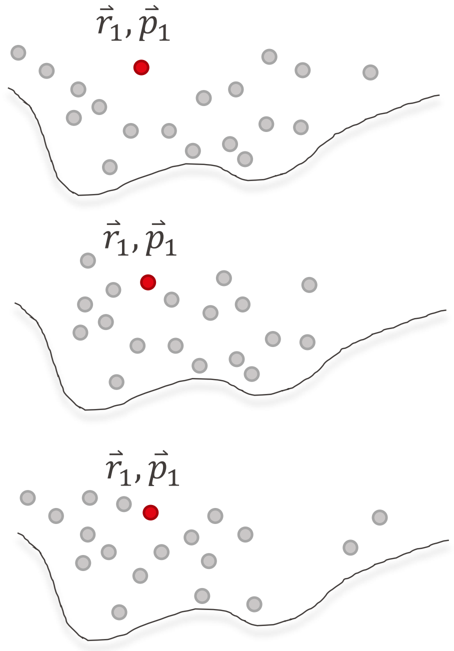
*the evolution of a system is uniquely determined by the initial conditions

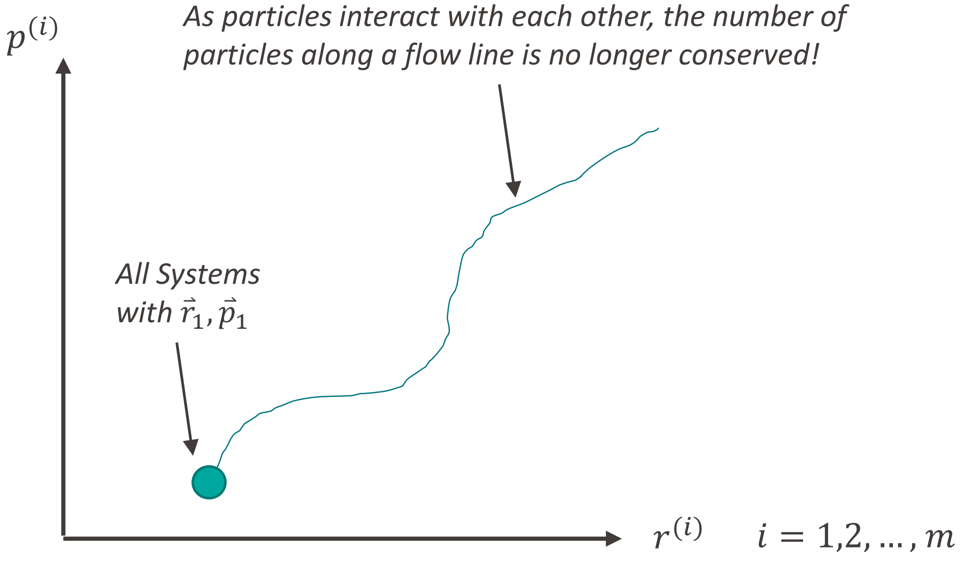
The Boltzmann Equation: from $2n$ to $2m$-dimensional space

1-particle in a system



$2m$-dimensional instead of $2n$-dimensional phase-space

Phase Space Representation



As particles interact with each other, the number of particles along a flow line is no longer conserved!

All Systems with $\vec{r}_1, \vec{p}_1$

We can perform the same averaging on the Liouville equation and we would obtain:

Boltzmann Equation

$$\frac{\partial f}{\partial t} + \frac{d\mathbf{r}}{dt} \bullet \nabla_{\mathbf{r}} f + \frac{d\mathbf{p}}{dt} \bullet \nabla_{\mathbf{p}} f = \boxed{\left(\frac{\partial f}{\partial t}\right)_c}$$

Scattering Term
Accounts for the collisions of this particle with all the other particles in the system (**non-conserving nature** of the 1-particle distribution function)

where

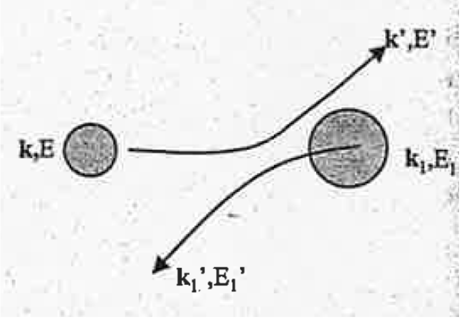
$$\nabla_{\mathbf{r}} f = \frac{\partial f}{\partial x}\hat{\mathbf{x}} + \frac{\partial f}{\partial y}\hat{\mathbf{y}} + \frac{\partial f}{\partial z}\hat{\mathbf{z}} \qquad \nabla_{\mathbf{p}} f = \frac{\partial f}{\partial p_x}\hat{\mathbf{p}}_x + \frac{\partial f}{\partial p_y}\hat{\mathbf{p}}_y + \frac{\partial f}{\partial p_z}\hat{\mathbf{p}}_z$$

The Scattering Integral – Relaxation-time Approximation

Let’s now look more closely at the scattering term in the Boltzmann equation and in particular let’s consider the collision between two particles:

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = \boxed{\left(\frac{\partial f}{\partial t}\right)_c}$$

↔



$$\left(\frac{\partial f}{\partial t}\right)_c = -\frac{f - f_0(T, E, \mu)}{\tau(\mathbf{r}, \mathbf{k})}$$

The scattering process can be caused by many different phenomena such as collision between equal particles (e.g. phonon-phonon), collision between different particles (e.g. electron-phonon), collision with boundaries or impurities.

Each process will have its own relaxation time τ_j and, **assuming that the scattering mechanisms are independent of each other**, we can calculate τ_t as:

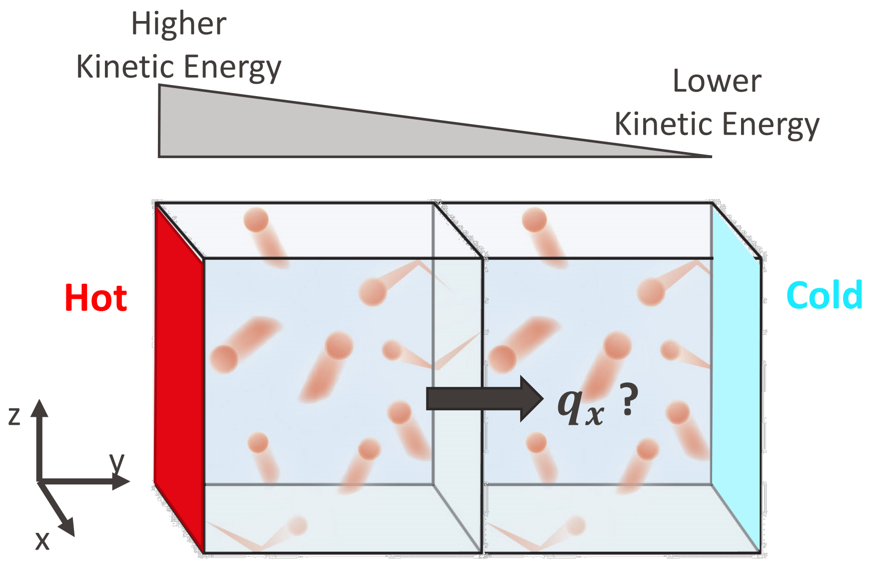
$$\frac{1}{\tau_t} = \sum_j \frac{1}{\tau_j}$$

Matthiessen rule

The Boltzmann Equation – From Phonons to Molecules

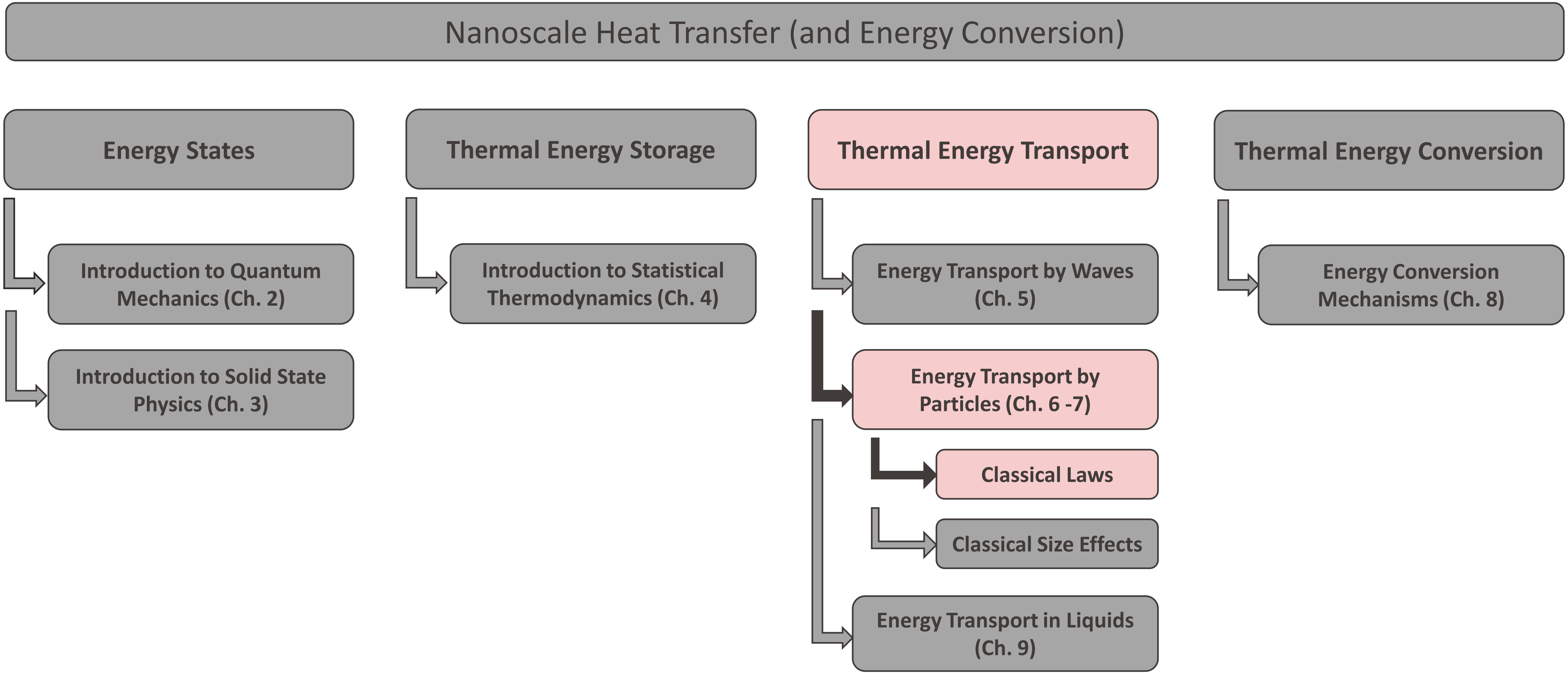
Particles	Boltzmann Equation	Scattering mechaninsms and relaxation time
Phonon	$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f = -\frac{f - f_0}{\tau}$	1. 3-phonon Umklapp process (volume) 2. Scattering from impurities (volume) 3. Boundary scattering (surface) $\tau_u^{-1} = B e^{-\theta_D / bT} T^3 \omega^2$ B and b are constants and θ_D is the Debye temperature. $\tau_I^{-1} = A\omega^4$ $\tau_b^{-1} = b_s v/L$ L is a characteristic length, b_s is a shape factor
Photon	$\frac{\partial I_\nu}{\partial s} = \frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{c,}$ $\frac{\partial I_\nu}{\partial s} = -K_{e\nu} I_\nu + \alpha_\nu I_{\nu 0} + \frac{\sigma_{s\nu}}{4\pi}\int I_\nu'(\hat{\Omega}')\phi(\hat{\Omega}' \to \Omega)d\Omega'$	Scattering can be elastic, inelastic outgoing, elastic incoming $\left(\frac{\partial I_\nu}{\partial t}\right)_{c,inelastic} = -\frac{I_\nu - I_{\nu 0}}{\Lambda}$ where $\Lambda = v\tau$ and $I_{\nu 0} = blackbody\ spectral\ intensity$ $\frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{\text{c,elastic}} = -\sigma_{s\nu} I_\nu + \frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{\text{c,elastic, in}}$ $\frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{\text{c,elastic,in}} = \frac{\sigma_{s\nu}}{4\pi}\int I_\nu'(\hat{\Omega}')\phi(\hat{\Omega}' \to \Omega)d\Omega'$ $\sigma_{s\nu}$ is the scattering coefficient
Electron	$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = -\frac{f - f_0}{\tau}$	Scattering dominated by electron-phonon interactions. In metals: $\frac{1}{\tau} \propto T$ In semiconductors complex processes.
Molecule	$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau}$	$\tau = \frac{\Lambda}{v}$ $\Lambda = \frac{m}{\pi\sqrt{2}\rho d^2}$ $\bar{v} = \int_0^\infty\int_0^\infty\int_0^\infty v f_0(v)\, dv_x\, dv_y\, dv_z = \sqrt{\frac{8\kappa_B T}{\pi m}}$

Energy Transport



How do classical laws emerge from the microscopic picture of energy transport?

This Week



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In This Lecture

- **Approximation of the Boltzmann Equation**
- Phonons - Fourier Law and Phonon Thermal Conductivity

The Approximated Boltzmann Transport Equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = \left(\frac{\partial f}{\partial t}\right)_c$$

$$\left(\frac{\partial f}{\partial t}\right)_c = -\frac{f - f_0(T, E, \mu)}{\tau(\mathbf{r}, \mathbf{k})}$$

We define: $g = f - f_0 = deviation\ from\ equilibrium$

➡
$$\frac{\partial g}{\partial t} + \frac{\partial f_0}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \mathbf{v} \bullet \nabla_{\mathbf{r}} g + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} g = -\frac{g}{\tau}$$

We now make the following assumptions:

1. Negligible transient terms $\frac{\partial f}{\partial t} \ll \frac{g}{\tau}$
2. The deviation from equilibrium is small $f_0 \gg g$
3. $\nabla g \ll \nabla f$ or alternatively $g \gg \nabla g$

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

Let’s now look more closely at the meaning of the approximation we made.

Note: we would have arrived to the same result doing a Taylor expansion of Boltzmann eqn. and keeping only the first order expansion of f , f_0 being the 0th order term

The Approximated Boltzmann Transport Equation

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

Let’s look more closely at the meaning of the three approximations we did to get to this result:

1. **Negligible transient terms** $\frac{\partial f}{\partial t} \ll \frac{g}{\tau}$

   If a transient phenomenon (e.g. a laser pulse) occurs with a characteristic time τ_c then this condition requires that: $\boldsymbol{\tau_c \gg \tau}$

   Therefore **the transient process must be slow compared to the relaxation time of the carriers**.

2. **The deviation from equilibrium is small** $\boldsymbol{f_0 \gg g}$

   If we look at the approximated Boltzmann equation we see that $f_0 \gg \tau \left(\mathbf{v} \bullet \nabla_{\mathbf{r}} f_0 + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f_0 \right)$

   Let’s then consider the case of phonons and let’s multiply the inequality by the phonon energy integrating then above all phonon states:

   $\sum_{\mathbf{k}} \hbar\omega f_0 \gg \sum_{\mathbf{k}} \hbar\omega\tau \mathbf{v} \bullet \nabla_{\mathbf{r}} f_0$ ➡ $U \gg -\frac{k}{\bar{v}} \frac{dT}{dx} \sim -C\Lambda \frac{dT}{dx}$ where $k = C\bar{v}\Lambda/3$ $\bar{v}$ is the average phonon velocity;

   If $U = CT$ ➡ $\frac{\Lambda}{T} \frac{dT}{dx} \ll 1$ therefore **the temperature variation within one mean free path must be small compared to the absolute temperature**

3. $\boldsymbol{\nabla g \ll \nabla f}$ **or alternatively** $\boldsymbol{g \gg \nabla g}$

   This condition can be rewritten also as $\frac{g}{\tau} \gg v \cdot \nabla g$. If we approximate $\nabla g \sim g/L$, where L is a characteristic length associated with the problem we get $\frac{\tau v}{L} = \frac{\Lambda}{L} \ll 1$

   Therefore **the characteristic length must be much larger than the mean free path of the carrier**.

In This Lecture

- Approximation of the Boltzmann Equation
- **Phonons - Fourier Law and Phonon Thermal Conductivity**

Phonons – Approximated Boltzmann Equation

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

For phonons :

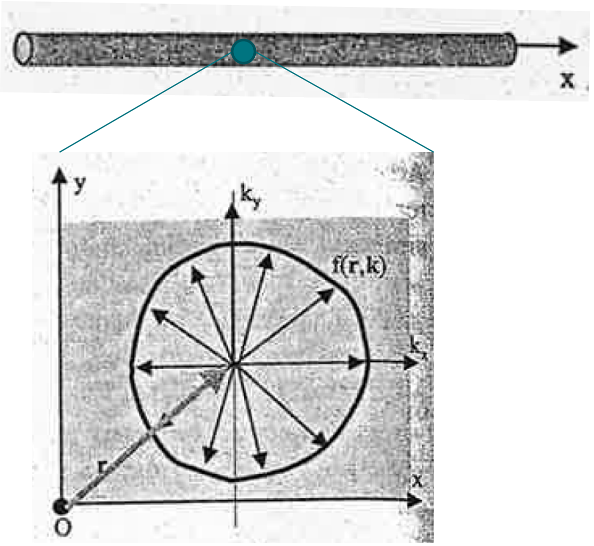
$$f_0 = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$$

$$\boldsymbol{F} = \mathbf{0}$$

$$f(\mathbf{r}, \mathbf{k}) = f_0 - \tau \frac{df_0}{dT} \mathbf{v} \bullet \nabla T$$

$$T = T(\vec{r}, t)$$

Phonons – Fourier Law and Thermal Conductivity



Let's consider the 1-dimensional problem of heat conduction along x-direction (i.e. temperature gradient along x). The **heat flux $J_{qx}(x)$** can be calculated as*:

$$J_{qx}(x) = \sum_s \left[\frac{1}{V} \sum_{k_{x1}=-\infty}^{\infty} \sum_{k_{y1}=-\infty}^{\infty} \sum_{k_{z1}=-\infty}^{\infty} v_x \hbar\omega f \right]$$

where $f(\mathbf{r},\mathbf{k}) = f_0 - \tau \frac{df_0}{dT}\mathbf{v} \bullet \nabla T$

velocity along x

Phonon energy

Nonequilibrium statistical distribution

Converting the sum into an integral**:

$$J_{qx}(x) = (1/V)\sum_s \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x \hbar\omega f \, dk_x \, dk_y \, dk_z/(2\pi/L)^3$$

Furthermore we use the density of states to go from an integral over k to an integral over ω, Ω where ω is the angular frequency and Ω is the solid angle:

$$J_{qx}(x) = \int_0^{\omega_{\max}} d\omega \left[\int_0^{2\pi} \left\{ \int_0^{\pi} v \cos\theta \hbar\omega f \frac{D(\omega)}{4\pi} \sin\theta d\theta \right\} d\varphi \right]$$

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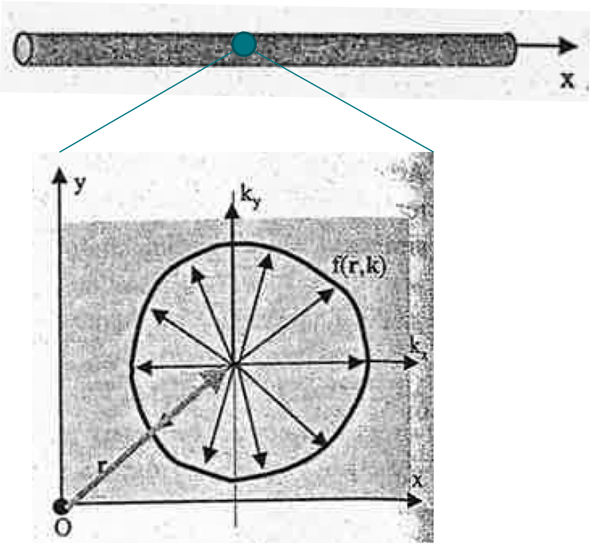
*compare the $J_{qx}(x)$ expression to L11, slide 7 (Landauer formalism). Observe that here we directly account for carrier moving in ALL directions at a given point.

** every point in k-space occupies a $(2\pi/L)^3$ space. Hence when we convert the discrete space into a continuum to obtain the correct number of points we need to use $d\vec{k}/(2\pi/L)^3$

Phonons – Fourier Law and Thermal Conductivity



We now insert the non-equilibrium statistical distribution $f(\mathbf{r},\mathbf{k}) = f_0 - \tau \frac{df_0}{dT}\mathbf{v} \bullet \nabla T$

$$J_{qx}(x) = \int_0^{\omega_{\max}} d\omega \left[\int_0^{2\pi} \left\{ \int_0^{\pi} v\cos\theta\hbar\omega \left[f_0 - \tau \frac{df_0}{dT}\frac{dT}{dx} v\cos\theta \right] \frac{D(\omega)}{4\pi} \sin\theta d\theta \right\} d\varphi \right]$$

The equilibrium distribution is isotropic and therefore the integral of f0 is zero.

➡ $$J_{qx}(x) = -\frac{1}{2}\frac{dT}{dx} \int_0^{\omega_{\max}} d\omega \left\{ \int_0^{\pi} \tau v^2 \sin\theta \cos^2\theta \times \hbar\omega D(\omega) \frac{df_0}{dT} d\theta \right\}$$

We immediately observe that this is exactly the classical Fourier Law: $J_{qx} = -k\frac{dT}{dx}$

where $$k = \frac{1}{2}\int_0^{\omega_{\max}} \left\{ \int_0^{\pi} \tau v^2 C_\omega \sin\theta \times \cos^2\theta d\theta \right\} d\omega$$ **Thermal Conductivity**

$C_\omega = \hbar\omega D(\omega) \boxed{df_0/dT}$ **Specific heat per unit frequency**

Phonons – Fourier Law and Thermal Conductivity

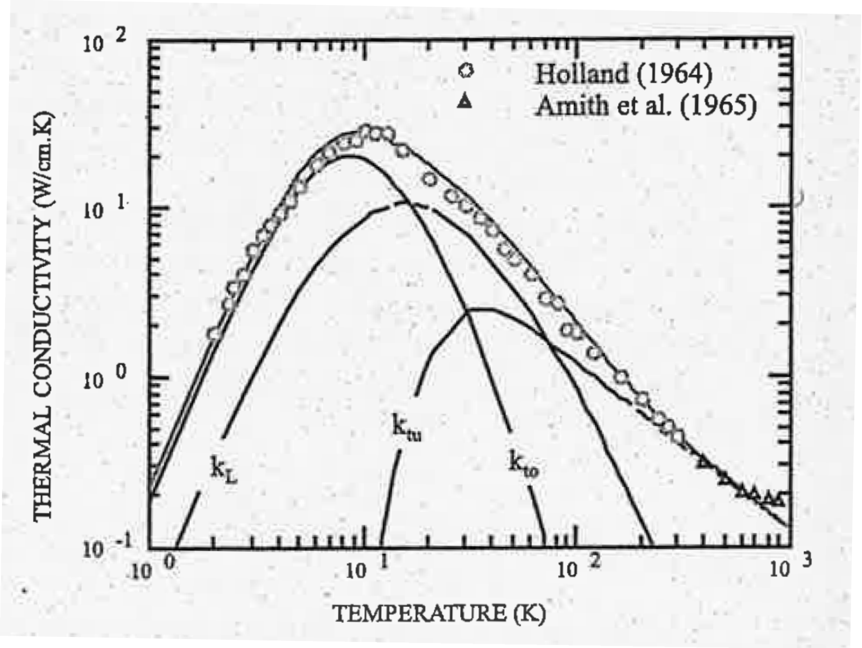
$$k = \frac{1}{2}\int_0^{\omega_{\max}}\left\{\int_0^{\pi}\tau v^2 C_\omega \sin\theta \times \cos^2\theta \, d\theta\right\} d\omega$$

- v, τ isotropic $\quad k = \frac{1}{3}\int \tau v^2 C_\omega \, d\omega$
- v, τ frequency independent $\quad k = \frac{1}{3} C v \Lambda \quad \Lambda = \tau v$

We know that the relaxation time an be expressed as: $\quad \frac{1}{\tau} = \frac{b_s v}{L} + A\omega^4 + B e^{-\theta_D/bT} T^3 \omega^2$

Therefore we can fit experimental data of the thermal conductivity to find the values of the coefficients and determine which scattering mechanism dominates at a given T. Yet, the simplest model $k = \frac{1}{3} C v \Lambda$, leads to major inaccuracies due to:

- Constant phase velocity instead of frequency dependent one (phonon dispersion)
- Optical phonons contribute to C but only very little to k because of low group velocities
- Phonon scattering is highly frequency dependent (high frequency phonons scatter more frequently)
- Although the normal 3-phonon scattering does not impede heat flow, the energy/momentum redistribution affects the likelihood of Umklapp processes.

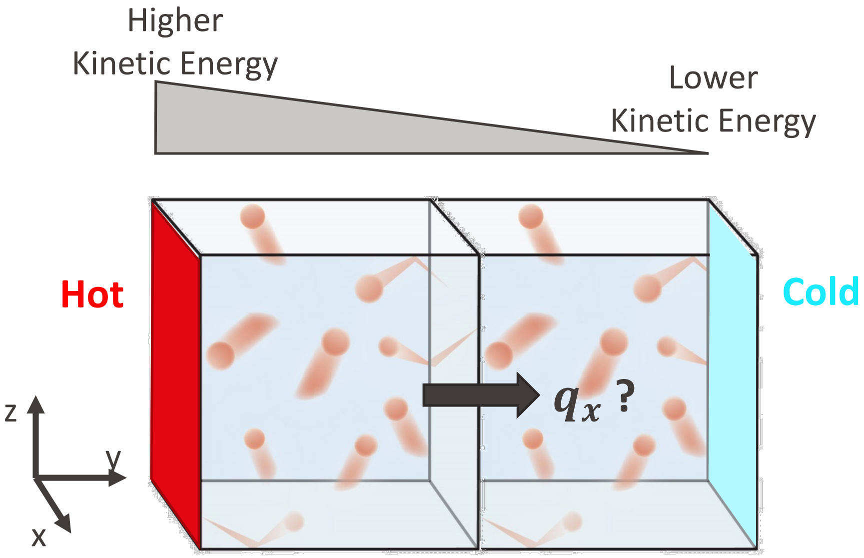


Thermal conductivity of GaAs fit with a model that accounts for the phonon dispersion as well as the different possible phonon branches.

Crystalline solids typically have a dome-shaped thermal conductivity with a peak at ~20K.

- At low T phonon-boundary scattering dominates and $k \propto C \propto T^3$.
- At high T phonon-phonon scattering dominates and $k \propto \frac{1}{T}$

Energy Transport



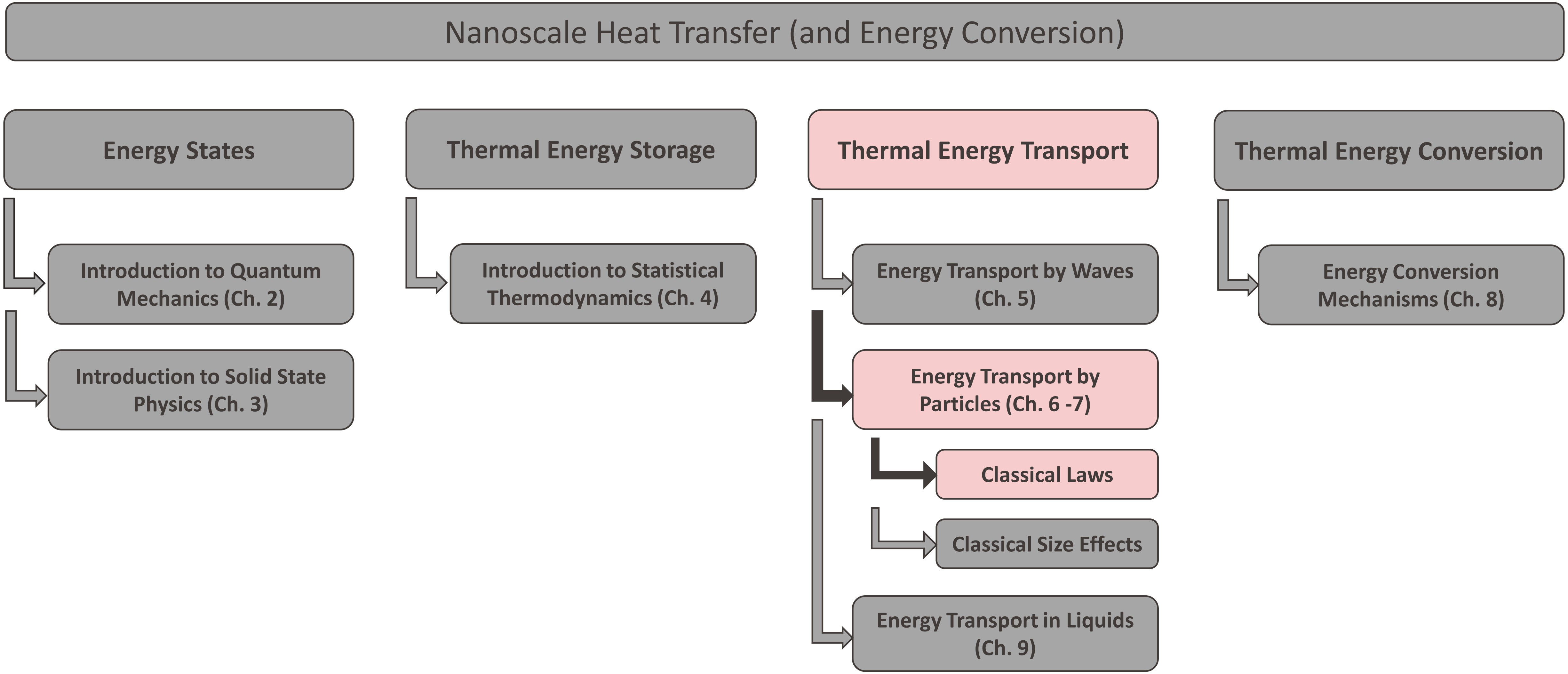
- The transient process must be slow compared to the relaxation time of the carriers.
- The temperature variation within one mean free path must be small compared to the absolute temperature
- The characteristic length must be much larger than the mean free path of the carrier.

➡

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

➡ **Phonons – Fourier Law and thermal conductivity**

In the Next Lecture



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