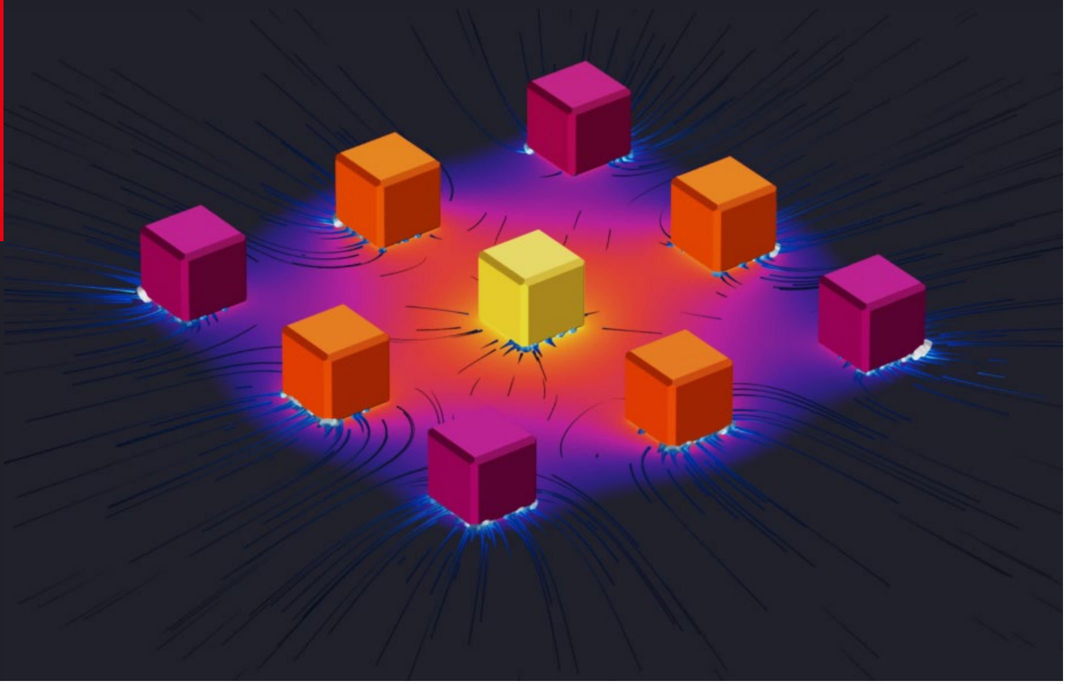
Nanoscale Heat Transfer (and Energy Conversion) ME469

Instructor: Giulia Tagliabue



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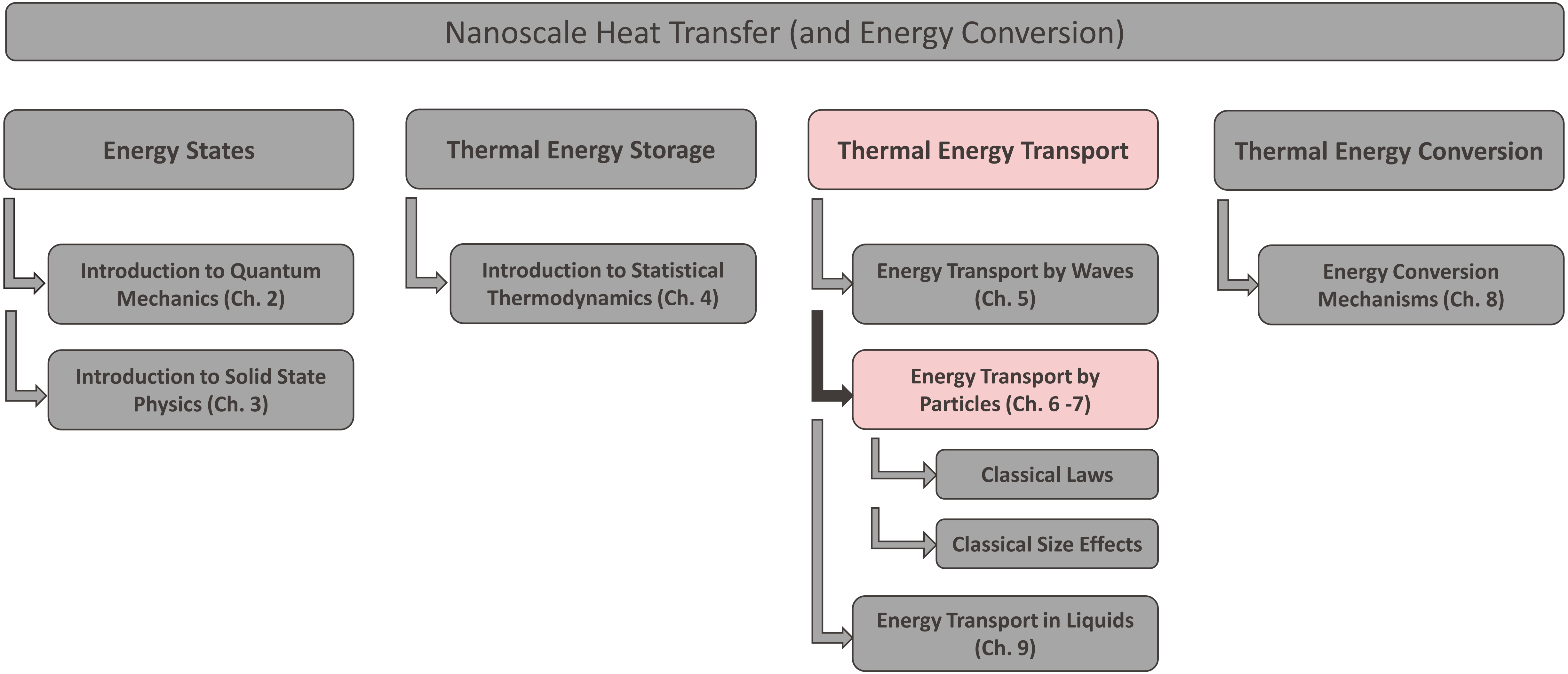
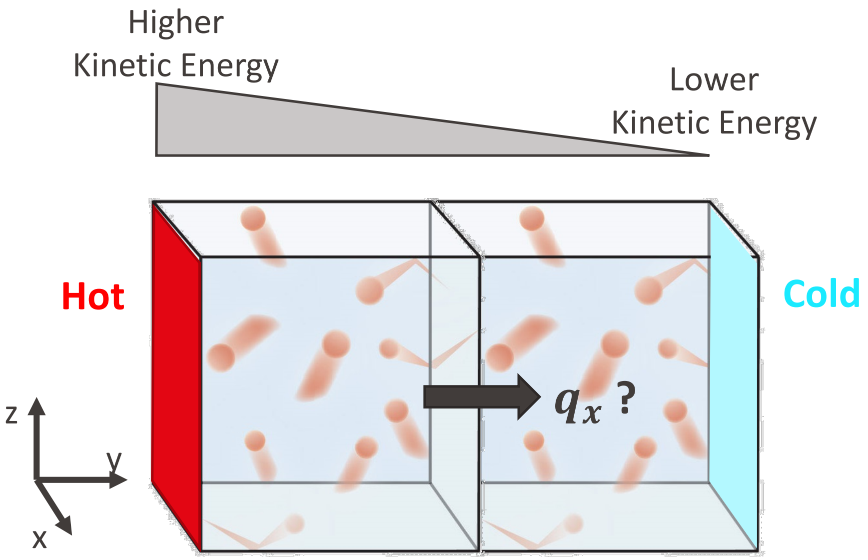
This Lecture

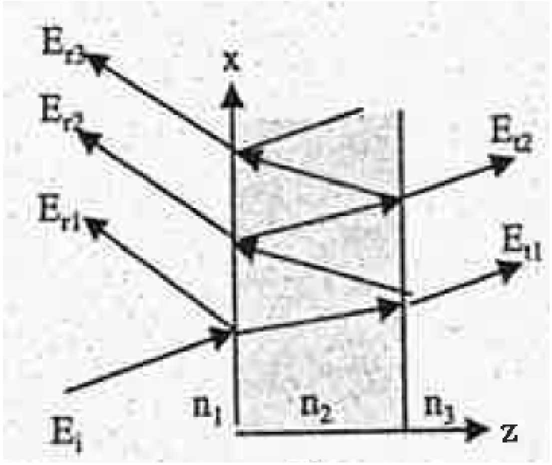


Nanoscale Heat Transfer (and Energy Conversion)

- 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



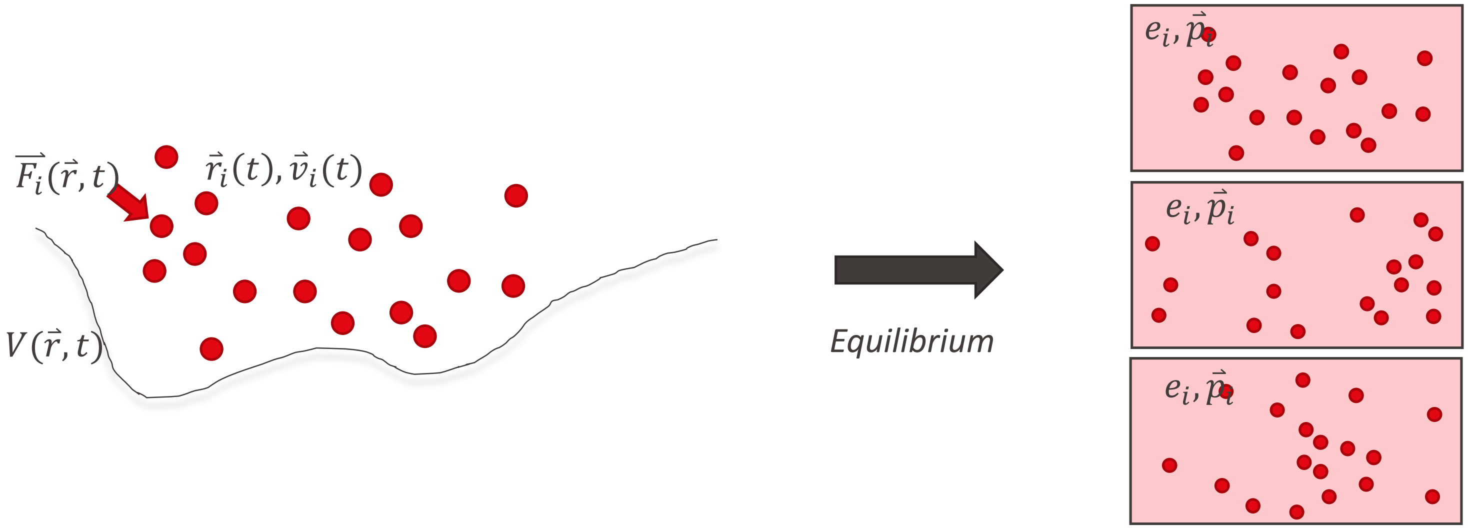


- If the phase of the carriers is important (interference effects), transport is coherent and the wave approach must be used (**ballistic transport**)
- **If the phase of the carriers in unimportant, a particle approach can be used (diffuse transport)**
- In between we have the **partially coherent regime**

In This Lecture …

- **The Boltzmann equation**
- Carrier Scattering (scattering integral and relaxation time approximation)

Systems at equilibrium and out-of-equilibrium

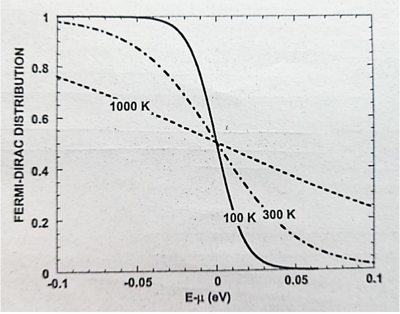


Fixed value of U, V, N, T …

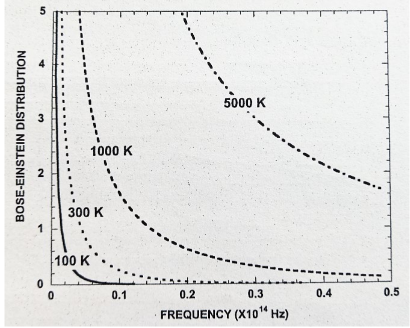
Fixed value of U, V, N, T …

Fixed value of U, V, N, T …

Fermi Dirac Distribution



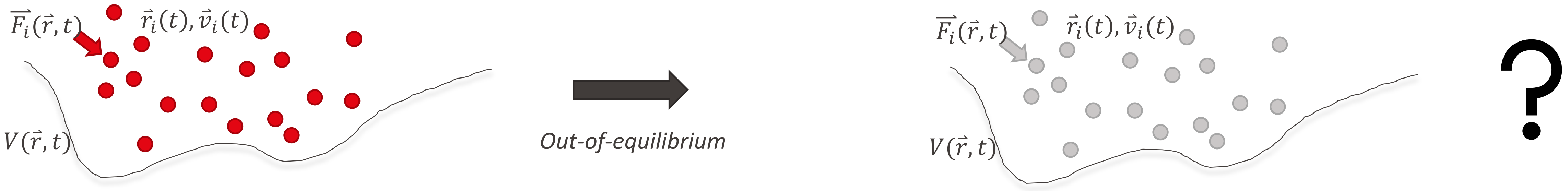
Bose Einstein Distribution



In statistical thermodynamics we considered a system at equilibrium.

We derived the equilibrium distribution functions that are dependent on the energy of the quantum state, the system temperature and the chemical potential.

Systems at equilibrium and out-of-equilibrium

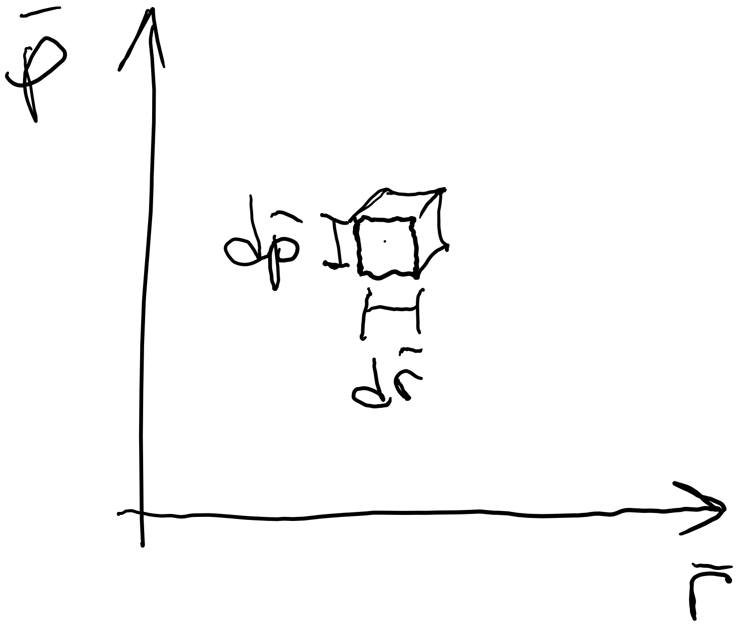


Out-of-equilibrium the derived distribution functions are no longer valid and in principle we would trace the trajectory of each particle in the system.

Because of the large number of atoms/molecules we again need to develop a statistical description of the particle trajectory.

We thus look for nonequilibrium distribution functions that depend on energy, temperature, position and other variables.

The Phase Space



The set of all possible positions **r** and momenta **p** is called the phase space of the system; in other words a set of three coordinates for each position coordinate *x, y, z*, and three more for each momentum component p_x, p_y, p_z. The entire space is 6-dimensional: a point in this space is $(\mathbf{r}, \mathbf{p}) = (x, y, z, p_x, p_y, p_z)$, and each coordinate is parameterized by time *t*. The small volume ("differential volume element") is written

$$d^3\mathbf{r}\, d^3\mathbf{p} = dx\, dy\, dz\, dp_x\, dp_y\, dp_z\,.$$

Since the probability of N molecules, which *all* have $\mathbf{r}$ and $\mathbf{p}$ within $d^3\mathbf{r}\, d^3\mathbf{p}$, is in question, at the heart of the equation is a quantity f which gives this probability per unit phase-space volume, or probability per unit length cubed per unit momentum cubed, at an instant of time t. This is a probability density function: $f(\mathbf{r}, \mathbf{p}, t)$, defined so that,

$$dN = f(\mathbf{r}, \mathbf{p}, t)\, d^3\mathbf{r}\, d^3\mathbf{p}$$

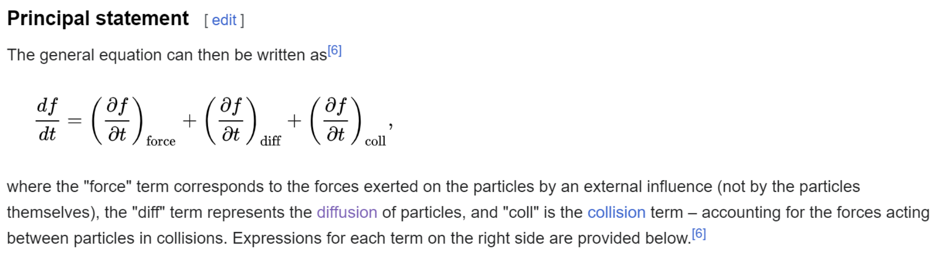
is the number of molecules which *all* have positions lying within a volume element $d^3\mathbf{r}$ about $\mathbf{r}$ and momenta lying within a momentum space element $d^3\mathbf{p}$ about $\mathbf{p}$, at time t.[5] Integrating over a region of position space and momentum space gives the total number of particles which have positions and momenta in that region:

$$\begin{aligned} N &= \int\limits_{\text{momenta}} d^3\mathbf{p} \int\limits_{\text{positions}} d^3\mathbf{r}\, f(\mathbf{r}, \mathbf{p}, t) \\ &= \iiint\limits_{\text{momenta}} \quad \iiint\limits_{\text{positions}} f(x, y, z, p_x, p_y, p_z, t)\, dx\, dy\, dz\, dp_x\, dp_y\, dp_z \end{aligned}$$

which is a 6-fold integral. While f is associated with a number of particles, the phase space is for one-particle (not all of them, which is usually the case with deterministic many-body systems), since only one $\mathbf{r}$ and $\mathbf{p}$ is in question. It is not part of the analysis to use $\mathbf{r}_1$, $\mathbf{p}_1$ for particle 1, $\mathbf{r}_2$, $\mathbf{p}_2$ for particle 2, etc. up to $\mathbf{r}_N$, $\mathbf{p}_N$ for particle *N*.

It is assumed the particles in the system are identical (so each has an identical mass m). For a mixture of more than one chemical species, one distribution is needed for each, see below.

The Boltzmann Equation

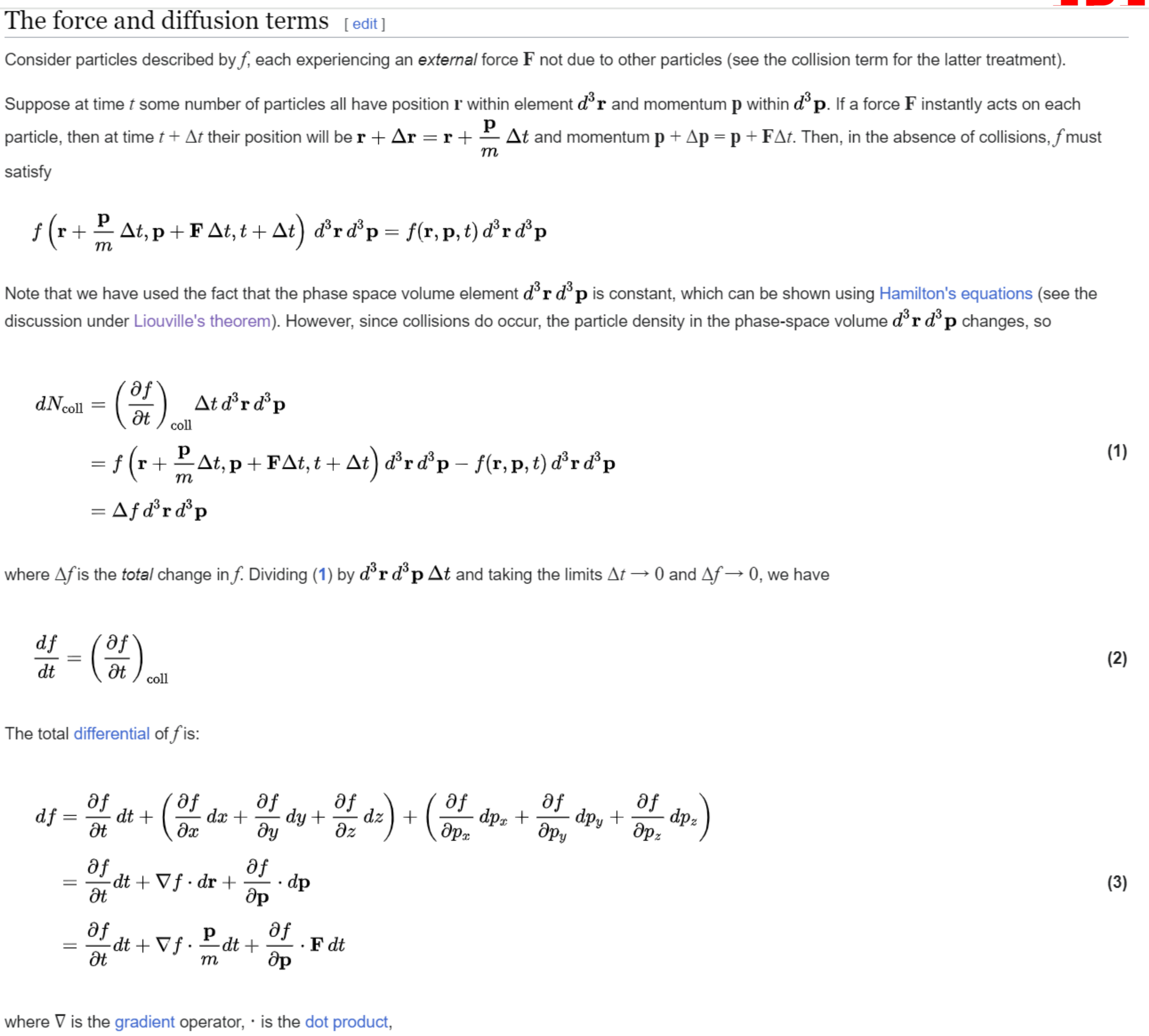


Principal statement [edit]

The general equation can then be written as[6]

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\text{force}} + \left(\frac{\partial f}{\partial t}\right)_{\text{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}},$$

where the "force" term corresponds to the forces exerted on the particles by an external influence (not by the particles themselves), the "diff" term represents the diffusion of particles, and "coll" is the collision term – accounting for the forces acting between particles in collisions. Expressions for each term on the right side are provided below.[6]



The force and diffusion terms [edit]

Consider particles described by f, each experiencing an *external* force $\mathbf{F}$ not due to other particles (see the collision term for the latter treatment).

Suppose at time t some number of particles all have position $\mathbf{r}$ within element $d^3\mathbf{r}$ and momentum $\mathbf{p}$ within $d^3\mathbf{p}$. If a force $\mathbf{F}$ instantly acts on each particle, then at time $t + \Delta t$ their position will be $\mathbf{r} + \Delta\mathbf{r} = \mathbf{r} + \frac{\mathbf{p}}{m}\Delta t$ and momentum $\mathbf{p} + \Delta\mathbf{p} = \mathbf{p} + \mathbf{F}\Delta t$. Then, in the absence of collisions, f must satisfy

$$f\left(\mathbf{r} + \frac{\mathbf{p}}{m}\,\Delta t, \mathbf{p} + \mathbf{F}\,\Delta t, t + \Delta t\right)\, d^3\mathbf{r}\, d^3\mathbf{p} = f(\mathbf{r}, \mathbf{p}, t)\, d^3\mathbf{r}\, d^3\mathbf{p}$$

Note that we have used the fact that the phase space volume element $d^3\mathbf{r}\, d^3\mathbf{p}$ is constant, which can be shown using Hamilton's equations (see the discussion under Liouville's theorem). However, since collisions do occur, the particle density in the phase-space volume $d^3\mathbf{r}\, d^3\mathbf{p}$ changes, so

$$\begin{aligned} dN_{\text{coll}} &= \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \Delta t\, d^3\mathbf{r}\, d^3\mathbf{p} \\ &= f\left(\mathbf{r} + \frac{\mathbf{p}}{m}\Delta t, \mathbf{p} + \mathbf{F}\Delta t, t + \Delta t\right) d^3\mathbf{r}\, d^3\mathbf{p} - f(\mathbf{r}, \mathbf{p}, t)\, d^3\mathbf{r}\, d^3\mathbf{p} \\ &= \Delta f\, d^3\mathbf{r}\, d^3\mathbf{p} \end{aligned} \tag{1}$$

where Δf is the *total* change in f. Dividing (1) by $d^3\mathbf{r}\, d^3\mathbf{p}\, \Delta t$ and taking the limits $\Delta t \to 0$ and $\Delta f \to 0$, we have

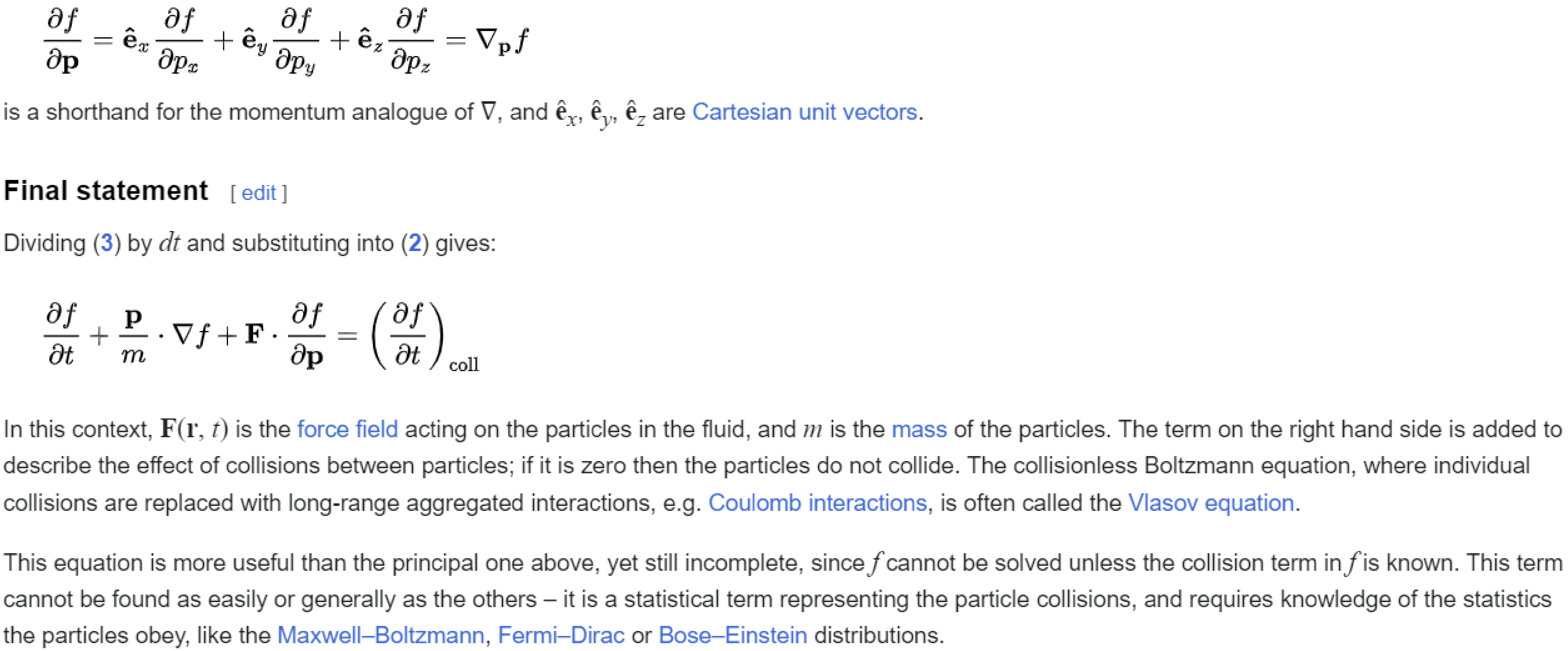
$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \tag{2}$$

The total differential of f is:

$$\begin{aligned} df &= \frac{\partial f}{\partial t}\, dt + \left(\frac{\partial f}{\partial x}\, dx + \frac{\partial f}{\partial y}\, dy + \frac{\partial f}{\partial z}\, dz\right) + \left(\frac{\partial f}{\partial p_x}\, dp_x + \frac{\partial f}{\partial p_y}\, dp_y + \frac{\partial f}{\partial p_z}\, dp_z\right) \\ &= \frac{\partial f}{\partial t} dt + \nabla f \cdot d\mathbf{r} + \frac{\partial f}{\partial \mathbf{p}} \cdot d\mathbf{p} \\ &= \frac{\partial f}{\partial t} dt + \nabla f \cdot \frac{\mathbf{p}}{m} dt + \frac{\partial f}{\partial \mathbf{p}} \cdot \mathbf{F}\, dt \end{aligned} \tag{3}$$

where ∇ is the gradient operator, $\cdot$ is the dot product,

The Boltzmann Equation



$$\frac{\partial f}{\partial \mathbf{p}} = \hat{\mathbf{e}}_x \frac{\partial f}{\partial p_x} + \hat{\mathbf{e}}_y \frac{\partial f}{\partial p_y} + \hat{\mathbf{e}}_z \frac{\partial f}{\partial p_z} = \nabla_{\mathbf{p}} f$$

is a shorthand for the momentum analogue of ∇, and $\hat{\mathbf{e}}_x$, $\hat{\mathbf{e}}_y$, $\hat{\mathbf{e}}_z$ are Cartesian unit vectors.

Final statement [edit]

Dividing (3) by dt and substituting into (2) gives:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla f + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}}$$

In this context, $\mathbf{F}(\mathbf{r}, t)$ is the force field acting on the particles in the fluid, and m is the mass of the particles. The term on the right hand side is added to describe the effect of collisions between particles; if it is zero then the particles do not collide. The collisionless Boltzmann equation, where individual collisions are replaced with long-range aggregated interactions, e.g. Coulomb interactions, is often called the Vlasov equation.

This equation is more useful than the principal one above, yet still incomplete, since f cannot be solved unless the collision term in f is known. This term cannot be found as easily or generally as the others – it is a statistical term representing the particle collisions, and requires knowledge of the statistics the particles obey, like the Maxwell–Boltzmann, Fermi–Dirac or Bose–Einstein distributions.

The Boltzmann Equation: Assumptions & Validity

The Boltzmann equation can be expressed in three different forms using the relationships $\vec{p} = m\vec{v}$ and $\vec{p} = \hbar\vec{k}$

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

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

Preferred for describing gases

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

Preferred for describing electrons/phonons

It is important to note that

$$\vec{v} = \nabla_k \omega = group\ velocity$$

$$\vec{p} = \hbar\vec{k} \rightarrow \vec{k} = \text{crystal momentum}$$

There is a major assumptions that underscore the derivation of the Boltzmann equation:

The N-particle distribution function can be expressed as the product distribution of each particle $f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)}) = f^{(1)}(t, \mathbf{r}_1, \mathbf{p}_1) f^{(1)}(t, \mathbf{r}_2, \mathbf{p}_2) \ldots f^{(1)}(t, \mathbf{r}_N, \mathbf{p}_N)$

- The particles in the system are quite independent of each other
- The distribution functions of one particle after collision are independent of the coordinate and momentum of the other particle (molecular chaos assumption)
- Collisions are infrequent
- **The Boltzmann equation is valid for dilute systems (molecular gases, electron/photon/phonon gases) but not for dense fluids (liquids)**

In addition the Boltzmann equation **does not account explicitly for wave effects** (i.e. interference & tunneling) .

The Boltzmann Equation: Average Quantities

The Boltzmann equation can be expressed in three different forms using the relationships $\vec{p} = m\vec{v}$ and $\vec{p} = \hbar\vec{k}$

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

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

Preferred for describing gases

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

Preferred for describing electrons/phonons

It is important to note that

$$\vec{v} = \nabla_k \omega = group\ velocity$$

$$\vec{p} = \hbar\vec{k} \rightarrow \vec{k} = \text{crystal momentum}$$

The Boltzmann equation gives us the distribution function. Similarly to the equilibrium, we can obtain the volume average of a microscopic quantity X as:

$$\langle X(\mathbf{r})\rangle = \frac{1}{V}\sum_{\mathbf{k},s} X(\mathbf{r},\mathbf{k}) f = \frac{1}{(2\pi)^3}\int X(\mathbf{r},\mathbf{k}) f d^3\mathbf{k}$$

Where s accounts for the polarization, if needed.

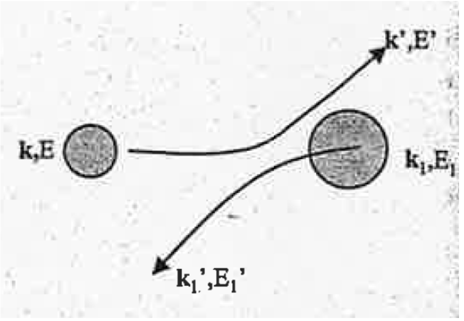
In This Lecture …

- The Boltzmann equation
- **Carrier Scattering (scattering integral and relaxation time approximation)**

The Scattering Integral

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:

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



Before the collision the two particles are in two quantum states characterized by $(\vec{k}, E)$ and $(\vec{k_1}, E_1)$. After the collision they are in $(\vec{k'}, E')$ and $(\vec{k'_1}, E'_1)$.

The scattering term in the Boltzmann equation describes the **net gain** of particles in one quantum state. Therefore, if we consider that a particle can be added or removed by the given quantum state due to scattering, we can write:

$$\left(\frac{\partial f}{\partial t}\right)_c = -\overbrace{\sum_{\mathbf{k}_1,\mathbf{k}',\mathbf{k}'_1} f(t,\mathbf{r},\mathbf{k})\, f(t,\mathbf{r},\mathbf{k}_1)\, W(\mathbf{k},\mathbf{k}_1 \to \mathbf{k}',\mathbf{k}'_1)}^{\textit{Particle scattered out of the state (loss)}} + \overbrace{\sum_{\mathbf{k}_1,\mathbf{k}',\mathbf{k}'_1} f(t,\mathbf{r},\mathbf{k}')\, f(t,\mathbf{r},\mathbf{k}'_1)\, W(\mathbf{k}',\mathbf{k}'_1 \to \mathbf{k},\mathbf{k}_1)}^{\textit{Particle scattered into the state (gain)}}$$

Distribution function
for the first particle

Distribution function
for the second particle

Transition rate
from the state $[\vec{k}, \vec{k}_1]$
To the state $[\vec{k}', \vec{k}'_1]$

Transition rate
from the state $[\vec{k}', \vec{k}'_1]$
to the state $[\vec{k}, \vec{k}_1]$

Note that we have used the same $\vec{r}$ for both particles, implicitly assuming that they do not have a finite volume.

The Scattering Integral

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:

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

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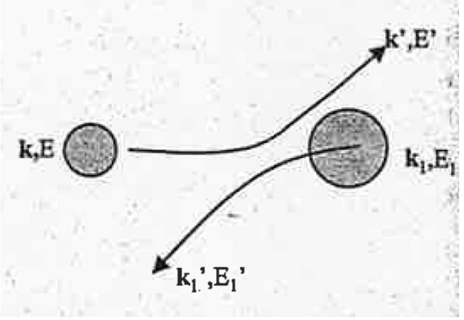


Before the collision the two particles are in two quantum states characterized by $(\vec{k}, E)$ and $(\overrightarrow{k_1}, E_1)$. After the collision they are in $(\overrightarrow{k'}, E')$ and $(\overrightarrow{k'_1}, E'_1)$.

The collision is a time-dependent process and to describe it, it is necessary to solve the time-dependent Schrodinger equation of the system of the two particles.

In the perturbation approximation, we can use the wave-functions of the **unperturbed** system to calculate the transition rate between the quantum states Ψ_i and Ψ_f using the Fermi Golden Rule:

$$W_i^f = \frac{2\pi}{\hbar}\left|\int \Psi_f^* H' \Psi_i d^3\mathbf{r}\right|^2 \delta(E_f - E_i)$$

$$M_{if} \equiv \langle i|H'|f\rangle \equiv \int \Psi_f^* H' \Psi_i d^3\mathbf{r}$$ ***Scattering matrix***

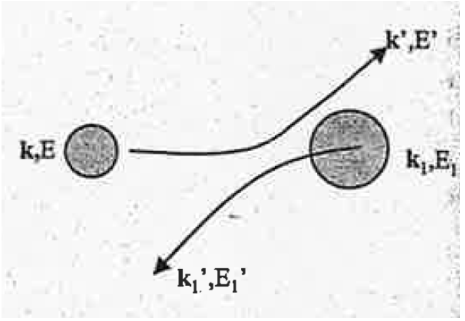
Eventually, accounting for energy and momentum conservation as well as reciprocity, it can be shown that:

$$\left(\frac{\partial f}{\partial t}\right)_c = -K \int W \times [f(t,\mathbf{r},\mathbf{k}) f(t,\mathbf{r},\mathbf{k}_1) - f(t,\mathbf{r},\mathbf{k}') f(t,\mathbf{r},\mathbf{k}_1')] d^3\mathbf{k}_1\, d^3\mathbf{k}' d^3\mathbf{k}_1'$$

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:

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



$$\left(\frac{\partial f}{\partial t}\right)_c = -K \int W \times [f(t, \mathbf{r}, \mathbf{k}) f(t, \mathbf{r}, \mathbf{k}_1) - f(t, \mathbf{r}, \mathbf{k}') f(t, \mathbf{r}, \mathbf{k}_1')] d^3 \mathbf{k}_1 \, d^3 \mathbf{k}' d^3 \mathbf{k}_1'$$

We observe that the scattering term requires an integral, making the Boltzmann equation an integral-differential equation with 7 variables that is hard to solve.
A drastic simplification that we will use in the following is based on the relaxation time approximation, giving:

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

If we ignore the spatial term, with this simplification the Boltzmann equation reduces to:

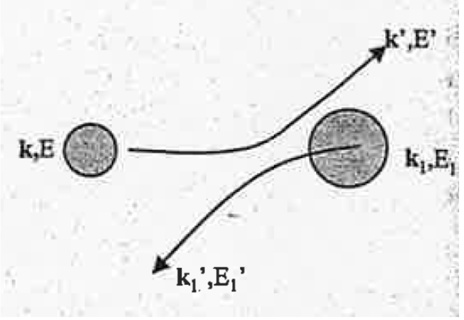
$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau} \Rightarrow f - f_0 = C e^{-t/\tau}$$

Relaxation-time
Time needed for a non-equilibrium system to relax back to the equilibrium distribution f_0

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:

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



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

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 Scattering Integral – Relaxation-time Approximation

We can therefore consider the following forms of the Boltzmann equation to analyze energy transport in a system accounting for scattering processes:

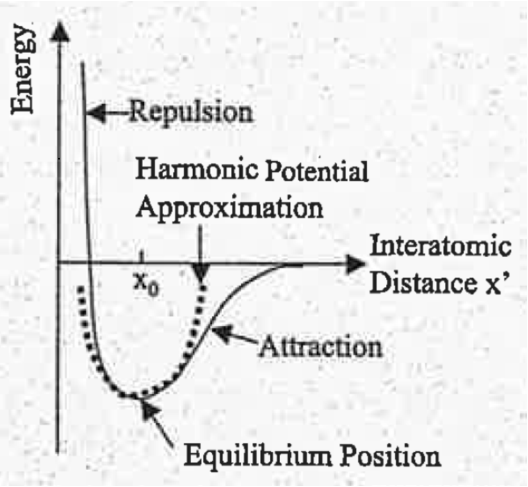
$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau}$$

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = -\frac{f - f_0}{\tau}$$

In This Lecture …

- The Boltzmann equation
- Carrier Scattering (scattering integral and relaxation time approximation)
    - ➢ **Phonons, Electrons and Molecules**

Scattering of Phonons



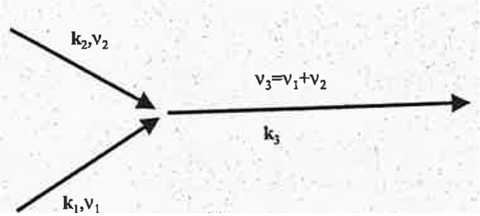
If the potential is purely harmonic, lattice waves are decomposed in normal modes that do not interact with each other. This implies that phonon propagation is unimpeded and thermal conductivity should be infinite

Instead, anharmonic terms of the inter-atomic potential are responsible for scattering of the phonons

$$U(x') = U(x_0) + \overbrace{\frac{1}{2}\left[\frac{d^2U}{dx'^2}\right]_{x'=x_0} (x'-x_0)^2}^{\text{Harmonic Potential}} + \overbrace{O[(x'-x_0)^3]}^{\text{Anharmonic Potential}}$$

$$H = H_0(\mathbf{r}) + H'(\mathbf{r}, t)$$

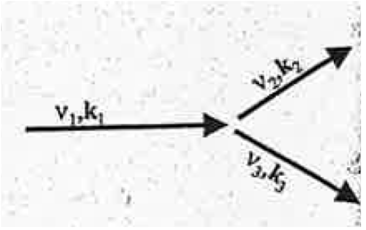
When using the Fermi golden rule with the third-order anharmonic potential as the perturbation Hamiltonian, it is found that this anharmonic force can result in:



Merging of two phonons (annihilation process)

$$h\nu_1 + h\nu_2 = h\nu_3$$

$$\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 = \mathbf{G}$$



Splitting of a phonon (generation process)

$$h\nu_1 = h\nu_2 + h\nu_3$$

$$\overrightarrow{k_1} - \overrightarrow{k_2} - \overrightarrow{k_3} = \overrightarrow{G}$$

Scattering of Phonons

Considering that phonons are massless and cannot be acted upon by an external force (quantization of the field), the Boltzmann equation reduces to:

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f = -\frac{f - f_0}{\tau}$$

The most important relaxation times that need to be considered are:

1. 3-phonon Umklapp process (volume) $\tau_u^{-1} = B e^{-\theta_D / bT} T^3 \omega^2$ B and b are constants and θ_D is the Debye temperature.
2. Scattering from impurities (volume) $\tau_I^{-1} = A \omega^4$
3. Boundary scattering (surface) $\tau_b^{-1} = b_s v / L$ L is a characteristic length, b_s is a shape factor

Typically, in a certain temperature range there is one scattering mechanism that dominates over the others.

Scattering of Electrons

For electrons, the Boltzmann transport equation expressed in the relaxation time approximation is:

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = -\frac{f - f_0}{\tau}$$

Electrons are predominantly scattered by phonons. Yet, in certain conditions, electron-electron scattering can become important.

For a phonon-creation process:

$$E_i = E_f + h\nu_p$$

$$\mathbf{k}_i = \mathbf{k}_f + \mathbf{k}_p + \mathbf{G}$$

$h\nu_p$ and $\mathbf{k}_p$ are the energy and wavevector of the created phonon

The dominant scattering process has $G = 0$.

In metals the number of phonons is proportional to the temperature (above the Debye temperature) and therefore: $\frac{1}{\tau} \propto T$

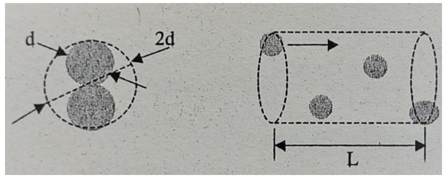
In semiconductors the presence of acoustic and optical phonons as well as the large amounts of impurities (dopants) give rise to very complex scattering interactions that require specific treatment.

Scattering of Molecules

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

In lecture 2, slide 9, we calculated the mean free path for a gas of molecules:

$$\boldsymbol{\Lambda} = \frac{\boldsymbol{m}}{\boldsymbol{\pi}\sqrt{2}\boldsymbol{\rho}\boldsymbol{d}^2}$$



Thus the mean free path can be obtained as :

$$\boldsymbol{\tau} = \frac{\boldsymbol{\Lambda}}{\boldsymbol{v}}$$

d = effective diameter of a molecule

m = molecular weight

$n = \frac{\rho}{m}$ = molecular number concentration

ρ = density

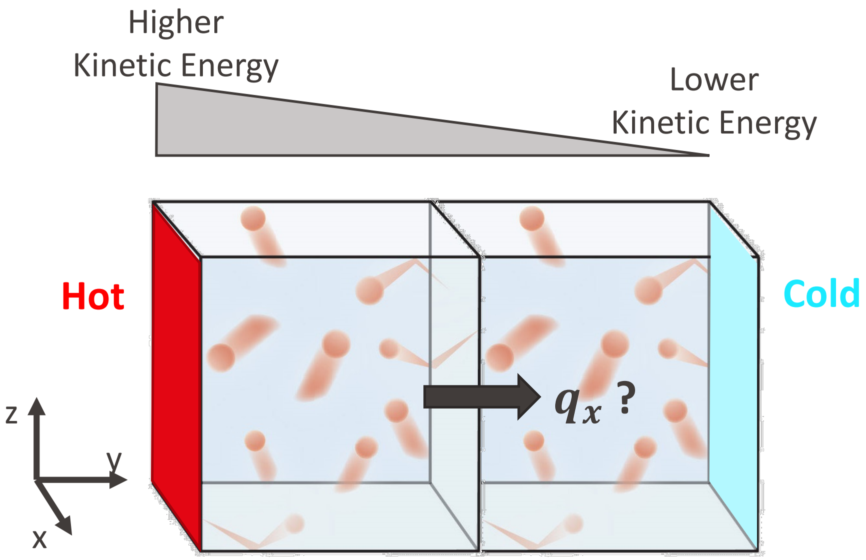
We now know that molecules will follow the Maxwell distribution and therefore their average velocity, at temperature *T*, will be:

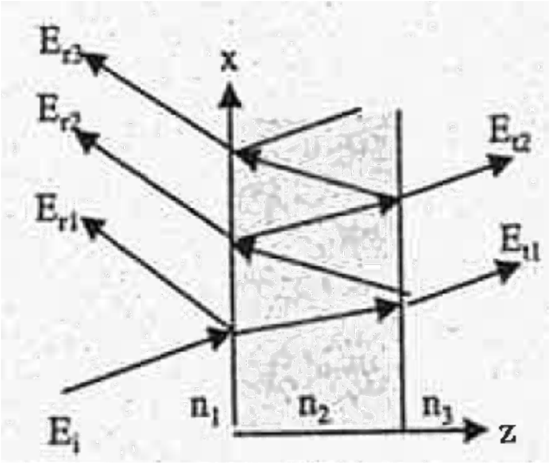
$$\bar{v} = \int_0^\infty \int_0^\infty \int_0^\infty v f_0(v)\, dv_x\, dv_y\, dv_z = \sqrt{\frac{8\kappa_B T}{\pi m}}$$

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) $\tau_u^{-1} = Be^{-\theta_D/bT} T^3 \omega^2$ 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
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	$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau}$	$\tau = \frac{\Lambda}{v}$ $\Lambda = \frac{m}{\pi\sqrt{2}\rho d^2}$ $\bar{v} = \int_0^\infty \int_0^\infty \int_0^\infty v f_0(v)\, dv_x\, dv_y\, dv_z = \sqrt{\frac{8k_B T}{\pi m}}$

Energy Transport



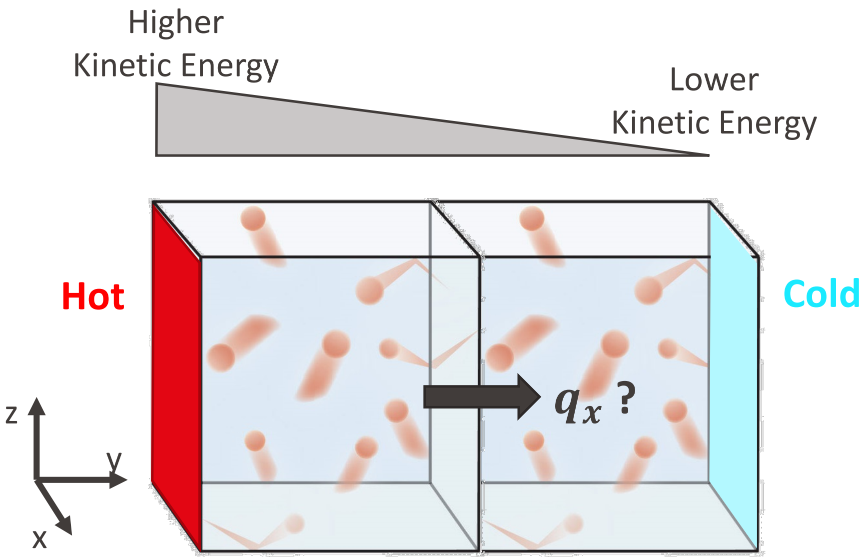


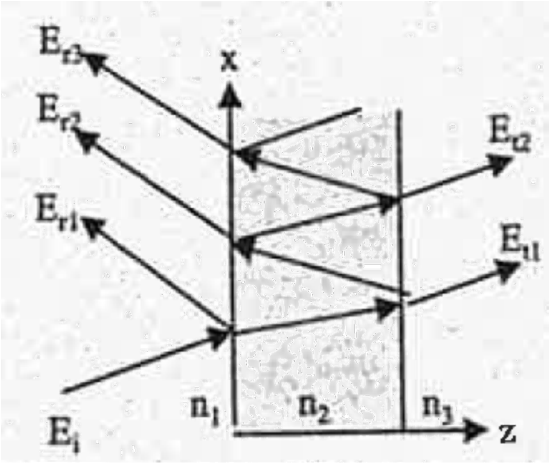
$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \bullet \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau}$$

$$\frac{\partial f}{\partial t} + \mathbf{v} \bullet \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{\hbar} \bullet \nabla_{\mathbf{k}} f = -\frac{f - f_0}{\tau}$$

Knowing the nonequilibrium statistical distribution f we can calculate the transport of energy within a material.

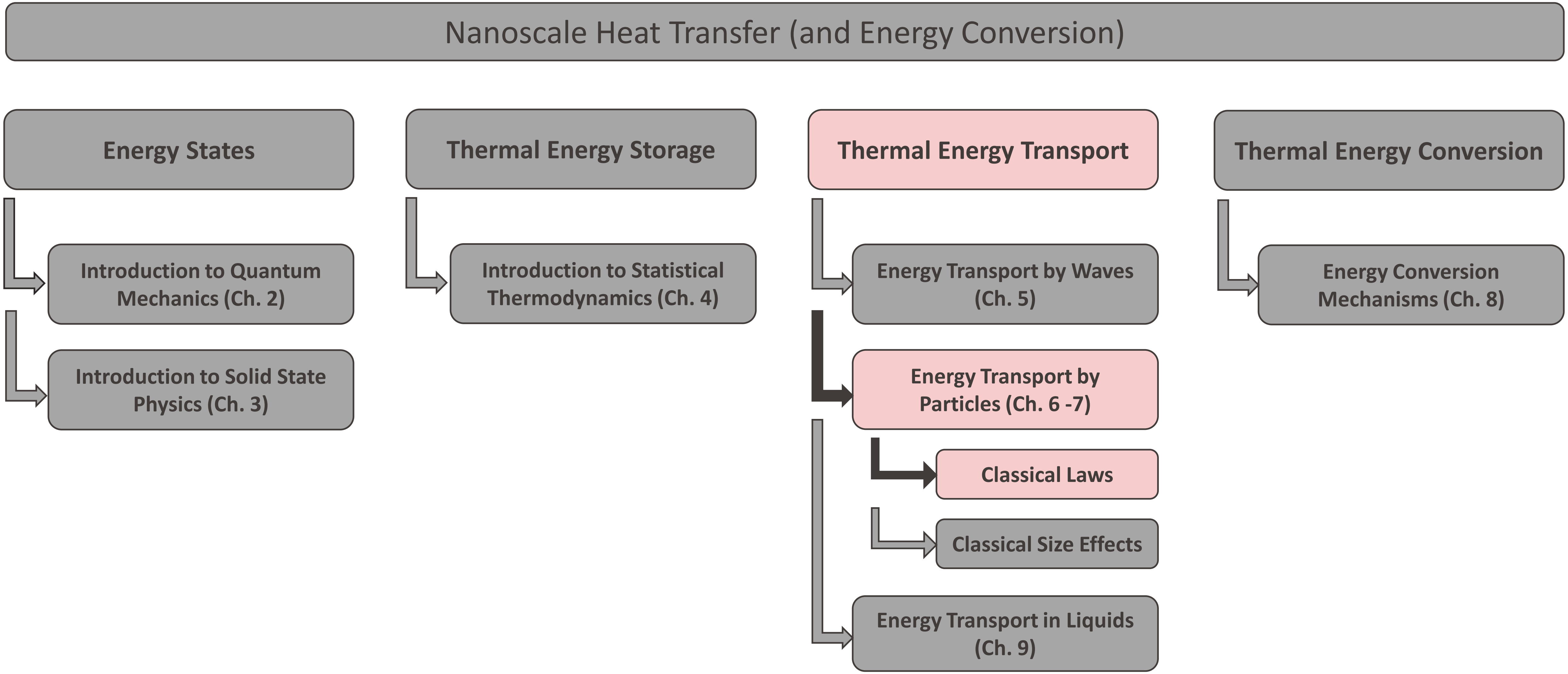
Energy Transport





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

Next Week



Nanoscale Heat Transfer (and Energy Conversion)

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

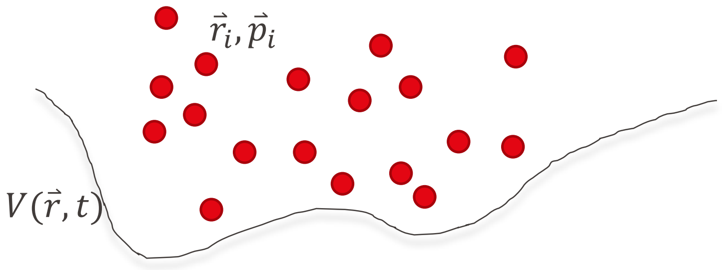
Thermal Energy Storage
- Introduction to Statistical Thermodynamics (Ch. 4)

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)

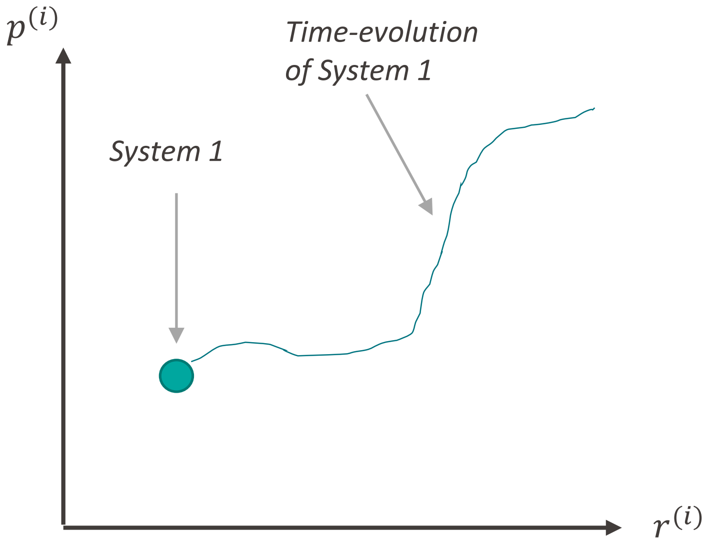
Thermal Energy Conversion
- Energy Conversion Mechanisms (Ch. 8)

Supplementary

The phase-space and the Liouville Equation



Phase Space Representation



$i = 1,2, \dots, n$
$n = mN$

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: $\vec{r_1} = (\underbrace{x_1, y_1, z_1}_{\textit{position}}, \underset{\substack{\downarrow \\ \textit{Vibrational} \\ \textit{coordinate}}}{\Delta r_1}, \underbrace{\theta_1, \varphi_1}_{\textit{rotation}})$ 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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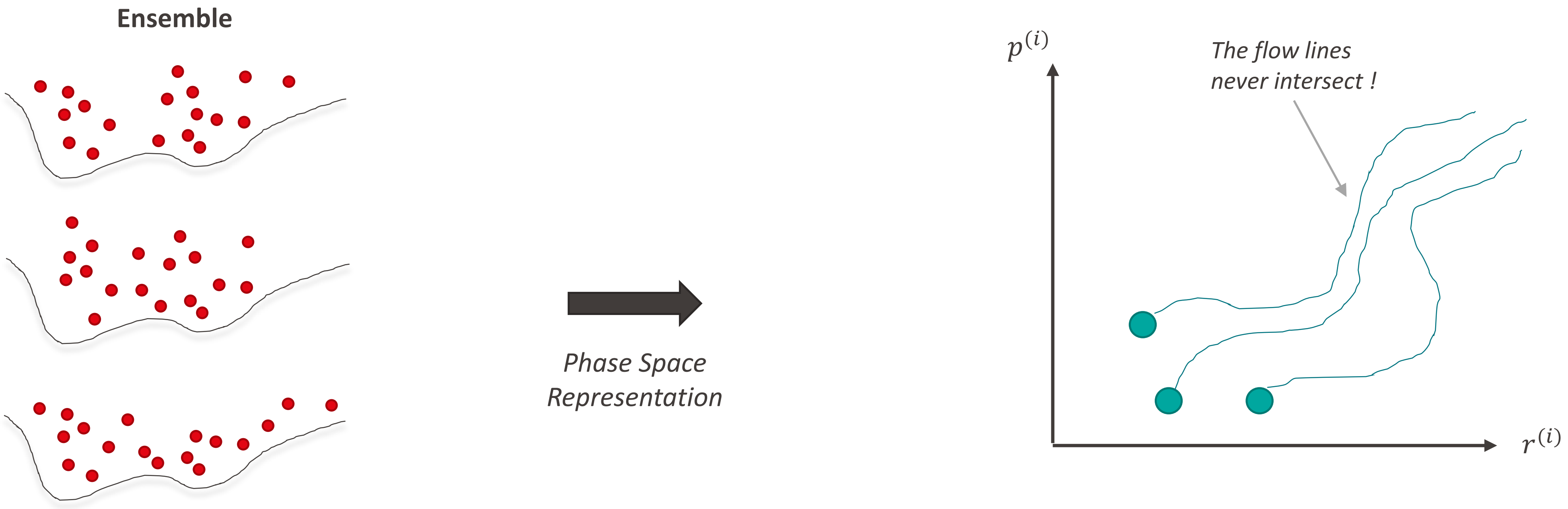
*the evolution of a system is uniquely determined by the initial conditions

The phase-space and the Liouville Equation



$$i = 1,2,\dots,n$$
$$n = mN$$

We now consider an **ensemble**. Each system in the ensemble is a point in the phase space and the trajectories of all these system do not intersect.

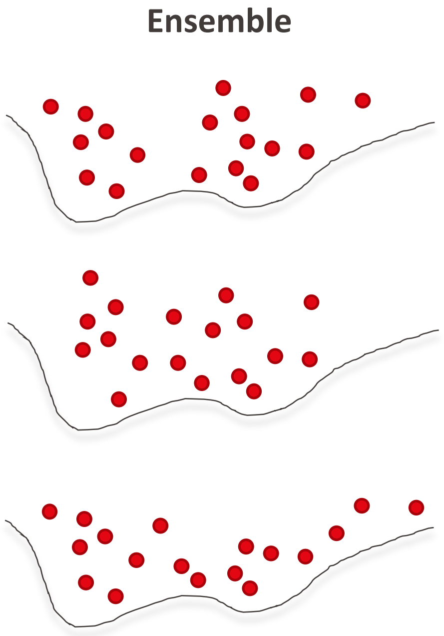
Given that the number of systems in an ensemble is very large, ($N_{systems} \gg N$), we can consider the points in phase-space to form a **continuum**.

Thus, we define a particle density $f^{(N)}$ in phase-space such as, surrounding any point $\left(\vec{r}^{(n)} = (r^1, r^2, \dots r^n), \vec{p}^{(n)} = (p^1, p^2, \dots, p^n)\right)$:

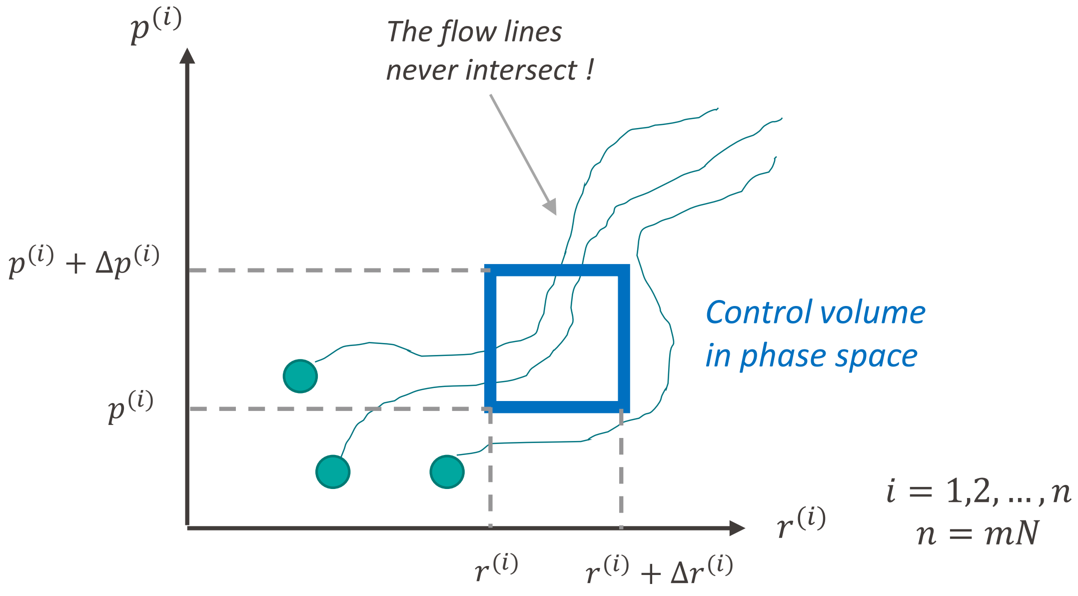
$$No.of\ systems = f^{(N)}\left(t, \vec{r}^{(n)}, \vec{p}^{(n)}\right) \Delta\vec{r}^{(n)} \Delta\vec{p}^{(n)}$$

- $f^{(N)}\left(t, \vec{r}^{(n)}, \vec{p}^{(n)}\right)$ is the **N-particle distribution function** and represent the probability density of finding a specific system at a specific state $\left(\vec{r}^{(n)}, \vec{p}^{(n)}\right)$
- For an ergodic ensemble $f^{(N)}\left(t, \vec{r}^{(n)}, \vec{p}^{(n)}\right)$ represent the **probability of observing one system** at a particular state over a period of time smaller than a characteristic time of the system.

The phase-space and the Liouville Equation


Ensemble

Phase Space Representation



$i = 1,2,\ldots,n$
$n = mN$

We now describe the evolution of the ensemble by describing the evolution of $f^{(N)}$ in phase-space. Given that the flow lines do not intersect and the points in phase-space are conserved we can use a control volume approach to derive the equation for the distribution function:

$$-\sum_{i=1}^{n} \frac{\partial}{\partial r^{(i)}}\left(f^{(N)} \frac{\partial r^{(i)}}{\partial t}\right) - \sum_{i=1}^{n} \frac{\partial}{\partial p^{(i)}}\left(f^{(N)} \frac{\partial p^{(i)}}{\partial t}\right) = \frac{\partial f^{(N)}}{\partial t}$$

where $\partial p^{(i)}/\partial t = \dot{p}^{(i)}$ and $\partial r^{(i)}/\partial t = \dot{r}^{(i)}$ *Flow rates of points*

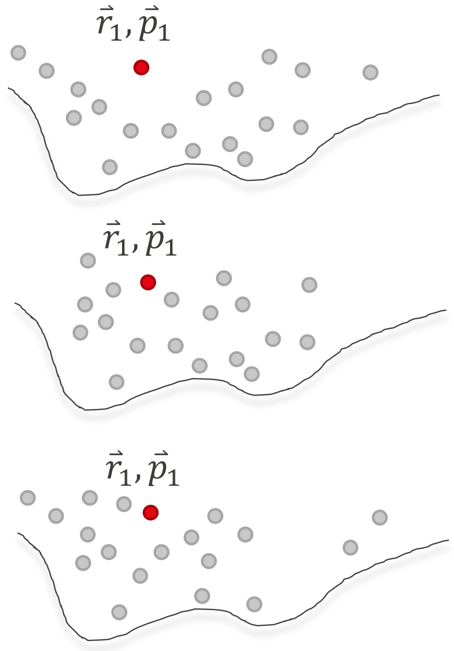
Using $\frac{\partial \dot{r}^{(i)}}{\partial r^{(i)}} + \frac{\partial \dot{p}^{(i)}}{\partial p^{(i)}} = 0$ we obtain:

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{i=1}^{n} \dot{r}^{(i)} \times \frac{\partial f^{(N)}}{\partial r^{(i)}} + \sum_{i=1}^{n} \dot{p}^{(i)} \times \frac{\partial f^{(N)}}{\partial p^{(i)}} = 0$$

Liouville equation
Valid for classic and quantum systems
The number of variables is $n \sim N_A$ (Avogadro's constant)

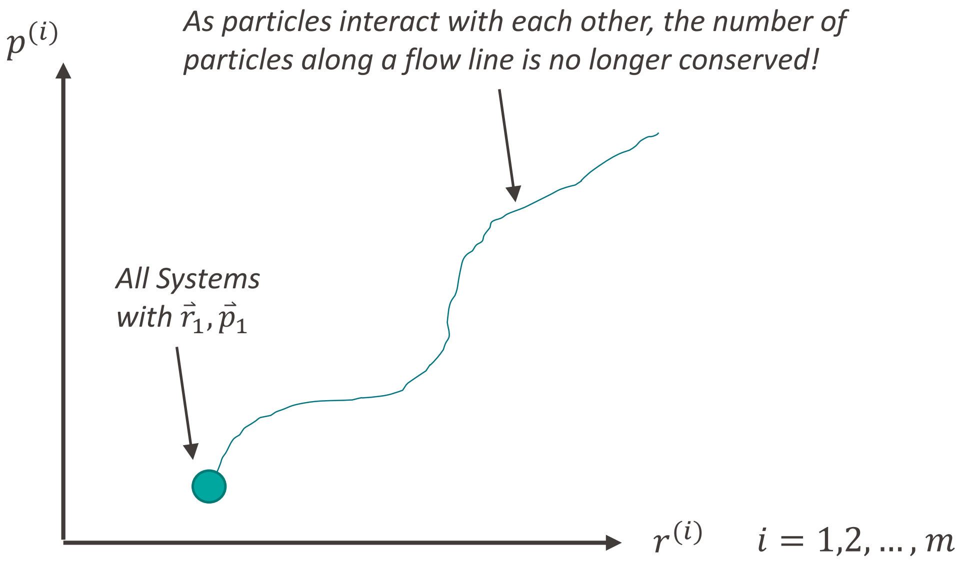
The Boltzmann Equation: from $2n$ to $2m$-dimensional space

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 consider a representative particle in a system and we average the N-particle distribution function over the N-1 particles to obtain a 1-particle distribution:

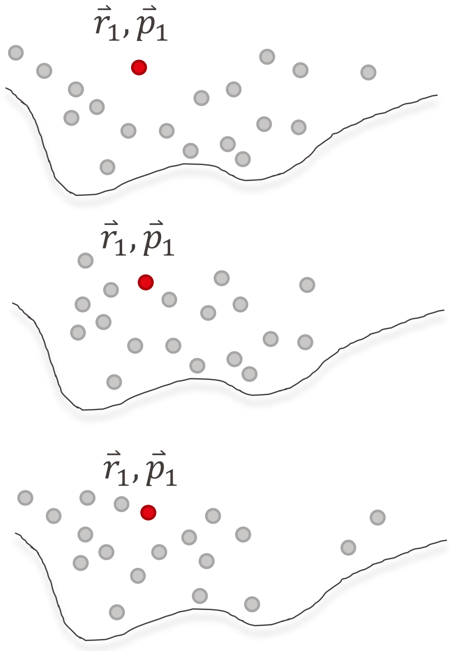
$$f^{(1)}(t, \mathbf{r}_1, \mathbf{p}_1) = \frac{N!}{(N-1)!} \int \dots \int f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)}) d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{p}_2 \dots d\mathbf{p}_N$$

➡ $f^{(1)}(t, \vec{r}_1, \vec{p}_1)$ is the **1-particle distribution function** and represent the number density of systems having coordinates $(\vec{r}_1, \vec{p}_1)$

$$f(t, \mathbf{r}, \mathbf{p}) d^3\mathbf{r} d^3\mathbf{p} = \text{number of systems in } d^3\mathbf{r} d^3\mathbf{p}$$

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

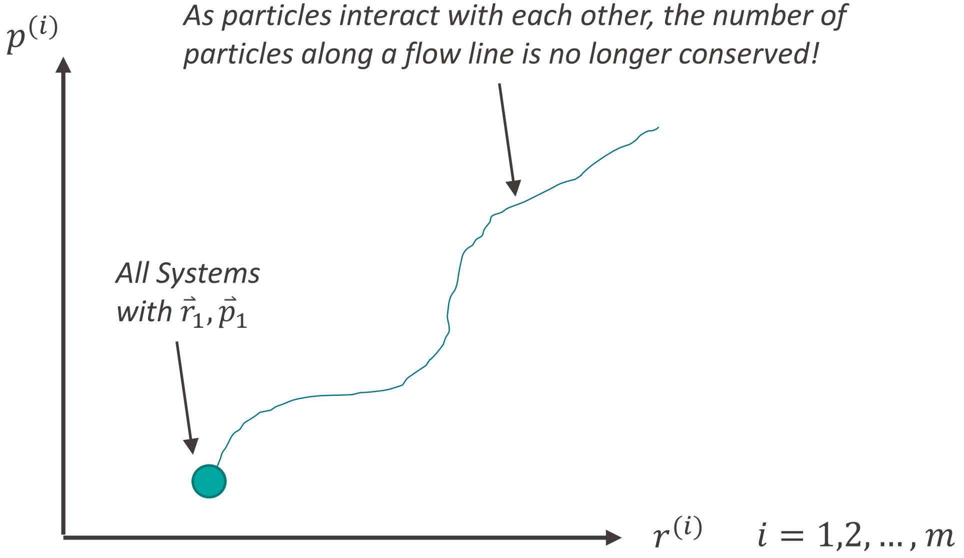
1-particle in a system



$2m$-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

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

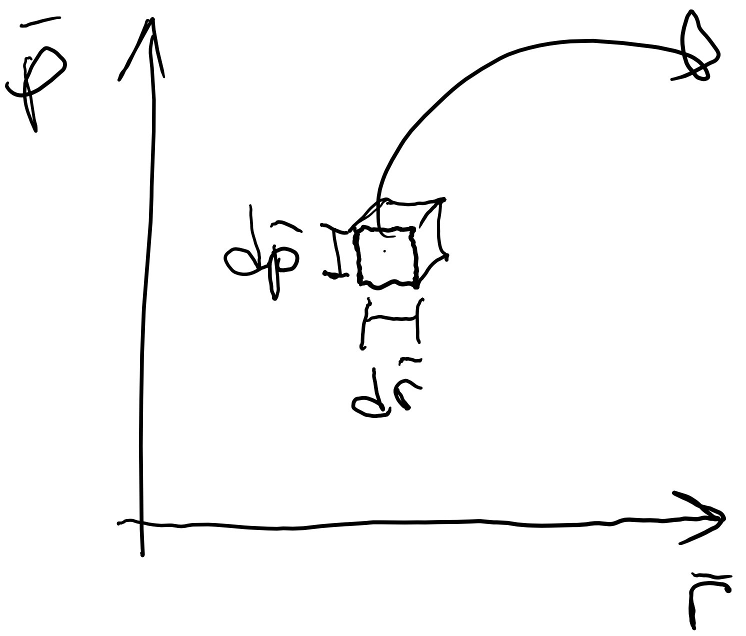
Scattering Term
Accounts for the collisions of this particle with all the other particles in the system (**non-conserving nature** of the 1-particle distribution function)

where

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

Boltzmann Equation

phase space $(\bar{r}, \bar{p}) = (x, y, z, p_x, p_y, p_z)$



? probability density fcn. f

$$N_{part} = f(\bar{r}, \bar{p}, t)\, d^3\bar{r}\, d^3\bar{p}$$

$$\bar{F} \to \begin{cases} \bar{r} \to \bar{r} + \Delta\bar{r} = \bar{r} + v\Delta t = \bar{r} + \frac{\bar{p}}{m}\Delta t \\ \bar{p} \to \bar{p} + \Delta\bar{p} = \bar{p} + \bar{F}\Delta t \end{cases}$$

$$f\left(\bar{r} + \frac{\bar{p}}{m}\Delta t, \bar{p} + F\Delta t, t + \Delta t\right) - f(\bar{r}, \bar{p}, t) = C$$

$$\boxed{\Delta N_{coll}} = \Delta f\, d^3p\, d^3r$$

$f(\bar r, \bar p, t)$

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{\partial f}{\partial t}\cancel{dt} + \underbrace{\left(\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz\right)}_{\nabla f \cdot \bar r} + \underbrace{\left(\frac{\partial f}{\partial P_x}dp_x + \dots\dots\right)}_{\frac{\partial f}{\partial \bar p}\cdot d\bar p}$$

$$\bar r \rightarrow \frac{\bar P}{m}\cancel{dt} \qquad \frac{\partial f}{\partial \bar p} \rightarrow \nabla_p f \qquad d\bar p \rightarrow \bar F \cancel{dt}$$

Non equilibrium !!

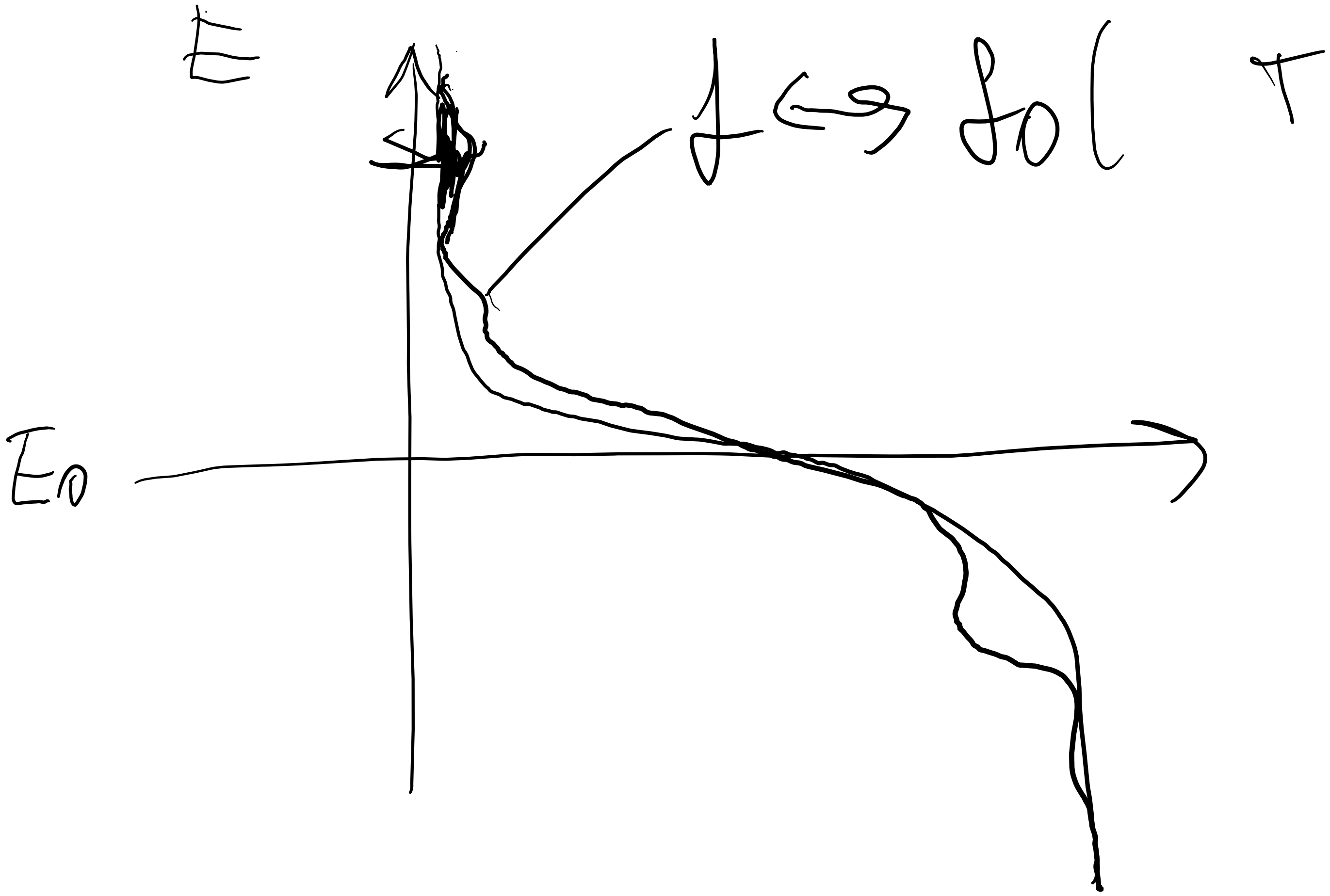
$f \neq f_0$ → Fermi Dirac
→ Bose-Einstein

Spatial changes in properties

external forces

$$\Rightarrow \frac{\partial f}{\partial t} + \frac{\bar p}{m}\cdot\nabla f + \bar F\cdot\nabla_p f = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

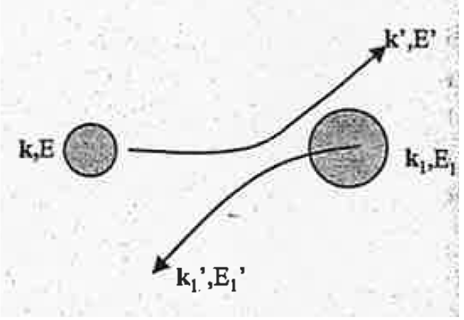
collisions


E
$f \leftrightarrow f_0($
T
E_0

The Scattering Integral

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:

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



Before the collision the two particles are in two quantum states characterized by $(\vec{k}, E)$ and $(\overrightarrow{k_1}, E_1)$. After the collision they are in $(\overrightarrow{k'}, E')$ and $(\overrightarrow{k'_1}, E'_1)$.

The collision is a time-dependent process and to describe it, it is necessary to solve the time-dependent Schrodinger equation of the system of the two particles.

The calculation can be simplified using the **perturbation method**, i.e. considering the Hamiltonian of the system composed of a non-interacting, steady state part and a small time-dependent perturbation term:

$$H = H_0(\mathbf{r}) + H'(\mathbf{r}, t)$$

where $H' \ll H_0$

In this approximation, we can thus use the wave-functions of the **unperturbed** system to calculate the transition rate between the quantum states Ψ_i and Ψ_f as:

Fermi golden rule

$$\begin{aligned} W_i^f &= \frac{2\pi}{\hbar} \left| \int \Psi_f^* H' \Psi_i d^3\mathbf{r} \right|^2 \delta(E_f - E_i) \\ &= \frac{2\pi}{\hbar} |\langle i | \mathrm{H}' | f \rangle|^2 \delta(E_f - E_i) \\ &= \frac{2\pi}{\hbar} M_{if}^2 \delta(E_f - E_i) \end{aligned}$$

$$M_{if} \equiv \langle i | H' | f \rangle \equiv \int \Psi_f^* H' \Psi_i d^3\mathbf{r}$$

Scattering matrix

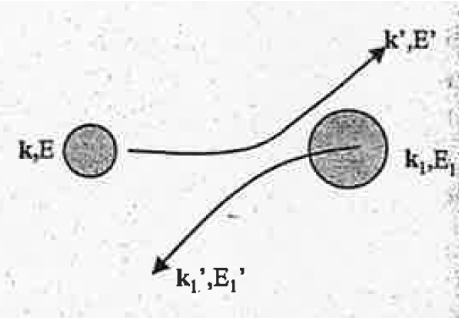
$$\delta(E_f - E_i) = \begin{cases} 1 & E_i = E_f \\ 0 & E_i \neq E_f \end{cases} \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(x) dx = 1$$

The Scattering Integral

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:

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

⟷



We re-write the scattering term as an integral:

$$\left(\frac{\partial f}{\partial t}\right)_c = -K \int f(t, \mathbf{r}, \mathbf{k}) f(t, \mathbf{r}, \mathbf{k}_1) W(\mathbf{k}, \mathbf{k}_1 \to \mathbf{k}', \mathbf{k}_1') d^3\mathbf{k}_1 d^3\mathbf{k}' d^3\mathbf{k}_1' + K \int f(t, \mathbf{r}, \mathbf{k}') f(t, \mathbf{r}, \mathbf{k}_1') W(\mathbf{k}', \mathbf{k}_1' \to \mathbf{k}, \mathbf{k}_1) d^3\mathbf{k}_1 d^3\mathbf{k}' d^3\mathbf{k}_1'$$

where $K = V^3/(2\pi)^9$

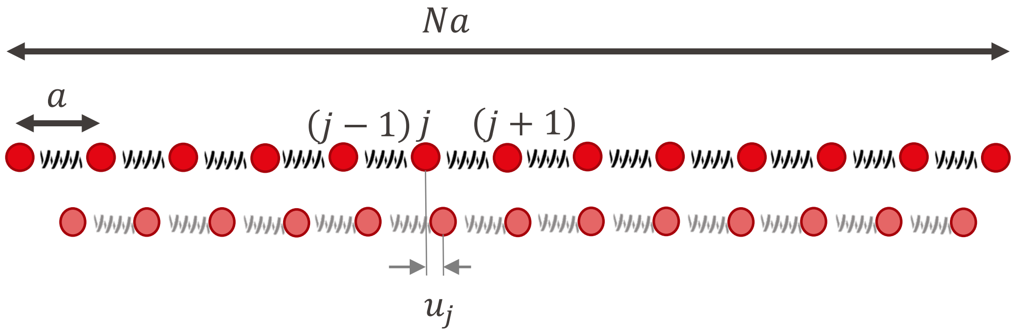
We also observe that the energy and momentum conservation require: $E(\mathbf{k}) + E(\mathbf{k}_1) = E(\mathbf{k}') + E(\mathbf{k}_1')$ $\mathbf{k} + \mathbf{k}_1 = \mathbf{k}' + \mathbf{k}_1'$

While a detailed balance analysis gives the reciprocity relation: $W(\mathbf{k}, \mathbf{k}_1 \to \mathbf{k}', \mathbf{k}_1') = W(\mathbf{k}', \mathbf{k}_1' \to \mathbf{k}, \mathbf{k}_1)$

Giving the final form of the collision integral:

$$\left(\frac{\partial f}{\partial t}\right)_c = -K \int W \times [f(t, \mathbf{r}, \mathbf{k}) f(t, \mathbf{r}, \mathbf{k}_1) - f(t, \mathbf{r}, \mathbf{k}') f(t, \mathbf{r}, \mathbf{k}_1')] d^3\mathbf{k}_1\, d^3\mathbf{k}' d^3\mathbf{k}_1'$$

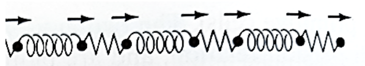
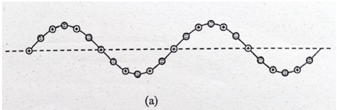
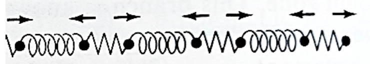
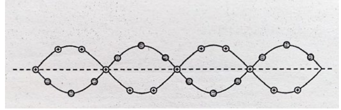
Scattering of Phonons



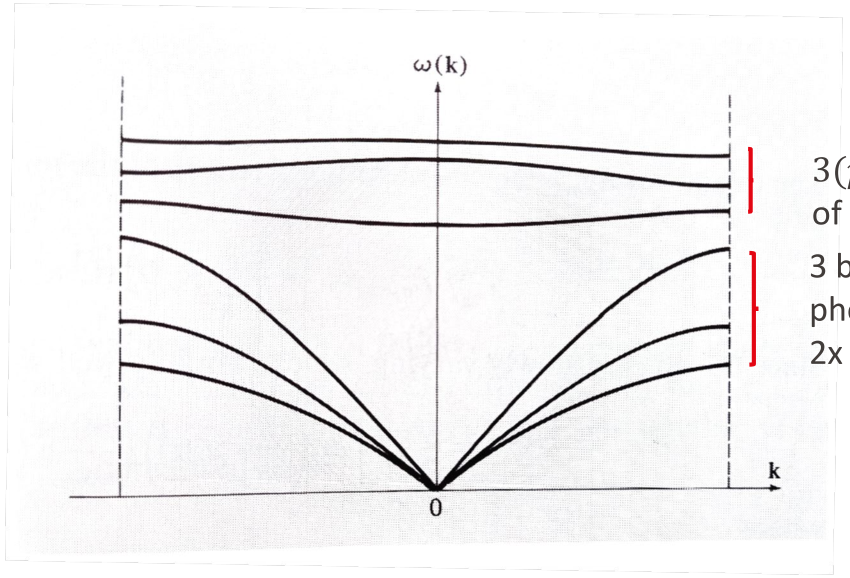
Hypothesis:

1. Force interactions occur only between nearest neighbors
2. **Harmonic** interaction force (Hooke's law)
3. Equal mass M and spring constant K

$$\left\{\begin{array}{ll} u_j = x_j - x_j^0 & \text{displacement} \\ U^{harm} = \frac{1}{2} K \sum_j \left[u_j - u_{j+1}\right]^2 & \text{potential} \\ F_j = -\frac{\partial \ U^{harm}}{\partial u_j} = K\left(u_{j+1} - u_j\right) - K\left(u_j - u_{j-1}\right) & \text{force} \end{array}\right.$$

	Longitudinal Waves	**Transversal Waves**
Acoustic Phonons		
Optical Phonons		

$p = \#atoms\ per\ lattice\ point$



$3(p-1)$ branches of optical phonons

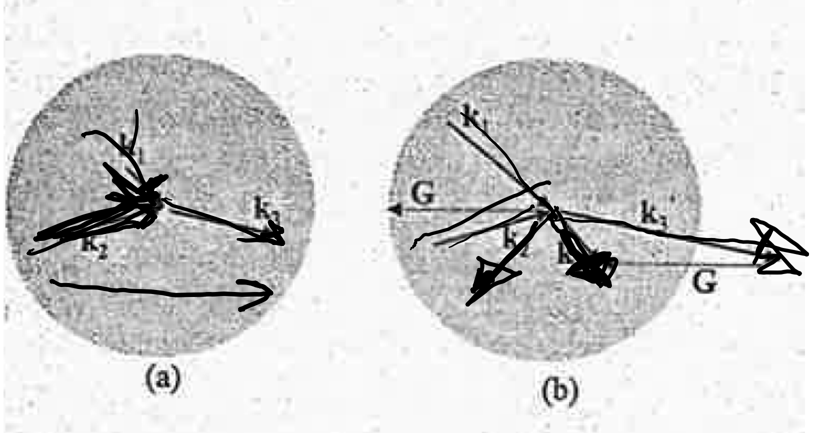
3 branches of acoustic phonons (1x longitudinal, 2x transversal)

If the potential is purely harmonic, lattice waves are decomposed in normal modes that do not interact with each other.

➡ **This implies that phonon propagation is unimpeded and thermal conductivity should be infinite**

Instead, anharmonic terms of the inter-atomic potential are responsible for scattering of the phonons

Scattering of Phonons



Let's consider the annihilation process.

Looking more closely at the momentum requirements, we observe that there are two possible cases:

a) $\boxed{k_1 + k_2} < k_{Brillouin}$. Therefore $G = 0$

b) $k_1 + k_2 > \underline{k_{Brillouin}}$. Therefore $G \neq 0$ and the process is called ***Umklapp process***

In case a) the resulting phonon continue to move along the same direction of the initial two phonons, hence heat is conducted in an unimpeded manner.

In case b) we observe that the addition of the reciprocal lattice wavevector, changes the net direction of the phonon propagation.

➡ It is the Umklapp process that gives rise to the thermal resistance

Scattering of Photons

Photons are also massless particles that cannot be acted upon by an external force, hence the Boltzmann equation is:

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

For photons, it is more common to consider the energy flux, i.e. the intensity, rather than the particle flux. $I_\nu = \frac{\text{Power}}{dA_\perp \, d\Omega \, d\nu}$

We observe that, along each wavevector direction, a photon will move at group velocity $\vec{v_g}(\vec{k})$.

Given the single-particle distribution, f, we can thus say that for a given quantum state the energy flux is $E \times \mathbf{v}_g(\mathbf{k}) \times f$

The rate of energy, i.e. intensity, propagating along a wavevector direction, per unit solid angle is $I(t, E, \mathbf{k}) = E \times v_g(\mathbf{k}) f(t, \mathbf{r}, \mathbf{k}) dD(E, \mathbf{k})$

We recall that $dD(E, \mathbf{k}) = \frac{\text{No. of States within } (E, E + dE) \text{ and } d\Omega}{V dE d\Omega} = \frac{D(E)}{4\pi}$ ➡ $I(t, E, \mathbf{k}) = \frac{1}{4\pi} E \times v_g(\mathbf{k}) f(t, \mathbf{r}, \mathbf{k}) D(E)$

Considering the steady state Boltzmann equation : $\mathbf{v} \bullet \nabla_{\mathbf{r}} f = \left(\frac{\partial f}{\partial t}\right)_c$ along the direction of propagation, *s*, we have: $\mathbf{v} \bullet \nabla_{\mathbf{r}} f = v \frac{\partial f}{\partial s}$ *v speed of light in medium*

Thus we can recast the steady-state Boltzmann equation in terms of intensity as:

$$\frac{\partial I_\nu}{\partial s} = \frac{1}{v} \left(\frac{\partial I_\nu}{\partial t}\right)_c$$

Scattering of Photons

$$\frac{\partial I_\nu}{\partial s} = \frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{c,}$$

Scattering of photons can be **elastic** or **inelastic** (absorption/emission).

For the inelastic term: $\left(\frac{\partial f}{\partial t}\right)_{c,\text{inelastic}} = -\frac{f - f_0}{\tau}$ ➡ $\left(\frac{\partial I_\nu}{\partial t}\right)_{c,inelastic} = -\frac{I_\nu - I_{\nu 0}}{\Lambda}$ where $\Lambda = v\tau$ and $I_{\nu 0} = blackbody\ spectral\ intensity$

In radiation it is more common to refer to the absorption coefficient: $\alpha_\nu = \frac{1}{\Lambda} = \frac{1}{v\tau} = \frac{4\pi k}{\lambda_0} = absorption\ coefficient$

For the elastic term there are two contributions, the **outgoing scattering**, proportional to the scattering coefficient, and the **incoming scattering** resulting from the fraction of the photons that are scattered from the direction Ω' to Ω per unit solid angle of the incident radiation, $\phi(\Omega' \to \Omega)$. We express these two terms as:

$$\frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{\text{c,elastic}} = -\sigma_{s\nu} I_\nu + \frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{\text{c,elastic, in}}$$

$$\frac{1}{v}\left(\frac{\partial I_\nu}{\partial t}\right)_{\text{c,elastic,in}} = \frac{\sigma_{s\nu}}{4\pi}\int I'_\nu(\hat{\Omega}')\phi(\hat{\Omega}' \to \Omega)d\Omega'$$

$\sigma_{s\nu} = scattering\ coefficient$

$\phi(\Omega' \to \Omega) = phase\ function$

$$\frac{\partial I_\nu}{\partial s} = -K_{e\nu} I_\nu + \alpha_\nu I_{\nu 0} + \frac{\sigma_{s\nu}}{4\pi}\int I'_\nu(\Omega')\phi(\Omega' \to \Omega)d\Omega'$$

Equation of the radiative transfer
(replaces Boltzmann transport)

$K_{e\nu} = \alpha_\nu + \sigma_{s\nu} = extinction\ coefficient$