<u>Recap:</u> Derivation of Boltzmann equation from BBGKY Hierarchy

c.f. appendix to chapter IV

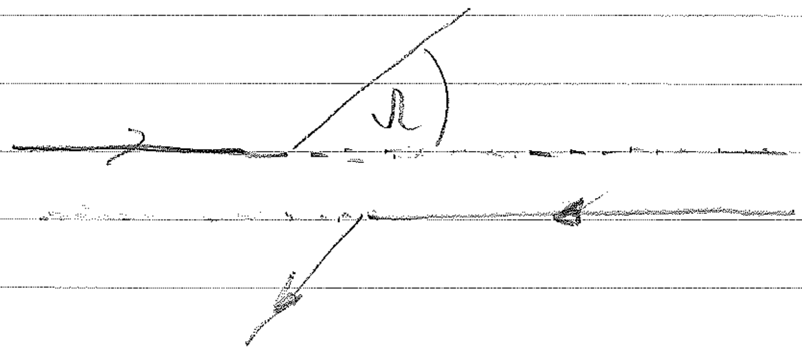
$$\left(\frac{\partial}{\partial t} + \vec{v}\vec{\nabla}_r + \vec{F}\vec{\nabla}_p\right) f = C[f]$$

$$C[f] = \frac{1}{2}\int_{p_2}\int_{p_3}\int_{p_4} \tilde{W}(p_1 p_2 \to p_3 p_4)\left[f_3 f_4 - f_1 f_2\right]$$

we learned that statistical weight

$$\frac{1}{2}\int_{p_3}\int_{p_4} \tilde{W}(p_1 p_2 \to p_3 p_4) = \int d\Omega \, \frac{d\sigma}{d\Omega}$$

where Ω denotes scattering angle



Will now proceed to study important formal properties Boltzmann equations, study approximations to near & far from equilibrium situations

Balance equations

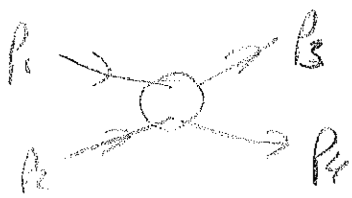
Conservation laws at microscopic level enter cross sections / transition rates

~~Consequences on~~ macroscopic level described by balance equations

$$\left(\frac{\partial}{\partial t} f_1\right)_{coll} = \int_{p_2}\int_{p_3}\int_{p_4} I(p_1,p_2,p_3,p_4)$$

$$I(p_1,p_2,p_3,p_4) = \left[f_3 f_4 - f_1 f_2\right] \tilde{W}(p_1 p_2 \to p_3 p_4)$$

Now



So generally $\tilde{W}$ will have symmetries

1) $(1,3) \leftrightarrow (2,4)$ trivial relabeling

2) $(1,2) \leftrightarrow (3,4)$ microreversibility (consequence of PCT)

So we have for

$$I(p_1,p_2,p_3,p_4) = +I(p_2,p_1,p_4,p_3) = -I(p_3,p_4,p_1,p_2)$$

We consider a function $\chi(\vec{p})$ which denotes a property that is conserved in a microscopic interaction,

e.g. $\chi(\vec{p}) = 1$ particle number

$\chi(\vec{p}) = \vec{p}$ momentum

$\chi(\vec{p}) = \frac{\vec{p}^2}{2m}$ energy

Now we know that since each microscopic scattering event conserves

$$\chi(p_1) + \chi(p_2) = \chi(p_3) + \chi(p_4)$$

i.e. χ is a collisional invariant

we expect some consequences on the level of Boltzmann equation

Idea: Look at what collisions do to first particle

$$\left(\frac{\partial \chi}{\partial t}\right)_{coll} = \int_{p_1} \chi(1) \left(\frac{\partial f_1}{\partial t}\right)_{coll} = \int_{p_1}\int_{p_2}\int_{p_3}\int_{p_4} \chi(p_1)\, I(p_1,p_2,p_3,p_4)$$

Now can change variables and use symmetries of $I(p_1,p_2,p_3,p_4)$ to rewrite as

$$\left(\frac{\partial \chi}{\partial t}\right) = \int_{p_1}\int_{p_2}\int_{p_3}\int_{p_4} \chi(p_2)\, I(p_2,p_1,p_4,p_3)$$

$$= \int_{p_1}\int_{p_2}\int_{p_3}\int_{p_4} \chi(p_2)\, I(p_1,p_2,p_3,p_4)$$

$$\left(\frac{\partial \chi}{\partial t}\right) = \int_{p_1}\int_{p_2}\int_{p_3}\int_{p_4} \chi(p_3)\, I(p_3,p_4,p_1,p_2)$$

$$= - \int_{p_1}\int_{p_2}\int_{p_3}\int_{p_4} \chi(p_3)\, I(p_1,p_2,p_3,p_4)$$

Same for p_4 :: Collect 1/4 of each term

$$\left(\frac{\partial \chi}{\partial t}\right)_{coll} = \frac{1}{4}\int_{p_1}\int_{p_2}\int_{p_3}\int_{p_4}\left[\chi(p_1)+\chi(p_2)-\chi(p_3)-\chi(p_4)\right] I(p_1,p_2,p_3,p_4)$$

$$= 0 \quad \text{because} \quad \chi(p_1)+\chi(p_2) = \chi(p_3)+\chi(p_4)$$

for collisional invariant

Physically: Collisions do not change the value of

$$X(t,\vec{r}) = \int_{\vec{p}} \chi(\vec{p})\, f_1(t,\vec{r},\vec{p})$$

$\Rightarrow$ can derive „simple" evolution equations for $X(t,\vec{r})$

Particle number balance:

Consider $\chi(\vec{p}) = 1$, the associated density is

particle number density $n(t,\vec{r}) = \int_{\vec{p}} f(t,\vec{r},\vec{p})$

$$\frac{\partial}{\partial t} n(t,\vec{r}) = \int_{\vec{p}} \frac{\partial}{\partial t} f(t,\vec{r},\vec{p}) = \int \frac{d^3p}{(2\pi\hbar)^3}\left[-\frac{\vec{p}}{m}\vec{\nabla}_r f(t,\vec{r},\vec{p}) - \underbrace{\vec{F}(\vec{r})\,\vec{\nabla}_p f(t,\vec{r},\vec{p})}_{\text{generates vanishing boundary term}} + \underbrace{\left(\frac{\partial f}{\partial t}\right)_{coll}}_{\text{vanishes upon integration as shown above}}\right]$$

$$= -\vec{\nabla}_r \underbrace{\int \frac{d^3p}{(2\pi\hbar)^3}\frac{\vec{p}}{m} f(t,\vec{r},\vec{p})}_{\text{average \# particles} \times \text{velocity}} = \vec{J}_N \text{ particle current}$$

$\Rightarrow$ Continuity equation

$$\boxed{\frac{\partial}{\partial t} n(t,\vec{r}) + \vec{\nabla}_r \vec{J}_N(t,\vec{r}) = 0}$$

Momentum balance:

$$\chi(\vec{p}) = \vec{p} \quad \Rightarrow \quad P^i(t,\vec{r}) = \int_{\vec{p}} p_i \, f(t,\vec{r},\vec{p})$$

where $P^i(t,\vec{r}) \hat{=}$ local momentum density

$$⓪ \quad -\frac{\partial}{\partial t} P^i(t,\vec{r}) = -\int_{\vec{p}} p_i \frac{\partial}{\partial t} f(t,\vec{r},\vec{p})$$

$$= \int_{\vec{p}} p_i \left[\underbrace{\frac{p_j}{m} \frac{\partial}{\partial r_j}}_{= \frac{\vec{p}}{m}\vec{\nabla}_r} f(t,\vec{r},\vec{p}) \; ① + \underbrace{F_j(\vec{r}) \frac{\partial}{\partial p_j}}_{= \vec{F}\vec{\nabla}_p} f(t,\vec{r},\vec{p}) \; ② - \left(\frac{\partial f}{\partial t}\right)_{coll} ③ \right]$$

③ vanishes according to discussions before

② perform integration by parts

→ generates new boundary terms from

$$\frac{\partial}{\partial p_j} p_i = \delta_{ij}$$

$$② \Rightarrow \; -\delta_{ij} F_j(\vec{r}) \int_{\vec{p}} f(t,\vec{r},\vec{p}) = -F_i(\vec{r}) \, n(t,\vec{r},\vec{p})$$

a la Newtons law for each particle

① Defines momentum flux

$$= \frac{\partial}{\partial r_j} \int_{\vec{p}} \underbrace{p_i}_{\text{momentum in } i\text{-direction}} \underbrace{\frac{p_j}{m}}_{\text{velocity in } j\text{-direction}} f(t,\vec{r},p) = \frac{\partial}{\partial r_j} J^{ij}_{\vec{p}}(t,\vec{r})$$

$\hat{=}$ momentum flux of i in j-direction

Collection ⓪, ①, ②, ③ gives us momentum balance equation for momentum

Denoting the momentum in terms of the <u>flow velocity</u>

$$v^i(t,\vec r) = \frac{P^i(t,\vec r)}{m\,n(t,\vec r)} = \frac{\int_{\vec p} \frac{p_i}{m} f(t,\vec r,\vec p)}{\int_{\vec p} f(t,\vec r,\vec p)}$$

we have

$$\boxed{\frac{\partial}{\partial t}\left(m\,n(t,\vec r)\, v^i(t,\vec r)\right) + \frac{\partial}{\partial r_j} J_{\vec p}^{\,ij}(t,\vec r) = n(t,\vec r)\, F^i(t,\vec r)}$$

Balance equations for $n(t,\vec r)$, $m\,n(t,\vec r)\vec v(t,\vec r)$ and $e(t,\vec r)$ represent the microscopically derived analogues of Balance equations in our macroscopic description

Similarly find for $e_{kin}(t,\vec r) = \int_{\vec p} \frac{\vec p^{\,2}}{2m} f(t,\vec r,\vec p)$

<u>Energy balance equation</u>

$$\boxed{\frac{\partial}{\partial t} e_{kin}(t,\vec r) + \vec\nabla_r \vec J_{e_{kin}}(t,\vec r) = \vec F(t,\vec r)\, \vec v(t,\vec r)\, n(t,\vec r)}$$

where $\vec J_{e_{kin}}(t,\vec r) = \int_{\vec p} \vec p \left(\frac{\vec p^{\,2}}{2m}\right) f(t,\vec r,\vec p)$

(see exercises)

Statistical entropy

Generally entropy characterizes information content of a distribution

<u>Example:</u> In equilibrium we only have a minimal amount of information $\{X_i\} = \{E, V, N\}$

$\Rightarrow$ Entropy is maximal

Existence of entropy function guaranteed by postulates of thermodynamics

$\Rightarrow$ Need to generalize this concept to <u>entropy functionals</u> which describe information content of

a) statistical phase space distributions (classical)

b) statistical / density operators (quantum)

Generally problem of defining entropy functional(s) for out-of-equilibrium systems derives from the fact that typically we don't even know

full ρ_N, f_N,

Generally concept of entropy is adopted from information theory

Shannon entropy:
$$S_{Shannon} = -\underbrace{K}_{constant} \sum_{m=1}^{N} p_m \log p_m$$

where $m = 1, \dots, N$ describes all possible outcomes of a measurement and $p_m \geq 0$ denotes their probability $\sum_m p_m = 1$

$$S_{Shannon} \geq 0 \qquad (\log(p_m) \leq 0;\ p_m \geq 0)$$

with $S_{Shannon} = 0$ only if $p_m = \delta_{mn}$ i.e. outcome entirely determined

Quantum Systems:

Von Neumann entropy
$$S_1 = -k_B \operatorname{Tr}(\hat{\rho} \log \hat{\rho})$$

where using $\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$ and evaluating the trace in the eigenbasis of density operator

One recovers Shannon formula, and one has

$S \geq 0$ with $S = 0$ corresponding to a pure state

Classical systems:

$$S_{cl} = -k_B \int d^{6N}V \; f_N(t, \{\vec{r}_i\}, \{\vec{p}_i\}) \log(f(t, \{\vec{r}_i\}, \{\vec{p}_i\}))$$

where f_N: characterises probability density to find N-particle system in given microstate $\{\vec{r}_i\}, \{\vec{p}_i\}$

Since probability density not bounded by 1 can find $S_{cl} < 0$ in fact $S \to -\infty$ possible in the limit where all coordinates and momenta are known exactly

Note that for microscopic N-body dynamics one has e.g. for quantum systems

$$S(t) = -k_B \mathrm{Tr}\left[\hat{\rho}(t) \log(\hat{\rho}(t))\right]$$
$$= -k_B \mathrm{Tr}\left[U(t)\hat{\rho}(0)U^\dagger(t) \log(U(t)\hat{\rho}(0)U^\dagger(t))\right]$$
$$\overset{UU^\dagger = \mathbb{1}}{=} -k_B \mathrm{Tr}\left[\hat{\rho}(0) \log(\hat{\rho}(0))\right] = S(0)$$

$$\Rightarrow \frac{dS}{dt} = 0$$

Entropy is conserved as long as full microscopic dynamics of all dof's is considered

$\Rightarrow$ no information is lost, dynamics is reversible

Entropy in Boltzmann equation / H-theorem

Now if we want to make use of entropy considerations in the Boltzmann equation, we face the challenge that we no longer know full N-body density fct

However in the spirit of information theory derivation, we can define a single particle entropy which employs $f_1(t, \vec{r}_1, \vec{p}_1)$ as statistical distribution

Boltzmann entropy:

$$S_B(t) \equiv -k_B \int \frac{d^3r \, d^3p}{(2\pi\hbar)^3} f(t, \vec{r}, \vec{p}) \log\left(f(t, \vec{r}, \vec{p})\right)$$

Will now show from Boltzmann equation that $\frac{dS_B}{dt} \geq 0$

Lohschmidt paradox: How can this be starting from reversible dynamics?

→ Molecular chaos ansatz singles out preferred time direction, neglecting correlations after they are necessarily introduced due to collisions (cf. assymmetric treatment in derivation)

Beyond Boltzmann information is shuffled into higher order correlation functions during non-equilibrium dynamics
→ reversibility saved but Boltzmann entropy can still increase

Boltzmann originally considered the dimensionless quantity

$$H(t) = \int \frac{d^3r\, d^3p}{(2\pi\hbar)^3}\, f(t,\vec{r},\vec{p})\, \log\left(f(t,\vec{r},\vec{p})\right)$$

$$S_B(t) = -k_B H(t) \quad (+\text{ constant})$$

Such that $\frac{dH}{dt} \leq 0$ can be proven as follows

$$\frac{d}{dt} H(t) = \int \underbrace{d^6V}_{= \frac{d^3r\, d^3p}{(2\pi\hbar)^3}} \frac{\partial}{\partial t}\left[f \log(f) \right]$$

$$= \int d^6V \frac{\partial f}{\partial t} \left(\log(f) + 1 \right)$$

Now $\frac{\partial f}{\partial t} = -\vec{v}\,\vec{\nabla}_r f + \vec{\dot{p}}\,\vec{\nabla}_p f + \left(\frac{\partial f}{\partial t}\right)_{coll}$

→ performing integrations by part only collisions contribute

e.g.

$$\int d^6V\, \vec{v}(\vec{\nabla}_r f)\left(\log(f) + 1\right)$$

$$= \underbrace{\int d^6V\, \vec{\nabla}_r (\vec{v} f)\left(\log(f) + 1\right)}_{=0 \ldots} - \underbrace{\int d^6V\, (\vec{v} f)\left(\vec{\nabla}_r \log(f)\right)}_{= \int d^6V\, \vec{v}(\vec{\nabla}_r f) = 0}$$

So

$$\frac{d}{dt} H(t) = \int d^6V \left(\frac{\partial f}{\partial t}\right)_{coll} \left(\log(f) + 1 \right)$$

$$= \int d^3r \left[\int_{p_1} \left(\frac{\partial f_1}{\partial t}\right)_{coll} \left(\log(f_1) + 1 \right) \right]$$

Term ($\propto 1$) does not contribute according to balance equation for particle number

$$= \int d^3r \int_{p_1} \left(\frac{\partial f_1}{\partial t}\right)_{coll} \log(f_1)$$

Now focus on

$$\int_{p_1} \left(\frac{\partial f_1}{\partial t}\right)_{coll} \log(f_1) = \int_{p_1 p_2 p_3 p_4} I(p_1, p_2, p_3, p_4) \log(f_1)$$

using same tricks as for balance equation

$$= \frac{1}{4} \int_{p_1 p_2 p_3 p_4} I(p_1, p_2, p_3, p_4) \left(\log(f_1) + \log(f_2) - \log(f_3) - \log(f_4) \right)$$

$$= \frac{1}{4} \int_{p_1 p_2 p_3 p_4} \left(f_3 f_4 - f_1 f_2 \right) \log\left(\frac{f_1 f_2}{f_3 f_4} \right) \tilde{w}(p_1 p_2 \to p_3 p_4)$$

$$= \frac{1}{4} \int_{p_1 p_2 p_3 p_4} \underbrace{f_3 f_4}_{\geq 0} \underbrace{\left(1 - \frac{f_1 f_2}{f_3 f_4} \right) \log\left(\frac{f_1 f_2}{f_3 f_4} \right)}_{(1-x)\log(x) \leq 0} \underbrace{\tilde{w}(p_1 p_2 \to p_3 p_4)}_{\geq 0} \leq 0$$

$\square$