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 $\dfrac{h}{\sqrt{2mE}}$

(for a particle of energy E). At finite temperature, all particles will typically have an average energy $E \sim kT$

$\Rightarrow$ the typical de Broglie wavelength is

$$\lambda_T = \frac{h}{\sqrt{2m\,kT}}$$ known as the thermal wavelength. The average distance between particles is

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

$\Rightarrow$ The classical regime is defined by the condition $\qquad d \gg \lambda_T$

$$\Rightarrow \quad \frac{h}{\sqrt{2m\,kT}} \left(\frac{N}{V}\right)^{1/3} \ll 1 \quad \Rightarrow \quad kT \gg \frac{h^2}{2m}\left(\frac{N}{V}\right)^{2/3}$$

In this regime quantum effects can be neglected. Notice that is also 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 $\sum \int f(\vec{r}, \vec{p}, t)\, \vec{r}\, \vec{p}$ is the # of particles at r~~ Since there are N particles in the volume V, we must impose the normalization condition

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

In ~~particular~~ particular for a uniform state

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

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

The main purpose of Kinetic Theory is to derive an equation of motion for $f(\vec{r}, \vec{p}, t)$ s.t. $\lim_{t \to \infty} f(\vec{r}, \vec{p}, t)$ 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

$$\vec{r} \to \vec{r} + \vec{v}\, \delta t \qquad \text{in } \delta t$$

$$\vec{p} \to \vec{p} + \vec{F}\, \delta t$$

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

$\Rightarrow$ after δt $\underline{\underline{all}}$ particles that were in $d^3p\, d^3r$ of $(\vec{r}, \vec{p})$ will be in a volume of phase space $d^3r'\, d^3p'$ of $(\vec{r} + \vec{v}\,\delta t,\; \vec{p} + \frac{\vec{F}}{m}\,\delta t)$

$\Rightarrow$ In the absence of collisions

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

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

$\Rightarrow$ $f(\vec{r} + \vec{v}\,\delta t,\; \vec{p} + \frac{\vec{F}}{m}\,\delta t, t+\delta t) = f(\vec{r}, \vec{p}, t)$ ($\overset{no}{\text{collisions}}$)

$\Rightarrow$ In the presence of collisions

$$f(\vec{r} + \vec{v}\,\delta t,\; \vec{p} + \frac{\vec{F}}{m}\,\delta t,\; t+\delta t) - f(\vec{r}, \vec{p}, t) = \left(\frac{\partial f}{\partial t}\right)_{collision} \delta t$$

(definition!)

$$\Rightarrow \boxed{\left\{\frac{\partial}{\partial t} + \frac{\vec{P}}{m} \cdot \vec{\nabla}_{\vec{r}} + \vec{F} \cdot \vec{\nabla}_{\vec{p}}\right\} f(\vec{r}, \vec{p}, t) = \left(\frac{\partial f}{\partial t}\right)_{coll}}$$

Q: How do we determine $\left(\frac{\partial f}{\partial t}\right)_{coll}$?

We can easily see that

$$\left(\frac{\partial f}{\partial t}\right)_{coll} \delta t = \overline{R} \,\delta t \, d^3 r \, d^3 p - \overline{\overline{R}} \,\delta t \, d^3 r \, d^3 p$$

↑
# of collisions in
$(t, t+\delta t)$ in which
one of the ~~final~~ final
particles is in $d^3 r \, d^3 p$

↑
# of collisions in
$(t, t+\delta t)$ in which
one of the ~~final~~ initial
particles is in $d^3 r \, d^3 p$

We will now resort to classical mechanics to

determine R and $\overline{R}$.

Consider the problem of elastic collisions of two

particles $\Rightarrow \quad \vec{P}_{1i} + \vec{P}_{2i} = \vec{P}_{1f} + \vec{P}_{2f}$

$$E_{1i} + E_{2i} = E_{1f} + E_{2f}$$

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

$$\vec{P} = \vec{P}_1 + \vec{P}_2 \qquad , \vec{p} = \frac{m_2 \vec{P}_1 - m_1 \vec{P}_2}{m_1 + m_2} \qquad \text{(rel. momentum)}$$

$$= \mu (\vec{v}_1 - \vec{v}_2)$$

$$\Rightarrow \quad \vec{P}_1 = \frac{m_1}{M}\hat{\vec{P}} - \vec{p} \qquad \vec{P}_2 = \frac{m_2}{M}\hat{\vec{P}} + \vec{p}$$

$$E = E_{1i} + E_{2i} = E_{1f} + E_{2f} = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^2}{2\mu} \quad \text{is conserved.}$$

$$\Rightarrow \text{ elastic collision} \Rightarrow \quad \vec{P}_i = \vec{P}_f \text{ and } |\vec{p}_i| = |\vec{p}_f|$$

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 $|1, 2\rangle_i$ be initial state of two particles

and $|1', 2'\rangle$ be the final state

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

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

$$T(E) = H' + H' \frac{1}{E - H_0 + i\varepsilon} H' + \cdots$$

$$(\text{Born series}) \qquad (\varepsilon \to 0^+)$$

A collision is a transition from some initial state to some other final state. For final states in $d^3p_1'\, d^3p_2'$ the rate is

$$dP_{12 \to 1'2'} = \frac{\# d^3p_1'\, d^3p_2'}{\mathcal{L}(normalization)}\; \delta^4(P_f - P_i)\; |T_{fi}|^2$$

(Fermi's Golden Rule)

~~$\delta^4 P_f \cdots \delta^2 \cdots = \cdots \delta^3 \vec{P}_f$~~

$$\delta^4(P_f - P_i) \equiv \delta^3(\vec{P}_f - \vec{P}_i)\; \delta(E_f - E_i')$$

But
$$dP_{12 \to 1'2'} = I\, d\sigma$$

I flux, σ cross section

$$I = \left(\frac{N}{V}\right)(\vec{v}_1 - \vec{v}_2) = \left(\frac{N}{V}\right)\left(\frac{\vec{P}_1 - \vec{P}_2}{m}\right)$$

$\Rightarrow$ integrating over $\vec{p}_1'$ (fixed by momentum conservation)

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

$$\Rightarrow I\frac{d\sigma}{d\Omega} = \int d^3P_2' \int d^3p_1'\; \delta^4(P_f - P_i)\; |T_{fi}|^2$$

Symmetries: T is invariant under rotations and spatial reflections, and time reversal

$$\Rightarrow \langle P_2'P_1' | T | P_1, P_2 \rangle = \langle R\vec{p}_2', R\vec{p}_1' | T | R\vec{P}_1, R\vec{P}_2 \rangle$$
$$= \langle -\vec{P}_2, -\vec{P}_1 | T | -\vec{p}_1', -\vec{p}_2' \rangle$$

$$\Rightarrow \quad \langle P_2', P_1' | T | \vec{P}_1, \vec{P}_2 \rangle = \langle \vec{P}_2, \vec{P}_{1g} | T | \vec{P}_1', \vec{P}_2' \rangle$$

$$\Rightarrow \quad T_{fi'} = T_{i'f}$$

The Boltzmann Transport Equation

We can now deduce the transport eqn. in general.

The # of transitions $12 \rightarrow 1'2'$ in d^3r at $\vec{r}$ due to collisions in δt is

$$dN_{12} \, dP_{12 \rightarrow 1'2'} \, \delta t$$

dN_{12} = # initial # of colliding pairs $(\vec{P}_1, \vec{P}_2)$

Let us define

$$dN_{12} = \underbrace{F(\vec{r}, \vec{P}_1, \vec{P}_2, t)}_{\text{2-particle correlation function.}} d^3r \, d^3p_1 \, d^3p_2$$

$$\Rightarrow R \, \delta t \, d^3r \, d^3P_1 = \delta t \, d^3r \, d^3p_1 \int d^3p_2 \, dP_{12 \rightarrow 1'2'} F(r, \vec{P}_1, \vec{P}_2)$$

$$\Rightarrow R = \int d^3P_2 \, d^3p_1' \, d^3p_2' \, \delta^4(P_f - P_i) \, |T_{fi}|^2 F(\vec{r}, \vec{P}_1, \vec{P}_2, t)$$

and

$$\bar{R} = \int d^3P_2 \, d^3p_1' \, d^3p_2' \, \delta^4(P_f - P_i) \, |T_{f0}|^2 F(\vec{r}, \vec{P}_1', \vec{P}_2', t)$$

$$\Rightarrow \left(\frac{\partial f}{\partial t}\right)_{coll} = \bar{R} - R$$

$$= \int d^3p_2\, d^3p_1'\, d^3p_2'\; \delta^4(P_f - P_i)\, |T_{fi}|\, (F_{1'2'} - F_{12})$$

integrating over $\vec{P}_1'$ and over $|\vec{P}_2|$ we get

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int d^3p_2\, d\Omega\, |\vec{v}_1 - \vec{v}_2| \left(\frac{d\sigma}{d\Omega}\right) (F_{1'2'} - F_{12})$$

$Q =$ What is the 2-particle ~~distribu~~ correlation function?

In the dilute limit the probability of a collision

is small $\Rightarrow$ we can approximate

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

hypothesis of

(i.e. the joint probability distrib. factorizes)

within this approximation we can write

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll} = \int d^3p_2\, d\Omega\, |\vec{v}_1 - \vec{v}_2| \left(\frac{d\sigma}{d\Omega}\right) (f_1' f_2' - f_1 f_2)$$

$\Rightarrow$ Boltzmann Transport Equation:

$$\left(\frac{\partial}{\partial t} + \frac{\vec{P}_1}{m}\cdot\vec{\nabla}_{\vec{r}} + \vec{F}\cdot\vec{\nabla}_{P_1}\right) f_1 = \int d^3p_2\, d^3p_1'\, d^3p_2'\; \delta^4(P_f - P_i)$$
$$|T_{fi}|^2 (f_2' f_1' - f_2 f_1)$$

$$f_1 = f(\vec{r}, \vec{P}_1, t)$$

The use of Quantum Mechanics here involves a subtlety. In the classical problem it is fine to use distribution functions $f(\vec{r}, \vec{p}, t)$ which are functions of $\vec{r}$ and $\vec{p}$. But in Q.M.'s $[\vec{r}, \vec{p}] \neq 0$. 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

$$\langle q | \hat{\rho} | q' \rangle \equiv \rho(q, q')$$

Let us define the Wigner function

$$f_W(p, q) \equiv \int \rho\left(q + \frac{\eta}{2}, q - \frac{\eta}{2}\right) e^{-i p \eta / \hbar} \, d\eta$$

$$\Rightarrow \int f_W(p, q) \frac{dp}{2\pi\hbar} = \int \rho\left(q + \frac{\eta}{2}, q - \frac{\eta}{2}\right) \delta(\eta) \, d\eta$$

$$= \rho(q, q) \qquad \text{the probability to find a particle at } q$$

$$\int f_W(q, p) \, dq = \int \left(\int dq \, \rho\left(q + \frac{\eta}{2}, q - \frac{\eta}{2}\right) \right) e^{-i p \eta / \hbar} \, d\eta$$

But $\rho(P, P') = \int \rho(q, q') \, e^{-\frac{i}{\hbar}(Pq - P'q')} \rho(q, q') \, dq \, dq'$

$$\Rightarrow \rho(p, p) = \int f_W(p, \bar{q}) \, d\bar{q} \qquad \left(\begin{array}{l} q = \bar{q} + \frac{\eta}{2} \\ q' = \bar{q} - \eta/2 \end{array} \right)$$

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 $\rho\left([\vec{q},\vec{p}],t\right)$? (of all q's and p's)

② Is the hypothesis of "molecular chaos" justified?

Let $\rho(1,\ldots,N;t) \equiv \rho(\vec{r}_1\ldots\vec{r}_N, \vec{p}_1,\ldots,\vec{p}_N;t)$

We know that ρ satisfies Liouville's Theorem.

i.e. $\dfrac{d\rho}{dt} = 0$ or

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

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

$$f_1(\vec{r},\vec{p},t) = \left\langle\sum_{i=1}^{N}\delta^3(\vec{r}-\vec{r}_i)\,\delta^3(\vec{p}-\vec{p}_i)\right\rangle$$

$$= N\int dr_2\wedge dp_2\ldots dr_N\wedge dp_N\;\rho(1,\ldots,N;t)$$

the n-particle distribution function is

$$f_s(1\ldots n,t) = \frac{N!}{(N-n)!}\int dr_{n+1}\wedge dp_{n+1}\ldots dr_N\wedge dp_N\;\rho(1,\ldots,N;t)$$

Let us rewrite Liouville's Thm in a more useful way

$$\frac{\partial \rho}{\partial t} = \sum_{i=1}^{N} \left(\vec{\nabla}_{\vec{P}_i} \rho \cdot \vec{\nabla}_{\vec{r}_i} H - \vec{\nabla}_{\vec{r}_i} \rho \cdot \vec{\nabla}_{\vec{P}_i} H \right)$$

If
$$H = \sum_{i=1}^{N} \frac{\vec{P}_i^{\,2}}{2m} + \sum_{i=1}^{N} U(\vec{r}_i) + \sum_{i<j} \upsilon(|\vec{r}_i - \vec{r}_j|)$$

$\underset{\text{external}}{\underset{\text{potential}}{\uparrow}}$ $\qquad\qquad$ $\underset{\text{pair}}{\underset{\text{interaction}}{\uparrow}}$

$$\Rightarrow \quad \vec{\nabla}_{\vec{P}_i} H = \frac{\vec{P}_i}{m}$$

$$\vec{\nabla}_{\vec{r}_i} H = + \underbrace{\vec{\nabla}_{r_i} U(\vec{r}_i)}_{-\vec{F}_i} + \underbrace{\sum_{\substack{j=1 \\ j \neq i}}^{N} \vec{\nabla}_{r_i} \upsilon(|\vec{r}_i - \vec{r}_j|)}_{\vec{K}_{ij}}$$

$$\Rightarrow \quad \text{Liouville's Thm is}$$

$$\left[\frac{\partial}{\partial t} + \sum_{i=1}^{N} \left(\frac{\vec{P}_i}{m} \cdot \vec{\nabla}_{r_i} + \vec{F}_i \cdot \vec{\nabla}_{\vec{P}_i} \right) + \frac{1}{2} \sum_{i \neq j=1}^{N} \overbrace{\vec{K}_{ij} \cdot (\vec{\nabla}_{P_i} - \vec{\nabla}_{P_j})}^{\mathcal{P}_{ij}} \right] \rho = 0$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{h_N}$$

$$\Rightarrow \quad \frac{\partial f_n}{\partial t} = \frac{N!}{(N-n)!} \int dr_{n+1} dp_{n+1} \cdots dr_N dp_N \, \frac{\partial \rho}{\partial t} =$$

$$= - \frac{N!}{(N-n)!} \int dr_{n+1} dp_{n+1} \cdots dr_N dp_N \, h_N \rho$$

But $\quad h_N(1,\cdots,N) = h_n(1\cdots s) + h_{N-n}(s+1\cdots N) +$

$$+ \sum_{i=1}^{n} \sum_{j=n+1}^{N} \mathcal{P}_{ij}$$

and $\int dr_{s+1} dp_{s+1} \cdots dr_N dp_N \, h_{N-n}(n+1\cdots N) \, \rho(1\cdots N) = 0$

$\qquad\qquad$ (it reduces to a boundary integral where $\rho \to 0$)

$\Rightarrow$

$$\left(\frac{\partial}{\partial t} + h_{s}\right) f_{s} = -\frac{N!}{(N-s)!} \int dr_{s+1} dp_{s+1} \cdots dr_{N} dp_{N} \sum_{i=1}^{s} \sum_{j=s+1}^{N} P_{ij} \, \rho(1 \cdots N)$$

$$= -\sum_{i=1}^{s} \int dr_{s+1} dp_{s+1} \; P_{i,s+1} \frac{N!}{(N-s+1)!} \int dr_{s+2} dp_{s+1} \cdots dr_{N} dp_{N} \, \rho(1 \cdots N)$$

$$= -\sum_{i=1}^{s} \int dr_{s+1} dp_{s+1} \; P_{i,s+1} \, f_{s+1} \, (1 \cdots s+1)$$

$$\Rightarrow \quad \overset{\text{streaming}}{\underset{\text{term}}{\big\uparrow}} \qquad\qquad\qquad \overset{\text{collision integral.}}{\underset{\downarrow}{}}$$

$$\left(\frac{\partial}{\partial t} + h_{s}\right) f_{s} = -\sum_{i=1}^{s} \int dr_{s+1} dp_{s+1} \; \vec{K}_{i,s+1} \cdot \vec{\nabla}_{p_{i}} f_{s+1} \, (1 \cdots s+1)$$

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

In particular

$$\left(\frac{\partial}{\partial t} + \frac{\vec{P}_{1}}{m} \cdot \nabla_{r_{1}} + \vec{F}_{1} \cdot \vec{\nabla}_{P_{1}}\right) f_{1} \, (\vec{r}, \vec{p}, t) =$$

$$= -\int dr_{2} dp_{2} \; \vec{K}_{12} \cdot \vec{\nabla}_{\vec{P}_{1}} f_{2} \, (r_{1} p_{1}, r_{2} p_{2}, t)$$

$$= \left(\frac{\partial f_{1}}{\partial t}\right)_{coll}$$

and

$$\left[\frac{\partial}{\partial t} + \frac{\vec{P}_{1}}{m} \cdot \vec{\nabla}_{r_{1}} + \frac{\vec{P}_{2}}{m} \cdot \vec{\nabla}_{r_{2}} + \vec{F}_{1} \cdot \vec{\nabla}_{P_{1}} + \vec{F}_{2} \cdot \vec{\nabla}_{P_{2}} + \frac{1}{2} \vec{K}_{12} \cdot \left(\vec{\nabla}_{P_{1}} - \vec{\nabla}_{P_{2}}\right)\right] f$$

$$= -\int dr_{3} dp_{3} \, \left(\vec{K}_{13} \cdot \vec{\nabla}_{P_{1}} + \vec{K}_{23} \cdot \vec{\nabla}_{\vec{P}_{2}}\right) f_{3} \, (1, 2, 3, t)$$

$$\vec{K} \cdot \vec{\nabla}_p f \sim \frac{1}{\tau_c} f \qquad \tau_c = \text{collision time}$$

$$\vec{F} \cdot \vec{\nabla}_p f \sim \frac{1}{\tau_e} f \qquad \tau_e = \text{time for a particle to traverse a distance over which } U \text{ varies}$$

$$\frac{\vec{p}}{m} \cdot \vec{\nabla}_r f \sim \frac{1}{\tau_s} f \qquad \tau_s = \text{time to traverse a distance over which } f \text{ varies significantly.}$$

The l.h.s of the eqn for f_2 has a collision term $\sim \frac{1}{\tau_c}$ 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 varies over some period τ_c and r_0 while f_1 varies much less rapidly.

If the interaction vanish (asymptotically) for $r \gg r_0$

$$\implies f_2 (r_1 p_1, r_2 p_2, t) \xrightarrow[|r_1 - r_2| \gg r_0]{} f_1 (r_1 p_1 t) f_1 (r_2 p_2 t)$$

It can be shown (see Huang) that this behavior 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-indep. 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 $f(\vec{p}, t)$ and we will denote by $f_0(\vec{p})$ as the time-independent solution.

$$\Rightarrow \quad \frac{\partial f_0}{\partial t} = 0 \quad \text{and}$$

$$\Rightarrow \quad 0 = \int d^3 p_2 \, d^3 p_1' \, d^3 p_2' \, \delta^4(\underline{P}_f - \underline{P}_i) \, |T_{fi}|^2 (f_2' f_1' - f_2 f_1$$

where $\vec{p}_1$ is a fixed momentum.

A sufficient condition for $f_0(\vec{p})$ is

$$f_0(\vec{p}_2') \, f_0(\vec{p}_1') - f_0(\vec{p}_2) \, f_0(\vec{p}_1) = 0$$

where $\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_1', \vec{p}_2'$ is any possible collision.

We will now show that this is also a
necessary condition. $\Rightarrow f_0(\vec{p})$ is independent
of the cross section $\frac{d\sigma}{d\Omega} \neq 0$. (In the dilute limit

Let us follow Boltzmann and define

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

where

$$\frac{\partial f}{\partial t}(\vec{p}_1, t) = \int d^3p_2 \; d^3p_2' \; d^3p_1' \; \delta^4(P_f - P_i) |T_{fi}|^2 \searrow$$

$$(f_2' f_1' - f_2 f_1)$$

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

$$\left. + f(\vec{p}, t) \frac{1}{f(\vec{p}, t)} \frac{\partial f}{\partial t}(\vec{p}, t) \right]$$

$$\frac{dH}{dt}(t) = \int d^3p_1 \; \frac{\partial f}{\partial t}(\vec{p}_1, t) \left[1 + \log f(\vec{p}_1, t) \right]$$

$$= \int d^3p_1 \; d^3p_2 \; d^3p_1' \; d^3p_2' \; \delta^4(P_f - P_i) \; |T_{fi}|^2$$

$$(f_2(\vec{p}_2', t) f(\vec{p}_1', t) - f(\vec{p}_2, t) f(\vec{p}_1, t))$$

$$(1 + \log f(\vec{p}_1, t))$$

Notice that $\quad \frac{\partial f}{\partial t} = 0 \Rightarrow \frac{dH}{dt} = 0$

We will prove that $\frac{dH}{dt} = 0 \implies \frac{\partial f}{\partial t} = 0$

But first

Boltzmann's H-Theorem:

We will show first that

$$\frac{dH}{dt} \leq 0 \qquad \text{if } f \text{ satisfies the Boltzmann}$$

$$\text{Equation} \implies \frac{dH}{dt} \leq 0$$

We can exchange $\vec{P_1} \leftrightarrow \vec{P_2}$ and write

$$\frac{dH}{dt} = \frac{1}{2}\left(\frac{dH}{dt}\right)_{P_1 P_2} + \frac{1}{2}\left(\frac{dH}{dt}\right)_{P_1 \leftrightarrow P_2} \qquad (\,|T_{fi}| \text{ is invariant}\,)$$

$$= \frac{1}{2}\int d^3P_2\, d^3P_1\, d^3P_2'\, d^3P_1'\, \delta^4(P_f - P_i)\, |T_{fi}|^2$$

$$(f_2'\, f_1' - f_2 f_1)(2 + \log(f_1 f_2))$$

which is invariant under $(P_1, P_2) \leftrightarrow (P_1', P_2')$

(the inverse collision has the same T-matrix)

$$\implies \frac{dH}{dt} = -\frac{1}{2}\int d^3P_2\, d^3P_1\, d^3P_2'\, d^3P_1'\, \delta^4(P_f - P_i)\, |T_{fi}|^2$$

$$(f_2' f_1' - f_2 f_1)(2 + \log(f_2' f_1'))$$

$$\Rightarrow \quad \frac{t}{2} \frac{dH}{dt} = \frac{1}{2} \frac{dH}{dt} + \frac{1}{2} \frac{dH}{dt}$$

$$\frac{dH}{dt} = \frac{1}{4} \int d^3p_1 \, d^3p_2 \, d^3p_1' \, d^3p_2' \; \delta^4(P_f - P_i) \; |T_{fi}|^2$$

$$(f_2' f_1' - f_2 f_1) \left[\log(f_2 f_1) - \log(f_2' f_1') \right]$$

$$\leq 0$$

since the integrand is ≤ 0

$$\Rightarrow \quad \frac{dH}{dt} = 0 \quad (\Rightarrow) \quad \text{the integrand} = 0$$

$$\Rightarrow \quad f_0(\vec{P_1}) \, f_0(\vec{P_2}) - f_0(\vec{P_1'}) \, f_0(\vec{P_2'}) = 0$$

$$\Rightarrow \quad \frac{\frac{dH}{dt} = 0}{\cancel{\frac{dH}{dt}}} \quad (\Rightarrow) \quad f_1 f_2 - f_1' f_2' = 0$$

$\Rightarrow$ since we also showed that $\frac{dH}{dt} \leq 0 \quad \forall t$

$$\Rightarrow \quad \frac{dH}{dt} = 0 \quad \text{only for } t \rightarrow \infty$$

$$\Rightarrow \quad f(\vec{P}, t) \xrightarrow[t \rightarrow \infty]{} f_0(\vec{P})$$

Maxwell - Boltzmann Distribution

$f_0(\vec{p})$ is the MB distribution.

$$f_0(\vec{p_1}) f_0(\vec{p_2}) = f_0(\vec{p_1'}) f_0(\vec{p_2'})$$

$$\Rightarrow \log f_0(\vec{p_1}) + \log f_0(\vec{p_2}) =$$
$$= \log f_0(\vec{p_1'}) + \log f_0(\vec{p_2'})$$

This is a conservation law since it is valid

for _any_ collision $(\vec{p_1}, \vec{p_2}) \rightarrow (\vec{p_1'}, \vec{p_2'})$

If $X(\vec{p})$ is any conserved quantity associated

with a particle of momentum $\vec{p}$ in a collision

s.t. $X(\vec{p_1}) + X(\vec{p_2})$ is conserved $\Rightarrow$ a solution

is $\qquad \log f_0(\vec{p}) = X(\vec{p})$

In general, if $X_1(\vec{p})$, $X_2(\vec{p})$, ... are conserved quantities

$$\Rightarrow \log f_0(\vec{p}) = X_1(\vec{p}) + X_2(\vec{p}) + \dots$$

$\Rightarrow X$ is a linear combination of $\vec{p}^2$ and

$\vec{p}$, up to a constant

$$\Rightarrow \log f_0(\vec{p}) = -A(\vec{p} - \vec{p_0})^2 + \log c$$

$$f_0(\vec{p}) = c \, e^{-A(\vec{p} - \vec{p_0})^2}$$

$$\Rightarrow \quad \int d^3p \; f_0(\vec{p}) = \frac{N}{V} = n$$

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

$$\text{and} \quad \langle \vec{p} \rangle = \frac{\int d^3p \; \vec{p} \; f_0(\vec{p})}{\int d^3p \; f_0(\vec{p})} = \vec{P_0}$$

$$\Rightarrow \quad \vec{P_0} = 0 \quad \text{if the system is at rest.}$$

$$\Rightarrow \quad \langle \varepsilon \rangle = \frac{\int d^3p \; \frac{\vec{p}^2}{2m} \; f_0(\vec{p})}{\int d^3p \; f_0(\vec{p})}$$

$$\Rightarrow \langle \varepsilon \rangle = \frac{3}{4Am} \qquad (\vec{P_0} = 0)$$

$$\Rightarrow \quad A = \frac{3}{4m \langle \varepsilon \rangle}$$

$$\text{and} \quad C = n \left(\frac{3}{4\pi \langle \varepsilon \rangle m}\right)^{3/2}$$

$$\text{Pressure} = P = \int_{P_x > 0} d^3p \; 2P_x \, v_x \, f_0(\vec{p}) = \frac{2}{3} n \langle \varepsilon \rangle$$

$$\Rightarrow \quad P = \frac{2}{3} n \langle \varepsilon \rangle$$

If we define $\quad P = nkT \quad$ (dilute gas)

$$\Rightarrow \quad \langle \varepsilon \rangle = \frac{3}{2} kT$$

and $f_0(\vec{p}) = \dfrac{n}{(2\pi m kT)^{3/2}} e^{-\frac{\vec{p}^2}{2mkT}}$

(Maxwell-Boltzmann)

is the probability of finding a ~~particle~~ particle with momentum $\vec{p}$ in equilibrium (for a dilute gas)

Most probable speed $\bar{v}$: the value at which

$4\pi p^2 f(\vec{p})$ is largest

in phase space

$\Rightarrow \bar{p} = \sqrt{2mkT}$ and $\bar{v} = \sqrt{\dfrac{2kT}{m}}$

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

Dilute Gas in an External Field

$\vec{F} = -\vec{\nabla}\phi$

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

This follows from the Boltzmann Equation.

This result follows from

① $\quad \dfrac{\partial f}{\partial t} = 0 \qquad$ since $\quad$ it is time-indep.

② $\quad \left(\dfrac{\partial f}{\partial t}\right)_{coll} = \int d^3 p_2' \, d^3 p_1' \, d^3 P_2 \; \delta^4(P_f - P_i) \, |T_{fi}|^2$

$$(f_2' f_1' - f_2 f_1)$$

$$\equiv e^{-2\phi(\vec{r})/kT} \int d^3 p_2' \, d^3 p_1' \, d^3 P_2 \, \delta^4(P_f - P_i) \, |T_{fi}|$$

$$\underbrace{(f_0(P_2') \, f_0(P_1') - f_0(P_2) \, f_0(P_1))}_{"_0}$$

$\Rightarrow \quad \left(\dfrac{\partial f}{\partial t}\right)_{coll} = 0$

and

③ $\quad f(\vec{r}, \vec{p}) = f_0(\vec{p}) \, e^{-\phi(\vec{r})/kT}$

$\quad$ satisfies $\quad \left(\dfrac{\vec{p}}{m} \cdot \vec{\nabla}_{\vec{r}} + \vec{F} \cdot \vec{\nabla}_{\vec{p}}\right) f(\vec{r}, \vec{p}) = 0$

$\quad$ since $\qquad \vec{F} = -\vec{\nabla}\phi$

$\qquad$ and $\quad \vec{\nabla} f_0 = \dfrac{\hat{p}}{2m \, kT} f_0$

$$\Rightarrow \quad f(\vec{r}, \vec{p}) = \frac{n(\vec{r})}{(2\pi m k T)^{3/2}} e^{-\vec{p}^2/2mkT}$$

with

$$n(\vec{r}) = n_o \, e^{-\phi(\vec{r})/kT} = \int d^3p \, f(\vec{p}, \vec{r})$$

(Boltzmann's formula)

Notice that all of these results ~~follow from~~ 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

$$H_0(t) = \int d^3p \, f_o(\vec{p}) \log f_o(\vec{p}) = -\frac{1}{kV} \underset{\uparrow}{S}$$

entropy

$$\Rightarrow \quad \lim_{t \to \infty} H(t) = -\frac{1}{kV} S$$

$\Rightarrow$ For an isolated gas S never decreases

i.e. the 2nd Law

What does the H-Theorem Mean?

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

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

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

"Molecular chaos": if $f(\vec{p}, t)$ is the probability to find a particle at time t and momentum $\vec{p}$ (within d^3p) $\Rightarrow$ the probability to find two particles at time t with moments $\vec{p}$ and $\vec{p}'$ is $f(\vec{p}, t) \, f(\vec{p}', t) \Leftrightarrow$ no correlation among the moments of $\neq$ particles.

what does this imply? Imagine that at $t = 0$ $f(\vec{p}, t)$ is $\underline{\underline{not}}$ Maxwell-Boltzmann $\Rightarrow$ at $t = 0^+$

$\frac{dH}{dt} \leq 0$. If the system is time-reversal invariant, the gas obtained by reversing all velocities has exactly the same properties and it also satisfies $\frac{dH}{dt} \leq 0$ for $t = 0^+$. But ~~the system with all velocities reversed is~~ since the equs of motion are T-invariant ⟹ the future of this new gas is the past of the old one ⟹

$$\frac{dH}{dt} \geq 0 \quad t \geq 0^-$$

⟹ molecular chaos ⟹ H is at a local peak

⟹ H cannot possibly be a simple differentiable function of time and $\left(\frac{\partial f}{\partial t}\right)_{coll}$ is not a "derivative"!

⟹ The ~~ac~~ actual time evolution of $H(t)$ is "noisy" reflecting the random nature of the microscopic forces

⟹ we are implicitly assuming that the system is non-deterministic (probabilistic) at the local ~~level~~. level. ⟹ only under these assumptions we can ~~poo~~ "derive" 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 Equ

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

$$\cancel{\frac{\partial f}{\partial t}}$$

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

can also be written as

$$\frac{\partial f}{\partial t} + \{ f, H \}_{PB} = \left(\frac{\partial f}{\partial t} \right)_{collision.}$$

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

$$\{ A, B \}_{PB} = \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \vec{r_i}} \cdot \frac{\partial B}{\partial \vec{P_i}} - \frac{\partial A}{\partial \vec{P_o}} \cdot \frac{\partial B}{\partial \vec{r_i}} \right)$$

The right hand side, the collision term, contains all the information about randomness at the

microscopic level. Recall that we wrote $\left(\frac{\partial f}{\partial t}\right)_{coll}$
as an integral involving the two-particle
distribution function and a matrix element (i.e.
~~the~~ the scattering cross-section). The hypothesis
about ~~random~~ microscopic motion ~~was~~ implied the
factorization of the 2-particle distribution
function, i.e. the momenta of colliding particles
are <u>uncorrelated</u>.

In the absence of random forces, i.e. for
a strictly ~~determinstic~~ deterministic system, $\left(\frac{\partial f}{\partial t}\right)_{coll} = 0$

(notice that H $\overset{still}{\text{contains}}$ interaction!)

$\Rightarrow$ the "deterministic Boltzmann Equation" is

simply
$$\frac{\partial f}{\partial t} = \{H, f\}$$

Let $\{X_i\}$ be $\overset{\text{a set of}}{\text{~~some~~}}$ conserved quantities,

$$\frac{\partial X_i}{\partial t} = \{H, X_i\} = 0$$

$\Rightarrow$ <u>any</u> function $F(X_1, \ldots, X_r, \ldots)$ also satisfies

the equation since

$$\frac{\partial F}{\partial t} = \sum_i \partial_i F \frac{\partial X_i}{\partial t} = \sum_i \partial_i F \{H, X_i\} = 0$$

i-th
variable

$\Rightarrow$ $f = F[X_i]$ *any* such function works!

If the system is at rest $(\vec{P}=0)$ and the

total angular momentum vanishes $(\vec{L}=0)$ $\Rightarrow$ the

only *generic* conservation law is energy

$\Rightarrow$ $f = F(H)$

$\Rightarrow$ $f(\vec{r}, \vec{p}, t) = e^{-H(\vec{r}, \vec{p})/kT}$ is *a* solution

But why is this particular form selected?, and what

is the "meaning" of T ~~is the~~ at the level of the

Boltzmann eqn.?

To understand these questions we must go

back to $\left(\frac{\partial f}{\partial t}\right)_{coll}$ and randomness. We

will begin with a simpler problem: Random Walks