3 Kinetic Theory

So far: equilibrium statistical mechanics

Goal now: theory of transport through gases and liquids

- Ch. 3: some basics on molecular collisions
- Ch. 4: equilibrium state of a dilute gas
- Ch. 5: Transport phenomena

Basic idea: kinetic theory explains the behavior of out-of-equilibrium systems as the consequence of collisions among the particles

collisions will be described by cross sections

Throughout, we will use classical framework.

point in phase space: $\underbrace{\vec{r}, \vec{p}}_{\text{6 degrees of freedom}}$

We are interested in distribution function $\underbrace{f(\vec{r}, \vec{p}, t)}_{\text{density of particles in phase space}}$

$f(\vec{r}, \vec{p}, t)\, d^3r\, d^3p$: # of particles at time t in the volume $d^3\vec{r}\, d^3\vec{p}$ at the phase space point $(\vec{r}, \vec{p})$

Want to calculate: spatio-temporal dynamics of the distribution function $f(\vec{r}, \vec{p}, t)$

We can define:

$$\boxed{n(\vec{r}, t) = \int f(\vec{r}, \vec{p}, t)\, d^3\vec{p}}$$: density in position space (at time t)

Instead of $f(\vec{r}, \vec{p}, t)$, we can use $f_v(\vec{r}, \vec{v}, t)$:

$$f_v(\vec{r}, \vec{v}, t) = m^3 f(\vec{r}, \vec{p}, t)$$

Let's assume, for a moment, that we do <u>not</u> have collisions, i.e., cross section $\sigma = 0$.

Particle with $\vec{r}, \vec{p}$ at time t will have the coordinates $(\vec{r} + \vec{v}\,dt,\ \vec{p} + \vec{F}\,dt)$ at time $t+dt$

$\vec{F}$: external force acting on the particle

$\vec{v} = \frac{\vec{p}}{m}$ $\hat{=}$ velocity

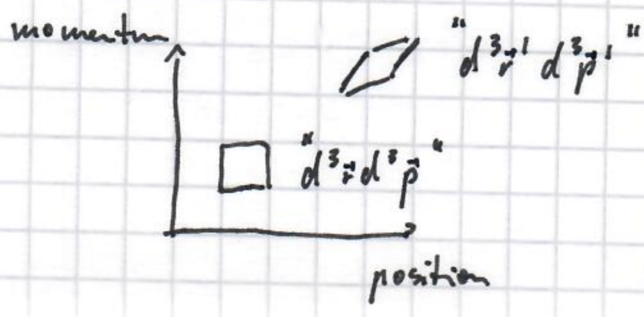
Since the number of particles in a volume element in phase space is constant, we have

$$f(\vec{r}(t+dt), \vec{p}(t+dt), t+dt)\, d^3\vec{r}\,'\, d^3\vec{p}\,'$$

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

$d^3\vec{r}\, d^3\vec{p}$: phase space volume at time t

$d^3\vec{r}\,'\, d^3\vec{p}\,'$: phase space volume at time $t+dt$



drawings in 6d are hard...

Due to Liouville's theorem ($d^3\vec{r}\, d^3\vec{p} = d^3\vec{r}\,'\, d^3\vec{p}\,'$):

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

Let's expand this to first order in dt:

$$\boxed{\underbrace{\left(\frac{\partial}{\partial t} + \underbrace{\frac{d\vec{r}}{dt}}_{\frac{1}{m}\vec{p}} \cdot \vec{\nabla}_{\vec{r}} + \underbrace{\frac{d\vec{p}}{dt}}_{\vec{F}} \cdot \vec{\nabla}_{\vec{p}}\right)}_{\text{"derivative in phase space"}} f(\vec{r}, \vec{p}, t) = 0}$$

recall: $G = 0$ (no collisions)

$$\frac{\partial}{\partial t} + \sum_\alpha \dot{r}_\alpha \partial_{r_\alpha} + \sum_\alpha \dot{p}_\alpha \partial_{p_\alpha}$$

$\alpha = 1, 2, 3$ or x, y, z

$\vec{r} = \begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix}$; "dot" $= \frac{d}{dt}$

this equation says: distribution function is constant along a trajectory in phase space.

Valid in the absence of interactions!

$\sigma \neq 0$:

$$\boxed{\left(\frac{\partial}{\partial t} + \frac{1}{m}\vec{p}\cdot\vec{\nabla}_{\vec{r}} + \vec{F}\cdot\vec{\nabla}_{\vec{p}}\right) f(\vec{r},\vec{p},t) = \left(\frac{\partial f}{\partial t}\right)_{coll}}$$

this equation <u>defines</u> the term $\left(\frac{\partial f}{\partial t}\right)_{coll}$

Note: This equation is based on the following hirarchy of time scales:

$$\boxed{\delta\tau \ll \tau^*}$$

$\delta\tau$: duration of collision

τ^*: time betw. collisions (for the most part the particles are free and independent)

E.g.: nitrogen under standard temperature and pressure

density $\sim 2.7 \cdot 10^{25}$ molecules$/m^3$

distance between molecules $d \sim n^{-1/3} \sim 3 \cdot 10^{-9}$ m

cross section $\sim 4 \cdot 10^{-19}\ m^2$ (from experimental data) corresponds to hard sphere radius $a \approx 1.8 \cdot 10^{-10}$ m

Then: $\tau^* \sim \frac{1}{n \langle v \rangle \sigma} \sim 2 \cdot 10^{-10}$ s

density

average velocity

cross section

average time between two successive collisions of the same particle

used $\langle v \rangle \sim 500$ m/s

$$l \sim \tau^* \langle v \rangle \sim \frac{1}{n\sigma} \sim 10^{-7} \text{ m}$$

mean free path

$$\delta\tau \sim \frac{a}{\langle v \rangle} \sim 3 \cdot 10^{-13} \text{ s}$$

So: $\delta\tau \ll \tau^*$

size of particle $\ll$ separation betw. particles $\ll$ mean free path

$$\underbrace{a \ll d \ll l}_{\text{length scale separation}}$$

note: if mean free path l becomes of the order of the system size, we will no longer have local equilibrium!

Our goal now is to find an explicit expression for $\left(\frac{\partial f}{\partial t}\right)_{coll}$.

the result is given at the top of page 299.

We write: $\left(\frac{\partial f}{\partial t}\right)_{coll} dt = (\bar{R} - R)\, dt$

$R\, dt\, d^3\vec{r}\, d^3\vec{p}$: # of collisions occuring during t and $t + dt$, in which one of the initial molecules is in $d^3\vec{r}\, d^3\vec{p}$ about $(\vec{r}, \vec{p})$

$\bar{R}\, dt\, d^3\vec{r}\, d^3\vec{p}$: # of collisions occuring during t and $t + dt$, in which one of the final molecules is in $d^3\vec{r}\, d^3\vec{p}$ about $(\vec{r}, \vec{p})$

$\rightsquigarrow$ essentially : "gain ~~minus~~ versus loss"

3.3 Boltzmann transport equation

Basic assumption: gas is so dilute that we only need to worry about binary collisions (higher-body / multi-body collisions are strongly suppressed due to diluteness)

Also: neglect effect of external forces on collisions.

Let's assume elastic collisions.

Moreover, assume the following:

$$\underbrace{F^{(2)}(\vec{r},}_{\text{two-particle distribution function}} \vec{p}_1, \quad \vec{p}_2, t) = f(\vec{r}, \vec{p}_1, t) f(\vec{r}, \vec{p}_2, t)$$

(the text uses F... but I want to explicitly distinguish this from the force...)

$F^{(2)}$ contains, in general, correlations the momenta of the two particles are uncorrelated

⇝ probability of finding them simultaneously is the probability of finding each alone

(assumption of "molecular chaos")

Then : $dN_{12} \quad dP_{12 \to 1'2'} \quad dt$ = # of transition $12 \to 1'2'$ in a volume element $d^3\vec{r}$ at $\vec{r}$ owing to collisions during the time interval dt

initial # of colliding pairs with $\vec{p}_1, \vec{p}_2$

$$dN_{12} = F^{(2)}(\vec{r}, \vec{p}_1, \vec{p}_2, t)\, d^3\vec{r}\, d^3\vec{p}_1\, d^3\vec{p}_2$$

$$\Rightarrow \quad R\, dt\, d^3\vec{r}\, d^3\vec{p}_1 = \int dP_{12 \to 1'2'}\, F^{(2)}(\vec{r}, \vec{p}_1, \vec{p}_2, t)\, d^3\vec{p}_2 \times$$

$$\times\, dt\, d^3\vec{r}\, d^3\vec{p}_1$$

$$dP_{12 \to 1'2'} = J\, d\sigma = \delta(\vec{P} - \vec{P}')\, \delta(E - E')\, |T_{fi}|^2\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}'$$

$\vec{P} = \vec{p}_1 + \vec{p}_2$ $\qquad$ $\vec{P}' = \vec{p}_1{}' + \vec{p}_2{}'$

$$\Rightarrow \quad R = \int \delta(\underline{\vec{P}} - \underline{\vec{P}}')\, \delta(E - E')\, |T_{fi}|^2\, F^{(2)}(\vec{r}, \vec{p}_1, \vec{p}_2, t)$$

$$d^3\vec{p}_2\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}'$$

momentum conservation

energy conservation

two-particle distribution fct. at time t

going from "initial" to "final"

$$\bar{R} = \int \delta(\underline{\vec{P}}' - \underline{\vec{P}})\, \delta(E' - E)\, |T_{if}|^2\, F^{(2)}(\vec{r}, \vec{p}_1{}', \vec{p}_2{}', t)$$

$$d^3\vec{p}_2\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}'$$

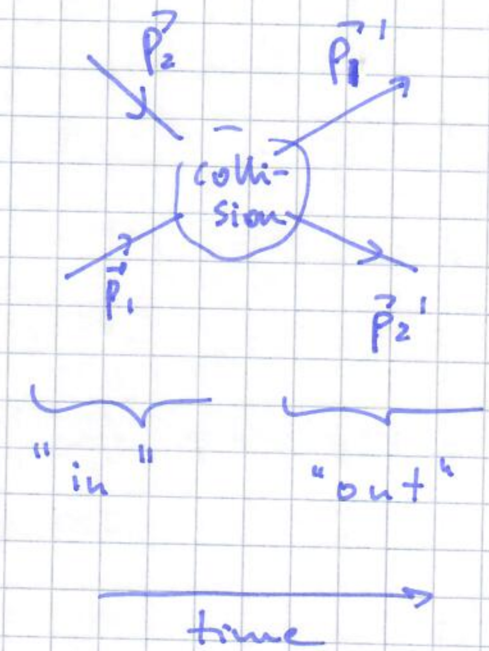
Rewriting $F^{(2)}$ in terms of product of two f functions we obtain:

$$\text{using} \begin{cases} \delta(\underline{\vec{P}}' - \underline{\vec{P}})\, \delta(E' - E) = \delta(\underline{\vec{P}} - \underline{\vec{P}}')\, \delta(E - E') \\ \left(\dfrac{\partial f}{\partial t}\right)_{coll} = \bar{R} - R \\ |T_{if}|^2 = |T_{fi}|^2 \end{cases}$$

$$\left(\frac{\partial}{\partial t} + \frac{1}{m}\,\vec{p}_1 \cdot \vec{\nabla}_{\vec{r}} + \vec{F} \cdot \vec{\nabla}_{\vec{p}_1}\right) f(\vec{r}, \vec{p}_1, t)$$

$$= \int \delta(\vec{P}' - \vec{P})\, \delta(E' - E)\, |T_{fi}|^2 \Big[f(\vec{r}, \vec{p}_1', t)\, f(\vec{r}, \vec{p}_2', t) - f(\vec{r}, \vec{p}_1, t)\, f(\vec{r}, \vec{p}_2, t) \Big]\, d^3\vec{p}_2\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}'$$

Boltzmann transport eq.



The momentum constraint (3-components) and energy constraint (1 equation) allow us to integrate over 4 degrees of freedom fairly straightforwardly → reduces r.h.s. of Boltzmann transport eq. to 5-dimensional integral

Results that follow from Boltzmann's transport equation: $\equiv$ integrodifferential eq. that describes the approach to equilibrium of the one-particle phase-space density fct. $f(\vec{r}, \vec{p}, t)$ of a dilute gas

- The only time-independent solution of the equation is the distribution

$$C \exp\left[-\frac{(\vec{p}^2/2m + U(\vec{r}))}{kT}\right]$$

equilibrium distribution function

↳ Maxwell-Boltzmann velocity distribution

- From Boltzmann eq., one can define entropy fct. with the following properties:
  * entropy fct. is equal to the logarithm of the phase-space volume available to a system with a given phase space density.
  * entropy increases steadily until the phase-space density function becomes equal to the Maxwell-Boltzmann distribution.
  * At equilibrium, the Boltzmann entropy fct. is equal to known thermodynamic entropy of an ideal gas.

4 The equilibrium state of a dilute gas

4.1 Boltzmann's H-theorem

equilibrium distribution fct. $\hat{=}$ solution of the Boltzmann transport equation that is independent of time

in most cases, this is the same as the distribution function in the $t \to \infty$ limit.

Let us make two assumptions:

- $\vec{F} = 0$ (no external force)
- $f(\vec{r}, \vec{p}, t) = \underbrace{f(\vec{p}, t)}_{\text{no dependence on } \vec{r} \text{ in equilibrium}}$

$$\Rightarrow \quad \frac{\partial}{\partial t} f(\vec{p}, t) = \int \delta(\vec{P}' - \vec{P})\, \delta(E' - E)\, |T_{fi}|^2 \times$$

$$\left[f(\vec{p}_1{}', t) f(\vec{p}_2{}', t) - f(\vec{p}_1, t) f(\vec{p}_2, t) \right] d^3\vec{p}_2\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}'$$

Let's denote the equilibrium solution by $f_0(\vec{p})$

$$\Rightarrow 0 = \int \delta(\vec{P}' - \vec{P})\, \delta(E' - E)\, |T_{fi}|^2 \times$$

$$\left[f_0(\vec{p}_1{}') f_0(\vec{p}_2{}') - f_0(\vec{p}_1) f_0(\vec{p}_2) \right] d^3\vec{p}_2\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}' \qquad (*)$$

no time-dependence

Clearly: if $f_0(\vec{p}_1{}') f_0(\vec{p}_2{}') - f_0(\vec{p}_1) f_0(\vec{p}_2) = 0$, then Eq. (*) is fulfilled, i.e., in this case $f_0(\vec{p})$ solves (*).

found in this way

sufficient condition

It turns out: $f_0(\vec{p}_1{}') f_0(\vec{p}_2{}') - f_0(\vec{p}_1) f_0(\vec{p}_2) = 0$

is also a necessary condition.

One can further show:

If f satisfies the Boltzmann transport equation, then $\frac{dH(t)}{dt} \leq 0$

$$\text{where } H(t) = \frac{1}{m}\int f(\vec{p},t)\,\log\big(f(\vec{p},t)\big)\,d^3\vec{p}\,.$$

Boltzmann's H-theorem

4.2 Maxwell Boltzmann distribution

So, we need: $f_0(\vec{p}_1)\,f_0(\vec{p}_2) = f_0(\vec{p}_1{}')\,f_0(\vec{p}_2{}')$

Goal: Want to find $f_0(\vec{p}) = \lim_{t\to\infty} f(\vec{p},t)$.

Take logarithm:

$$\log(f_0(\vec{p}_1)) + \log(f_0(\vec{p}_2)) = \log(f_0(\vec{p}_1{}')) + \log(f_0(\vec{p}_2{}'))$$

Solution in terms of the temperature T, average momentum $\vec{p}_0$, and particle density n:

$$\boxed{f_0(\vec{p}) = n\,(2\pi m k T)^{-3/2}\exp\left[-\frac{(\vec{p}-\vec{p}_0)^2}{2mkT}\right]}$$

Maxwell Boltzmann distribution

assuming no external forces

$\equiv$ probability of finding a molecule/particle with momentum $\vec{p}$ in the gas

If we have an external force $\vec{F}$, we find:

$$\vec{F} = -\nabla \phi(\vec{r})$$ ← this is how we can parametrize $\vec{F}$

$$\Rightarrow f(\vec{r},\vec{p}) = \frac{n(\vec{r})}{(2\pi m k T)^{3/2}} \exp\left[-\frac{(\vec{p}-\vec{p}_0)^2}{2mkT}\right]$$

$$\text{with } n(\vec{r}) = n_0 \exp\left(-\frac{\phi(\vec{r})}{kT}\right)$$

Importantly: Maxwell - Boltzmann distribution is independent of details of interactions (but we require interactions since we need a non-zero cross section ⇝ if the cross section was zero, we wouldn't have collisions that drive the system into equilibrium).

Note: $H = -\dfrac{S}{Vk}$

this is straightforward to show for ideal gas but holds more generally

Thus: $\boxed{\frac{dH}{dt} \leq 0}$ => $\boxed{-\frac{1}{Vk} \frac{dS}{dt} \leq 0}$

assume: fixed volume (isolated gas)

⇝ entropy never decreases

(this is the 2nd law of thermodynamics)

4.4 Analysis of the H-theorem
(or: physical implications)

Recall:

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

time dependence of H is governed / determined by time dependence of $f(\vec{p}, t)$

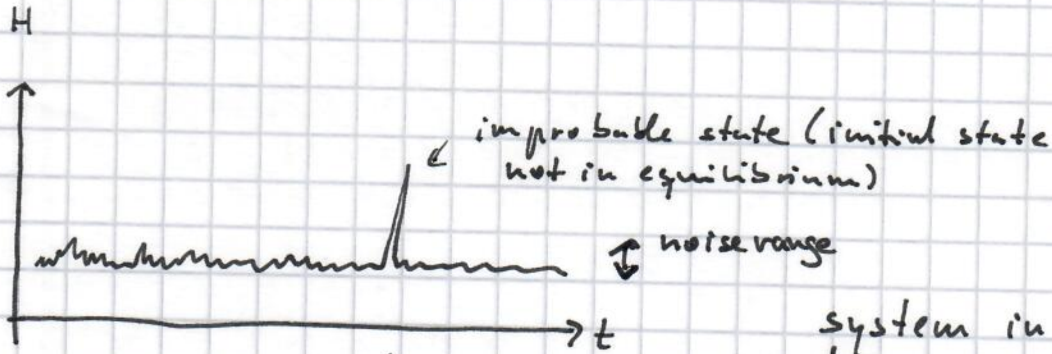
in general, $f(\vec{p}, t)$ does not satisfy Boltzmann transport equation

!!! it satisfies the Boltzmann transport equation only when the assumption of molecular chaos happens to be valid

The H-theorem states that if at a given instant t the state of the gas satisfies the assumption of molecular chaos, then at the instant $t+\varepsilon$ ($\varepsilon > 0$ and $\varepsilon \to 0$) we have:

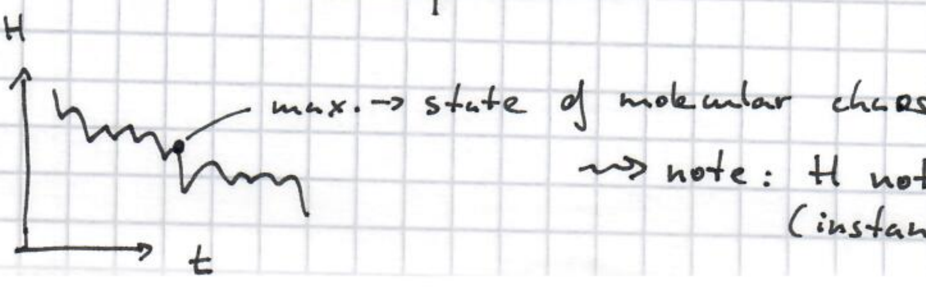
(a) $$\frac{dH(t)}{dt} \leq 0$$

(b) $$\frac{dH(t)}{dt} = 0$$ if and only if $f(\vec{p}, t)$ is the Maxwell-Boltzmann distribution.



system in thermodynamic equilibrium never goes out of equilibrium

after a few collisions, system will be back in equilibrium



⇝ note: H not continuous (instantaneous collisions)