Kinetic Theory and Statistical Mechanics

Consider a system of point particles ("atoms") in the dilute limit. The de Broglie wavelength of a particle of mass \( m \) is \( \frac{\hbar}{\sqrt{2mE}} \) (for a particle of energy \( E \)). At finite temperature, typically average all particles will have an energy \( E \approx kT \).

\[ \lambda_T = \frac{\hbar}{\sqrt{2m kT}} \]

\( \lambda_T \) is known as the thermal average wavelength. The distance between particles is

\[ d \approx \left( \frac{1}{n} \right)^{1/3} \text{, where } n = \frac{N}{V} \text{ is the density.} \]

\( \Rightarrow \) The classical regime is defined by the condition

\[ d \gg \lambda_T \]

\[ \Rightarrow \quad \frac{\hbar}{\sqrt{2m kT}} \left( \frac{N}{V} \right)^{1/3} \ll 1 \Rightarrow \quad kT \gg \frac{\hbar^2}{2m} \left( \frac{N}{V} \right)^{2/3} \]

In this regime quantum effects can be neglected. Notice that this works at high temperature at fixed density.
Let $f(\vec{r}, \vec{p}, t)$ be the classical distribution function, i.e. $f(\vec{r}, \vec{p}, t) \, d^3r \, d^3p$ is the number of particles at time $t$ within $d^3r$ of $\vec{r}$ and within $d^3p$ of $\vec{p}$. (Once again $d^3r$ and $d^3p$ are large enough to have a large # of particles in that region of phase space).

More precisely $\int f(\vec{r}, \vec{p}, t) \, d^3r \, d^3p$ is the # of particles.

Since there are $N$ particles in the volume $V$, we must impose the normalization condition

$$\int f(\vec{r}, \vec{p}, t) \, d^3r \, d^3p = N$$

In particular, for a uniform state

$$f(\vec{r}, \vec{p}, t) = f(\vec{p}, t)$$

$$\Rightarrow \int f(\vec{p}, t) \, d^3p = \left(\frac{N}{V}\right) = n$$

The main purpose of Kinetic Theory is to derive an equation of motion for $f(\vec{r}, \vec{p}, t)$ such that $f(\vec{r}, \vec{p}, t)$ is the equilibrium distribution.
Let us derive this equation of motion. Consider a volume $d^3r \, d^3p$ of phase space. In the absence of interactions, things are simple. A particle with coord. $\vec{r}$ and momentum $\vec{p}$ at time $t$ will evolve to

$$\vec{r} \rightarrow \vec{r} + \vec{v} \, dt$$

$$\vec{p} \rightarrow \vec{p} + \vec{F} \, dt$$

where $\vec{v} = \vec{p} / m$

$$\Rightarrow$$ after $dt$ all particles that were in $d^3r \, d^3p$ of $$(\vec{r}, \vec{p})$$ will be in a volume of phase space $d^3r', d^3p'$ of $$(\vec{r} + \vec{v} \, dt, \vec{p} + \frac{\vec{F}}{m} \, dt)$$

$$\Rightarrow$$ In the absence of collisions

$$f(\vec{r} + \vec{v} \, dt, \vec{p} + \frac{\vec{F}}{m} \, dt, t+dt) \, d^3r' \, d^3p' = f(\vec{r}, \vec{p}, t) \, d^3r \, d^3p$$

since $d^3r \, d^3p = d^3r' \, d^3p'$ (Liouville Theorem)

$$\Rightarrow$$

$$f(\vec{r} + \vec{v} \, dt, \vec{p} + \frac{\vec{F}}{m} \, dt, t+dt) = f(\vec{r}, \vec{p}, t)$$ (collisions)

$$\Rightarrow$$ In the presence of collisions

$$f(\vec{r} + \vec{v} \, dt, \vec{p} + \frac{\vec{F}}{m} \, dt, t+dt) - f(\vec{r}, \vec{p}, t) = \left( \frac{\partial f}{\partial t} \right) \, dt$$ (definition)
\[ \Rightarrow \left\{ \frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla \mathbf{r} + \mathbf{f} \cdot \nabla \mathbf{p} \right\} f(\mathbf{r}, \mathbf{p}, t) = (\frac{\partial f}{\partial t})_{\text{coll}}. \]

**Q:** How do we determine \((\frac{\partial f}{\partial t})_{\text{coll}}\)?

We can easily see that

\[
\frac{\partial f}{\partial t}_{\text{coll}} = \int \frac{\partial f}{\partial t} \, d^3 \mathbf{r} \, d^3 \mathbf{p} - \int \frac{\partial f}{\partial t} \, d^3 \mathbf{r} \, d^3 \mathbf{p}
\]

we will now resort to classical mechanics to determine \(R\) and \(\bar{R}\).

Consider the problem of elastic collisions of two particles \(\Rightarrow \mathbf{p}_{1f} + \mathbf{p}_{2f} = \mathbf{p}_{1i} + \mathbf{p}_{2i}\)

\[
E_{1f} + E_{2f} = E_{1i} + E_{2i}
\]

\[
M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}
\]

\[
\mathbf{p} = \mathbf{p}_i + \mathbf{p}_{\text{rel}}, \quad \mathbf{P} = \frac{m_2 \mathbf{p}_{1i} - m_1 \mathbf{p}_{2i}}{m_1 + m_2} \quad \text{(rel. momentum)}
\]

\[
= \mu (\mathbf{\tilde{v}}_1 - \mathbf{\tilde{v}}_2)
\]
\[ \vec{p}_1 = \frac{m_1}{M} \vec{P} - \vec{p} \quad \vec{p}_2 = \frac{m_2}{M} \vec{P} + \vec{p} \]

\[ E = E_{1i} + E_{2i} = E_f + E_f = \frac{\vec{P}^2_{1i}}{2M} + \frac{\vec{P}^2_{2i}}{2\mu} \text{ is conserved.} \]

- elastic collision \( \Rightarrow \vec{P}_i = \vec{P}^* \quad \text{and} \quad |\vec{P}_i| = |\vec{P}^*| \)

The dynamics of the collision is encoded in the differential cross section \( \frac{d\sigma}{d\Omega} \)

In quantum mechanics, the quantity that matters in a scattering process is the T-matrix.

Let \( |1, 2\rangle \) be initial state of two particles, and \( |1', 2'\rangle \) be the final state.

\[ \Rightarrow T_{fi} = \langle 1', 2' | T(E) | 1, 2 \rangle \]

If \( H_0 \) is the unperturbed Hamiltonian and \( H' \) is the interaction potential (which causes the scattering), \( \Rightarrow \)

\[ T(E) = H + H' \frac{1}{E - H_0 + i\epsilon} H' + \cdots \]

(Born series) \( \quad (E \to 0^+) \)
A collision is a transition from one initial state to some other final state. For final states \( \vec{dP}_1', \vec{dP}_2' \) the rate is

\[
d\sigma_{12 \rightarrow 1'2'} = \frac{\hbar}{2} \frac{d^3\vec{p}_1'}{d^3\vec{p}_2'} \delta^4(P_f - P_c') \left| T_{fi} \right|^2
\]

(\text{Fermi's Golden Rule})

\[
\delta^4(P_f - P_c') \equiv \delta^3(\vec{P}_f - \vec{P}_c') \delta(E_f - E_c')
\]

But

\[
d\sigma_{12 \rightarrow 1'2'} = \frac{I}{\nu} \frac{d\sigma}{\mu^2} \text{ cross section}
\]

\[
I = \left( \frac{N}{\nu} \right) (\nu_1 - \nu_2) = \left( \frac{N}{\nu} \right) \left( \frac{\vec{P}_1 - \vec{P}_2}{m} \right)
\]

\[
\Rightarrow \text{integrating } \frac{d\sigma}{\mu^2} \text{ over } \vec{P}_1' \text{ (fixed by momentum conservation)}
\]

and \( \vec{P}_2' \) (fixed by energy conservation)

\[
\Rightarrow I \frac{d\sigma}{d\omega^2} = \int d^3\vec{P}_2' \int d^3\vec{P}_1' \delta^4(P_f - P_c') \left| T_{fi} \right|^2
\]

Symmetries: \( T \) is invariant under rotation and spatial reflection, and time reversal

\[
\langle P_{2f}' P_1' | T | P_{1p} P_2 \rangle = \langle R \bar{P}_{2f}' , R \bar{P}_1' | T | R \bar{P}_{1p} , R \bar{P}_2 \rangle = \langle \bar{P}_2 , \bar{P}_1 | T | \bar{P}_1 , \bar{P}_2 \rangle
\]
\[ \Rightarrow \langle p'_2, p'_1 | T | p_i, p_2 \rangle = \langle \tilde{p}_2, \tilde{p}_1, \tilde{p}_2 | T | \tilde{p}_1, \tilde{p}_2 \rangle \]

\[ = \frac{T_{fi'}}{T_{if}} \]

The Boltzmann Transport Equation

We can now deduce the transport eqn. in general.

The \# of transitions \( 12 \rightarrow 1'2' \) in \( d^3r \) at \( r \) due to collisions with \( r' \) is

\[ dN_{12} = \text{# initial } \# \text{ of colliding pairs } (p_i, \tilde{p}_2) \]

Let us define

\[ dN_{12} = F(\tilde{r}, \tilde{p}_1, \tilde{p}_2, t) \ d^3r \ d^3p_1 \ d^3p_2 \]

2-particle correlation function.

\[ \Rightarrow R \delta t \ d^3r \ d^3p_1 = \delta t \ d^3r \ d^3p_1 \int d^3p_2 \ dP_{12 \rightarrow 1'2'} F(\tilde{r}, \tilde{p}_1, \tilde{p}_2, t) \]

\[ \Rightarrow R = \int d^3p_2 \ d^3p_1' \ d^3p_2' \ \delta^4(p_f - p_i) \ |T_{fi}|^2 \ F(\tilde{r}, \tilde{p}_1, \tilde{p}_2, t) \]

and

\[ \tilde{R} = \int d^3p_2' \ d^3p_1' \ d^3p_2' \ \delta^4(p_f - p_i) \ |T_{fi}|^2 \ F(\tilde{r}, \tilde{p}_1', \tilde{p}_2', t) \]
\[
\frac{\partial f}{\partial t} + \nabla \cdot (\vec{V} f) = \frac{1}{m} \left( \frac{\partial}{\partial t} + \vec{F} \cdot \vec{V} \right) \frac{\partial}{\partial \vec{V}} \left( \frac{\partial f}{\partial \vec{V}} \right) = \left[ \frac{\partial}{\partial t} + \vec{F} \cdot \vec{V} + \nabla \cdot (\vec{F} \cdot \vec{V}) \right] f
\]

\[
f = f(\vec{r}, \vec{p}, t)
\]

\[
\Rightarrow \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \bar{F} - \bar{F}
\]

\[
= \int d^3 p_2 d^3 p'_2 d^3 p'_2 \ \delta^4(\vec{p}_f - \vec{p}'_2) \ |T_f| \bar{f} \left( F_{12}' - F_{12} \right)
\]

integrating over \( \vec{p}'_2 \) and over \( \bar{f} \) we get

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d^3 p_2 \ \bar{f} \left( \bar{F}_1 - \bar{F}_2 \right) \ (F_{12}' - F_{12})
\]

Q: What is the 2-particle correlation function?

In the dilute limit the probability of a collision is small \(\Rightarrow\) we can approximate hypothesis of

\[
F_{12}(\vec{r}, \vec{p}_1, \vec{p}_2, t) \approx f(\vec{r}, \vec{p}_1, t) f(\vec{r}, \vec{p}_2, t) \quad \text{"molecular chaos"}
\]

(i.e. the joint probability distribution factorizes)

within this approximation we can write

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d^3 p_2 \ \bar{f} \left( \bar{F}_1 - \bar{F}_2 \right) \ (f'_1 f'_2 - f_1 f_2)
\]

\[
\Rightarrow \text{ Boltzmann Transport Equation:}
\]

\[
\left( \frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \cdot \nabla f + \vec{F} \cdot \nabla f \right) = \int d^3 p_2 d^3 p'_2 d^3 p'_2 \ \delta^4(\vec{p}_f - \vec{p}'_2) \ \bar{f} \left( f'_1 f'_2 - f_1 f_2 \right)
\]

\[
f_1 = f(\vec{r}, \vec{p}_1, t)
\]
The use of Quantum Mechanics here involves a subtlety. In the classical problem it is fine to use distribution functions \( f(\vec{r}, \vec{p}) \) which are functions of \( \vec{r} \) and \( \vec{p} \). But in Q.M., \( [\vec{r}, \vec{p}] \neq 0 \). Can we still define a suitable distribution? The answer is the **Wigner function**, defined as follows.

Let \( \hat{\rho} \) be the density matrix and its matrix elements in the coordinate representation are

\[
\langle \vec{r} | \hat{\rho} | \vec{r}' \rangle = \rho(\vec{r}, \vec{r}')
\]

Let us define the Wigner function

\[
f_w(p, \vec{r}) = \int \rho \left( \vec{r} + \frac{\vec{p}}{2}, \frac{\vec{r} - \vec{p}}{2} \right) e^{-i \vec{p} \cdot \frac{\vec{r}}{\hbar}} d\vec{r}
\]

\[
\Rightarrow \int f_w(p, \vec{r}) \frac{dp}{2\pi \hbar} = \int \rho \left( \vec{r} + \frac{\vec{p}}{2}, \frac{\vec{r} - \vec{p}}{2} \right) \delta(\vec{p}) d\vec{r}
\]

\[
= \rho(\vec{r}, \vec{r}) \quad \text{the probability to find a particle at } \vec{r}
\]

\[
\int f_w(\vec{r}, p) d\vec{r} = \int \left( \int d\vec{r} \rho \left( \vec{r} + \frac{\vec{p}}{2}, \frac{\vec{r} - \vec{p}}{2} \right) \right) e^{-i \vec{p} \cdot \frac{\vec{r}}{\hbar}} d\vec{r}
\]

But \( \rho(p, p') = \int \rho(\vec{r}, \vec{r}') e^{-i \frac{\vec{p} \cdot (\vec{r} - \vec{r}')}{\hbar}} d\vec{r} d\vec{r}' \)

\[
\Rightarrow \rho(p, p') = \int f_w(p, \vec{r}) d\vec{r} \quad \left( \frac{\vec{r} = \frac{\vec{r} + \vec{p}}{2}}{\frac{\vec{r}}{2} = \frac{\vec{r} - \vec{p}}{2}} \right)
\]
Notice that the Wigner function is not necessarily positive = it is not a probability.

There is an number of questions we must now address:

1. How are $f_1$ and $F_2$ related to the distribution function $P(\vec{r}, \vec{p}, t)$? (of all $\vec{r}$'s and $\vec{p}$'s)

2. Is the hypothesis of "molecular chaos" justified?

Let $P(\vec{r}, \ldots, \vec{r}_N, \vec{p}, \ldots, \vec{p}_N, t) = P(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N, t)

We know that $P$ satisfies Liouville's theorem.

i.e. $\frac{df}{dt} = 0$ or

$$\frac{dP}{dt} = -\frac{1}{i} \sum_{i=1}^{3N} \left( \frac{\partial}{\partial r_i} \vec{r}_i + \frac{\partial}{\partial p_i} \vec{p}_i \right)$$

Let us define the one-particle distribution function $f_1(\vec{r}, \vec{p}, t)$ to be

$$f_1(\vec{r}, \vec{p}, t) = \left\langle \delta^3(\vec{r} - \vec{r}_i) \delta^3(\vec{p} - \vec{p}_i) \right\rangle$$

$$= \frac{1}{N} \int d\vec{r}_2 d\vec{p}_2 \ldots d\vec{r}_N d\vec{p}_N \ P(1, \ldots, N; t)$$

The $n$-particle distribution function is

$$f_n(1, \ldots, n; t) = \frac{N!}{(N-n)!^n} \int d\vec{r}_1 d\vec{p}_1 \ldots d\vec{r}_n d\vec{p}_n P(1, \ldots, N; t)$$
Let us rewrite Liouville's Theorem in a more useful way:

\[ \frac{\partial \rho}{\partial t} = \sum_{i=1}^{N} \left( \frac{\partial}{\partial \vec{r}_i} \cdot \vec{p}_i - \frac{\partial}{\partial \vec{p}_i} \cdot \vec{r}_i \right) H = \sum_{i=1}^{N} \vec{F}_i \cdot \vec{p}_i - H \]

If \( H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^{N} U(\vec{r}_i) + \sum_{i=1}^{N} U(1\vec{r}_i - \vec{r}_j) \)

\[ \vec{F}_i = \frac{\partial}{\partial \vec{r}_i} H = \sum_{i=1}^{N} \vec{F}_i \cdot \vec{p}_i + \sum_{j=1, j \neq i}^{N} \vec{K}_{ij} \cdot \left( \vec{r}_i - \vec{r}_j \right) \]

\[ \sum_{i=1}^{N} \frac{\vec{F}_i \cdot \vec{p}_i}{m} = \sum_{i=1}^{N} \vec{K}_{ij} \cdot \left( \vec{r}_i - \vec{r}_j \right) \]

Liouville's Theorem:

\[ \left[ \frac{\partial}{\partial t} + \sum_{i=1}^{N} \left( \frac{\vec{F}_i \cdot \vec{r}_i}{m} + \vec{K}_{ij} \cdot \vec{r}_j \right) \right] f = 0 \]

\[ \frac{\partial h_n}{\partial t} = \frac{N!}{(N-n)!} \int d\vec{r}_1 d\vec{p}_1... d\vec{r}_n d\vec{p}_n \frac{\partial \rho}{\partial t} = \]

\[ = - \frac{N!}{(N-n)!} \int d\vec{r}_1 d\vec{p}_1... d\vec{r}_n d\vec{p}_n h_n f \]

But

\[ h_n (1,...,N) = h_n(1...N) + h_{n-1}(1...N) + \]

\[ + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \vec{P}_{ij} \]

and

\[ \int d\vec{r}_1 d\vec{p}_1... d\vec{r}_n d\vec{p}_n h_{n-1}(1...N) f(1...N) = 0 \]

(If reduces to a boundary integral when \( n \to 0 \))
\[
\left( \frac{\partial}{\partial t} + \nabla \cdot \mathbf{u} \right) \tilde{f}_S = - \frac{N!}{(N-1)!} \sum_{i=1}^{N} \sum_{j=1}^{N} P_{ij} \int \cdots \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \int d\mathbf{r}_{N+1} \frac{N!}{(N-1)!} \int d\mathbf{r}_{N+2} \cdots d\mathbf{r}_{N+1} \mathcal{P}(1 \cdots N)
\]

\[
= - \sum_{i=1}^{N} \int d\mathbf{r}_{N+1} \frac{P_{c_i} \mathcal{P}_{c_i}}{N-1} \int d\mathbf{r}_{N+2} \cdots d\mathbf{r}_{N+1} \mathcal{P}(1 \cdots N)
\]

\[
= - \sum_{i=1}^{N} \int d\mathbf{r}_{N+1} \mathcal{P}_{c_i} \mathcal{P}_{c_i+1} \tilde{f}_{c_i+1} (1 \cdots N+1)
\]

This is the BBGKY Hierarchy (Bogoliubov - Born - Green - Kirkwood - Yvon)

In particular

\[
\left( \frac{\partial}{\partial t} + \frac{\mathbf{P}_1 \cdot \nabla \mathbf{P}_1}{m} + \mathbf{F}_1 \cdot \nabla \mathbf{P}_1 \right) \tilde{f}_S (\mathbf{r}, \mathbf{p}, t) = \]

\[
= - \int d\mathbf{r}_2 \frac{\mathbf{K}_{12} \cdot \nabla \mathbf{P}_2}{m} \tilde{f}_2 (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_2, t)
\]

\[
= \left( \frac{\partial}{\partial t} \right) \text{coll}
\]

and

\[
\left[ \frac{\partial}{\partial t} + \frac{\mathbf{P}_1 \cdot \nabla \mathbf{P}_1}{m} + \frac{\mathbf{P}_2 \cdot \nabla \mathbf{P}_2}{m} + \mathbf{F}_1 \cdot \nabla \mathbf{P}_1 + \mathbf{F}_2 \cdot \nabla \mathbf{P}_2 + \frac{1}{2} \mathbf{K}_{12} \cdot (\nabla \mathbf{P}_1 - \nabla \mathbf{P}_2) \right] \tilde{f}_S \]

\[
= - \int d\mathbf{r}_3 \frac{d\mathbf{r}_3}{d\mathbf{r}_3} \left( \mathbf{K}_{13} \cdot \nabla \mathbf{P}_1 + \mathbf{K}_{23} \cdot \nabla \mathbf{P}_2 \right) \tilde{f}_3 (1, 2, 3, t)
\]
\[ f \sim |f| \]

\[ T_c = \text{collision time} \]

\[ T_e = \text{time for a particle to traverse a distance over which } V \text{ varies} \]

\[ T_s = \text{time to traverse a distance over which } f \text{ varies significantly} \]

The l.h.s of the eqn for \( f_2 \) has a collision term \( \sim \frac{1}{T_c} \)

whereas its r.h.s. \( \sim n r_0^3 \) where \( r_0 \) is the range of the pair interaction. For dilute systems,

\[ n r_0^3 \ll 1 \quad (\sim 10^{-5}) \implies \text{we can neglect the right hand side. } f_2 \text{ varies over some period } T_c \]

and \( r_0 \) while \( f_1 \) varies much less rapidly.

If the interaction vanishes (asymptotically) for \( r \gg r_0 \)

\[ \implies f_2 (r, \mathbf{p}_1, \mathbf{p}_2, t) \rightarrow f_1 (r, \mathbf{p}, t) f(r_0, \mathbf{p}, t) \]

\[ 1_{r-r_0 \ll r_0} \]

It can be shown (see Huang) that this behaviour implies the validity of the Boltzmann Equation.
The H-Theorem

We will now address the problem of the approach to equilibrium. We will define the equilibrium distribution as the time-independent solution to the Boltzmann Transport Equation. We will assume that there are no external forces. Hence the equilibrium solution will be uniform (by symmetry). Let us consider solutions of the form $f(p, t)$ and we will denote by $f_0(p)$ as the time-independent solution.

$\Rightarrow \frac{df_0}{dt} = 0 \quad \text{and}$

$\Rightarrow 0 = \int d^3p_2 \, d^3p_1' \, d^3p_2' \, \delta^4(p_f - p_2) \, \delta^4(p_i - p_1') \, (f_2 f_1' - f_2' f_1)$

when $p_1'$ is a fixed momentum.

A sufficient condition for $f_0(p)$ is

$\int f_0(p_2') f_0(p_1') - f_0(p_2) f_0(p_1') \, dp_1' = 0$

where $p_1, p_2 \rightarrow p_1', p_2'$ is any possible collision.
We will now show that this is also a necessary condition. \( \Rightarrow \frac{\partial f}{\partial t} \) is independent of the cross section \( \frac{d\sigma}{dt} \neq 0 \). (In the dilute limit.

Let us follow Boltzmann and define

\[
H(t) = \int d^3 \vec{p} \ f(\vec{p}, t) \log f(\vec{p}, t)
\]

where

\[
\frac{\partial f(\vec{p}, t)}{\partial t} = \int d^3 \vec{p}' \ d^3 \vec{p}_2 \ d^3 \vec{p}_1 \ \delta^4(\vec{p}_1 - \vec{p}_2) \left( f(\vec{f}, t) \right)^2 f(\vec{p}, t)
\]

\[
\Rightarrow \quad \frac{dH(t)}{dt} = \int d^3 \vec{p} \left[ \frac{\partial f(\vec{p}, t)}{\partial t} \log f(\vec{p}, t) \right.
\]

\[
\quad \quad \quad \quad \quad + f(\vec{p}, t) \frac{1}{f(\vec{p}, t)} \frac{\partial f(\vec{p}, t)}{\partial t}
\]

\[
\frac{dH(t)}{dt} = \int d^3 \vec{p}_2 \ \frac{\partial f(\vec{p}, t)}{\partial t} \left[ 1 + \log f(\vec{p}, t) \right]
\]

\[
= \int d^3 \vec{p}_1 \ d^3 \vec{p}_2 \ d^3 \vec{p}_1' \ d^3 \vec{p}_2' \ \delta^4(\vec{p}_1 - \vec{p}_2) \left( f_2(\vec{p}_2', t) f(\vec{p}_2, t) - f(\vec{p}_1, t) f(\vec{p}_2, t) \right)
\]

\[
\quad \quad \quad \quad \quad \left( 1 + \log f(\vec{p}, t) \right)
\]

Notice that \( \frac{\partial f}{\partial t} = 0 \Rightarrow \frac{dH}{dt} = 0 \)
We will prove that \( \frac{dH}{dt} = 0 \Rightarrow \frac{df}{dt} = 0 \)

But first

**Boltzmann's H-Theorem:**

We will show first that

\[
\frac{dH}{dt} \quad \text{if } f \text{ satisfies the Boltzmann equation} \Rightarrow \quad \frac{dH}{dt} \leq 0
\]

We can exchange \( P_i \leftrightarrow P_j \) and write

\[
\frac{dH}{dt} = \frac{1}{2} \left( \frac{dH}{dt} \right) + \frac{1}{2} \left( \frac{dH}{dt} \right)
\]

\[
P_j \quad P_2 \quad P_i \leftrightarrow P_j
\]

\[
= \frac{1}{2} \int d^3P_2 \ d^3P_1 \ d^3P'_2 \ d^3P'_1 \ \delta^4(P_2 - P'_2) \ |T_{fi}|^2
\]

\[
(f_2 f'_1 - f_1 f'_2) \ (2 + \log(f_1 f'_2))
\]

which is invariant under \( (P_i, P_{2}) \leftrightarrow (P'_i, P'_2) \)

(The inverse collision has the same \( T \)-matrix)

\[
\Rightarrow \quad \frac{dH}{dt} = -\frac{1}{2} \int d^3P_2 \ d^3P_1 \ d^3P'_2 \ d^3P'_1 \ \delta^4(P_2 - P'_2) \ |T_{fi}|^2
\]

\[
(f_2 f'_1 - f_1 f'_2) \ (2 + \log(f_2 f'_1))
\]
\[
\frac{dH}{dt} = \frac{1}{4} \int d^3p_1 \ d^3p_2 \ d^3p'_1 \ d^3p'_2 \ \delta^4(p - p') \ \delta^4(p' - p'_1) \ \frac{\delta^4(p'_1)}{2} \ \\
(f_1 f'_1 - f_1 f'_1) \left[ \log (f_2 f_1) - \log (f'_2 f'_1) \right] \ \\
\leq 0
\]

since the integrand is \leq 0

\[
\Rightarrow \frac{dH}{dt} = 0 \quad \Rightarrow \text{the integrand} = 0
\]

\[
\Rightarrow \ f_0(p_1) f_0(p_2) - f_0(p'_1) f_0(p'_2) = 0
\]

\[
\Rightarrow \ \frac{dH}{dt} = 0
\]

\[
\Rightarrow \ f_1 f_2 - f'_1 f'_2 = 0
\]

\[
\Rightarrow \ \text{since we also showed that} \ \frac{dH}{dt} \leq 0 \ \forall t
\]

\[
\Rightarrow \ \frac{dH}{dt} = 0 \ \text{only for} \ t \to \infty
\]

\[
\Rightarrow \ f(p_{1 t}) \to f_0(p)
\]
Maxwell-Boltzmann Distribution

\[ f_0(p_1) \text{ is the MB distribution.} \]
\[ f_0(p_1) f_0(p_2) = f_0(p_1') f_0(p_2') \]

\[ \Rightarrow \log f_0(p_1) + \log f_0(p_2) = \]
\[ = \log f_0(p_1') + \log f_0(p_2') \]

This is a conservation law since it is valid for any collision \((p_1, p_2) \rightarrow (p_1', p_2')\)

If \(X(p)\) is any conserved quantity associated with a particle of momentum \(p\) in a collision, s.t. \(X(p_1) + X(p_2)\) is conserved \(\Rightarrow\) a solution is \(\log f_0(p) = X(p)\)

In general, if \(X_1(p), X_2(p), \ldots\) are conserved quantities,

\(\Rightarrow\) \(\log f_0(p) = X_1(p) + X_2(p) + \ldots\)

\(\Rightarrow\) \(X\) is a linear combination of \(p^2\) and \(\bar{p}\), up to a constant

\(\Rightarrow\) \(\log f_0(p) = -A(p - \bar{p})^2 + \log C\)

\[ f_0(p) = C e^{-A(p - \bar{p})^2} \]
\[ \Rightarrow \int d^3 p \ f_0(\vec{p}) = \frac{N}{V} = n \]

\[ \Rightarrow n = C \left( \frac{\pi}{A} \right)^{3/2} \]

and

\[ \langle \vec{p} \rangle = \frac{\int d^3 p \ \vec{p} \ f_0(\vec{p})}{\int d^3 p \ f_0(\vec{p})} = \vec{p}_0 \]

\[ \Rightarrow \vec{p}_0 = 0 \quad \text{if the system is at rest} \]

\[ \Rightarrow \langle E \rangle = \frac{\int d^3 p \ \frac{\vec{p}^2}{2m} \ f_0(\vec{p})}{\int d^3 p \ f_0(\vec{p})} \]

\[ \Rightarrow \langle E \rangle = \frac{3}{4Am} \quad (\vec{p}_0 = 0) \]

\[ \Rightarrow A = \frac{3}{4m \langle E \rangle} \]

and

\[ C = n \left( \frac{3}{4\pi \langle E \rangle m} \right)^{3/2} \]

Pressure \[ P = \frac{\int d^3 p \ 2p_x u_x f_0(\vec{p})}{P_x > 0} = \frac{2}{3} n \langle E \rangle \]

\[ \Rightarrow P = \frac{2}{3} n \langle E \rangle \]

If we define \[ P = n kT \quad (dilute \ gas) \]

\[ \Rightarrow \langle E \rangle = \frac{3}{2} kT \]
and \( f_0(\vec{p}) = \frac{n}{(2\pi m kT)^{3/2}} e^{-\frac{\vec{p}^2}{2mkT}} \) (Maxwell-Boltzmann) is the probability of finding a \( \vec{p} \) particle with momentum \( \vec{p} \) in equilibrium (for a dilute gas).

Most probable speed \( \bar{v} \): the value at which \( 4\pi \rho^2 f(\vec{p}) \) is largest in phase space.

\( \Rightarrow \bar{p} = \sqrt{2mkT} \) and \( \bar{v} = \sqrt{\frac{2kT}{m}} \)

and \( v_{rms} = \left[ \int d^3p \frac{v^2 f_0(\vec{p})}{\int d^3p f_0(\vec{p})} \right]^{1/2} = \sqrt{\frac{3kT}{m}} \)

Dilute Gas in an External Field

\( \vec{F} = -\vec{\nabla} \phi \)

\( \Rightarrow f(\vec{r}, \vec{p}) = f_0(\vec{p}) e^{-\phi(\vec{r})/kT} \)

This follows from the Boltzmann Equation.
This result follows from

1. \( \frac{df}{dt} = 0 \) since it is time-indep.

2. \( \frac{d\rho}{dt} \) = \( \int d^3p_2 \int d^3p' \int d^3p'' \delta^4(p_f - p_i) \left( f_2 f_1' - f_2' f_1 \right) \)

and \( e^{-2\Phi(\vec{r})/kT} \int d^3p_2 \int d^3p' \int d^3p'' \delta^4(p_2 - p_2') \left( f_o(p_2) f_o(p_2') - f_0(p_2) f_o(p_2) \right) \)

\( \Rightarrow \frac{d\rho}{dt} \) = 0

and

3. \( f(\vec{r}, \vec{p}) = f_o(\vec{p}) e^{-\Phi(\vec{r})/kT} \)

satisfies \( \frac{\vec{p}}{m} \cdot \nabla f_o + \vec{F} \cdot \nabla f_o \) = 0

since \( \vec{F} = -\nabla \Phi \)

and \( \nabla f_o = \frac{\vec{p}}{m} f_o \)
\[ f(\vec{r}, \vec{p}) = \frac{n(\vec{r})}{(2\pi mkT)^{3/2}} e^{-\frac{\vec{p}^2}{2mkT}} \]

with

\[ n(\vec{r}) = n_0 e^{-\frac{\Phi(\vec{r})}{kT}} = \int d^3p f(\vec{p}, \vec{r}) \]

(Bohr's formula)

Notice that all of these results also hold for the ideal gas in an external field in the canonical ensemble.

In particular, the quantity

\[ H(t) = \int d^3p f(\vec{p}, t) \log f(\vec{p}, t) \]

in the equilibrium state becomes

\[ H_0 = \int d^3p f_0(\vec{p}) \log f_0(\vec{p}) = -\frac{1}{kT} S \]

\[ \lim_{t \to \infty} H(t) = -\frac{1}{kT} S \]

\[ \Rightarrow \text{For an isolated gas, } S \text{ never decreases} \]

i.e., the 2nd Law
What does the H-Theorem mean?

\[ H = \int d^3p \ f(\vec{p}, t) \log f(\vec{p}, t) \]

\[ \Rightarrow \text{the time-evolution of } f(\vec{p}, t) \text{ determines the time-evolution of } H. \text{ In general } f(\vec{p}, t) \text{ is not a solution of the Boltzmann equation but it is if the hypothesis of "molecular chaos" holds.} \]

\[ \Rightarrow \text{The H-theorem actually says that if at some time } t \text{ "molecular chaos" holds } \Rightarrow \text{ at } t + \varepsilon, \ \frac{dH}{dt} < 0 \text{ and } \frac{dH}{dt} = 0 \Leftrightarrow f \text{ is MB} \]

"Molecular chaos": if \( f(\vec{p},t) \) is the probability to find a particle at time \( t \) and momentum \( \vec{p} \) (within \( d\vec{p} \) ) \Rightarrow the probability to find two particles at time \( t \) with momenta \( \vec{p} \) and \( \vec{p}' \) is \( f(\vec{p},t) f(\vec{p}',t) \Leftrightarrow \text{no correlation among the momenta of } 2 \text{ particles.} \)

What does this imply? Imagine that at \( t = 0 \)

\( f(\vec{p},t) \) is not Maxwell-Boltzmann \Rightarrow at \( t = 0^+ \)
\[ \frac{dH}{dt} \leq 0 . \quad \text{If the system is time-reversal invarient, the gas obtained by reversing all velocities has exactly the same properties and it also satisfies } \frac{dH}{dt} \leq 0 \text{ for } t=0^+. \quad \text{But the system with all velocities reversed is}
\]

\[ \Rightarrow \text{molecular chaos } \Rightarrow \text{H is at a local peak}
\]

\[ \Rightarrow \text{H cannot possibly be a simple differentiable function and } \frac{\partial f}{\partial t} \text{ is not a "derivative"!}
\]

\[ \Rightarrow \text{The actual time evolution of } H(t) \text{ is "wrong" reflecting the random nature of the microscopic forces}
\]

\[ \Rightarrow \text{we are implicitly assuming that the system is non-deterministic (probabilistic) at the local particle level. } \Rightarrow \text{only under these assumptions we can speak "coarse" Statistical Mechanics from strictly microscopic physics.} \]

Brownian Motion, the Langevin and Fokker-Planck Eqns.

Our discussion of the Boltzmann Equation led us to the conclusion that in order to be able to find an equilibrium state some notion of randomness must be invoked at the microscopic level. Indeed the Boltzmann Eqn

\[ \frac{\partial f}{\partial t} + \sum_{i=1}^{N} \left[ \frac{\partial f}{\partial p_i} \cdot \frac{\partial H}{\partial r_i} + \frac{\partial f}{\partial r_i} \cdot \frac{\partial H}{\partial p_i} \right] = \left( \frac{\partial f}{\partial t} \right)_{\text{collision}} \]

can also be written as

\[ \frac{\partial f}{\partial t} + \{ f, H \}_{PB} = \left( \frac{\partial f}{\partial t} \right)_{\text{collision}} \]

where \( \{ A, B \}_{PB} \) is the Poisson Bracket

\[ \{ A, B \}_{PB} = \sum_{i=1}^{N} \left( \frac{\partial A}{\partial p_i} \cdot \frac{\partial B}{\partial r_i} - \frac{\partial A}{\partial r_i} \cdot \frac{\partial B}{\partial p_i} \right) \]

The right hand side, the collision term, contains all the information about randomness at the
microscopic level. Recall that we wrote \( \frac{df}{dt} \) as an integral involving the two-particle distribution function and a matrix element (i.e., the scattering cross-section). The hypothesis about random microscopic motion implied the factorization of the 2-particle distribution function, i.e., the moments of colliding particles are uncorrelated.

In the absence of random forces, i.e., for a strictly deterministic system, \( \frac{df}{dt} = 0 \) (notice that \( H \) contains interactions!)

\( \Rightarrow \) the "deterministic Boltzmann Equation" is simply \[ \frac{df}{dt} = \{ H, f \} \]

Let \( \{ X_i \} \) be a set of conserved quantities,
\[ \frac{dx_i}{dt} = \{ H, X_i \} = 0 \]

\( \Rightarrow \) any function \( F(X_1, \ldots, X_r, \ldots) \) also satisfies
The equation reads
\[ \frac{\partial \mathbf{F}}{\partial t} = \sum \frac{\partial \mathbf{F}}{\partial x_i} \frac{\partial x_i}{\partial t} = \sum_i \frac{\partial \mathbf{F}}{\partial x_i} \{ \mathbf{H}, \dot{\mathbf{X}}_i \} = 0 \]

for the \( i \)-th variable.

\[ \Rightarrow f = F [X_i] \quad \text{any such function works!} \]

If the system is at rest (\( \dot{\mathbf{P}} = 0 \)) and the total angular momentum vanishes (\( \mathbf{L} = 0 \)) \( \Rightarrow \) the only generic conservation law is energy

\[ \Rightarrow f = F (\mathbf{H}) \]

\[ \Rightarrow f (\mathbf{r}, \mathbf{p}, t) = e^{-\frac{\mathbf{H} (\mathbf{r}, \mathbf{p})}{kT}} \text{ is a solution} \]

But why is this particular form selected? And what is the "meaning" of \( T \) at the level of the Boltzmann equ.?

To understand these questions we must go back to \( \frac{\partial f}{\partial t} \) and randomness. We will begin with a simple problem: Random Walks.