Theo. 4 Statistical Physics.

Lecture 11.

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Last time: Consequences of Liouville's theorem, ergodicity

Streaming + collision

Today: The BBGKY hierarchy

The Boltzmann equation.

From last time, we found that an s-particle density obeyed a time-evolution of

$$\frac{\partial f_s}{\partial t} - \{H_s, f_s\} = \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial V(\vec{q}_n - \vec{q}_{s+1})}{\partial \vec{q}_n} \frac{\partial f_{s+1}}{\partial \vec{p}_n}$$

with $f_s = \frac{N!}{(N-s)!} \rho_s$. ρ_s fixes the first s coordinates in phase space to the given $(\vec{p}_i, \vec{q}_i)$ with $i = 1, s$.

The LHS are streaming terms, since this is the expected behavior from simple time evolution, $\frac{\partial \rho}{\partial t} = -\{\rho, H\}$. The modification to "free-streaming" of the s-particles comes from "collision" terms on the RHS, which are non-zero if any of the s-particles "hits" the s+1st particle (which takes into account any of the remaining N-s particles by exchange symmetry.). Necessarily, the RHS is proportional to an s+1 joint PDF.

This structure is attributed to Bogoliubov, Born, Green, Kirkwood, and Yvon, since we can now characterize the time length scales of each set of terms.

Note each term has units of $(\text{time})^{-1}$.

For concreteness, we consider the BBGKY hierarchy eqn. for $s=1$ and $s=2$:

$$\star \quad \left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1}\right] f_1 = \int dV_2 \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial f_2}{\partial \vec{p}_1}.$$

$$\star\star \quad \left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} - \frac{\partial U}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2} + \frac{\vec{p}_1}{m}\frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m}\frac{\partial}{\partial \vec{q}_2}\right.$$

$$\left. - \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right)\right] f_2$$

$$= \int dV_3 \left[\frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_3)}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\partial \mathcal{V}(\vec{q}_2-\vec{q}_3)}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2}\right] f_3$$

where we have used a symmetric potential,

$$\mathcal{V}(\vec{q}_1-\vec{q}_2) = \mathcal{V}(\vec{q}_2-\vec{q}_1) \quad \text{s.t.} \quad \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1} = -\frac{\partial \mathcal{V}(\vec{q}_2-\vec{q}_1)}{\partial \vec{q}_2}$$

In terms of gas molecules, we can estimate the time scale of each term from empirical observation. Typical velocities of gas molecules a room temp. are $\mathcal{O}(10^2)\ \text{m/s}$ (using $\langle K.E.\rangle = \frac{3}{2}k_B T = \frac{1}{2}mv^2$ monatomic).

The term: $\frac{\partial U}{\partial \vec{q}}\cdot\frac{\partial}{\partial \vec{p}}$. The first part is the variation of the external potential w.r.t. spatial distance, which we can rescale freely by changing system size.

If $L \sim 10^{-3}m$, then $\frac{1}{\tau_u} \sim \frac{1}{L} \cdot v \Rightarrow \tau_u \sim 10^{-5}s$.

In comparison, $\frac{1}{\tau_c} \sim \frac{\partial V}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}}$ is the inverse collision duration for the interatomic potential V, which extends roughly over $d \sim 10^{-10}m$, so $\tau_c \sim 10^{-12}s$. This is applicable to short-range interactions, like the van der Waals force & Lennard-Jones potential. A different behavior is seen for long-range forces, such as the Coulomb gas in a plasma. [Neutral plasma uses Debye screening length λ instead of d.]

Collision terms on RHS are

$$\frac{1}{\tau_x} \sim \int dV \frac{\partial V}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \frac{f_{s+1}}{f_s} \sim \int dV \frac{\partial V}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} N \frac{\rho_{s+1}}{\rho_s}$$

Here, the volume integral gives a factor d^3, and $\frac{f_{s+1}}{f_s} \sim$ prob. of finding another particle per unit volume, so $\frac{f_{s+1}}{f_s} \sim n = \frac{N}{V} \sim 10^{26}/m^3$.

$$\frac{1}{\tau_x} \sim d^3 \cdot n \cdot \underbrace{\frac{1}{\tau_c}}_{\text{from before}} \Rightarrow \tau_x \sim \frac{\tau_c}{nd^3} \sim \frac{1}{nvd^2}$$

$$\sim \frac{m^3}{10^{26}} \cdot \frac{1}{10^2}\frac{s}{m} \cdot \frac{1}{10^{-20}m^2}$$

$$\sim 10^{-8}s$$

This $\tau_x \sim 10^{-8}s \gg \tau_c \sim 10^{-12}s$, and $nd^3 \sim 10^{-4} \ll 1$.

So, RHS has terms $\frac{1}{\tau_x} \sim \frac{10^8}{s}$ scaling while

LHS has terms $\frac{1}{\tau_c} \sim \frac{10^{12}}{s}$ scaling, so we can solve the nested/iterative system of equations by truncating after the f_2 eqn. Remark: the f_1 eqn. has <u>no</u> collision terms on LHS.

So, we set RHS of $\star\star = 0$, and this means that f_2 evolves as an isolated two-particle system with time constant τ_u for the CoM of the two particles and τ_c for the relative coordinates. We will thus assume

$$f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t) \to f_1(\vec{p}_1, \vec{q}_1, t)\, f_1(\vec{p}_2, \vec{q}_2, t)$$

for $|\vec{q}_2 - \vec{q}_1| \gg d$.

We can solve for the f_2 dependence on relative coordinates + momenta by considering the steady state behavior,

$$\left[\frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial\vec{q}_1} + \frac{\vec{p}_2}{m}\cdot\frac{\partial}{\partial\vec{q}_2} - \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial\vec{q}_1}\cdot\left(\frac{\partial}{\partial\vec{p}_1} - \frac{\partial}{\partial\vec{p}_2}\right)\right] f_2 = 0$$

f_2 should vary slowly over CoM coordinate $\vec{Q} = \frac{\vec{q}_1 + \vec{q}_2}{2}$ and greatly over $\vec{q} = \vec{q}_2 - \vec{q}_1$, so $\frac{\partial f_2}{\partial\vec{q}} \gg \frac{\partial f_2}{\partial\vec{Q}}$,

$\frac{\partial f_2}{\partial\vec{q}_2} \simeq -\frac{\partial f_2}{\partial\vec{q}_1} = \frac{\partial f_2}{\partial\vec{q}}$, giving

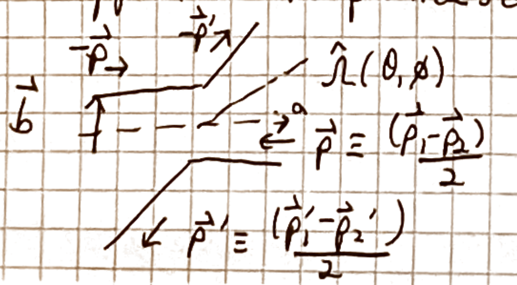
$$\frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial\vec{q}_1}\left(\frac{\partial}{\partial\vec{p}_1} - \frac{\partial}{\partial\vec{p}_2}\right) f_2 = -\left(\frac{\vec{p}_1 - \vec{p}_2}{m}\right)\cdot\frac{\partial}{\partial\vec{q}} f_2$$

Collision term on RHS of $\star$ is

$$\left.\frac{df_1}{dt}\right|_{coll.} = \int d^3\vec{p}_2\, d^3\vec{q}_2\, \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial\vec{q}_1}\cdot\left(\frac{\partial}{\partial\vec{p}_1} - \frac{\partial}{\partial\vec{p}_2}\right) f_2$$

$$\simeq \int d^3\vec{p}_2\, d^3\vec{q}_2 \left(\frac{\vec{p}_2 - \vec{p}_1}{m}\right) \underbrace{\frac{\partial}{\partial\vec{q}}}_{\text{total deriv.}} f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2; t)$$

Appeal to two particle scattering. Introduce impact parameter $\vec{b}$ and coord. a is ~~pos.~~ neg. before collision & pos. after.



$$\left.\frac{df_1}{dt}\right|_{coll.} = \int d^3\vec{p}_2 \, \overbrace{d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2|}^{\text{flux on area } d^2\vec{b}} \left[f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, +; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \right]$$

for $|\vec{v}_1 - \vec{v}_2| = \frac{1}{m} |\vec{p}_1 - \vec{p}_2|$ relative velocity.

Integration over "a" is $-\infty$ to $+\infty$, but will already approximate for "a" few d from collision. Still work at small separations so can ignore difference of $\vec{q}_1$ + $\vec{q}_2$. (Coarse-graining variations smaller than d.)

Complication: f_2 densities treated differently before and after collision. Collisions tend to randomize momenta + give more isotropic dist. Densities f_2 before + after related by streaming, so $f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, +; t) = f_2(\vec{p}_1{}', \vec{q}_1{}', \vec{p}_2{}', \vec{b}, -; t)$

We get

$$\left.\frac{df_1}{dt}\right|_{coll.} = \int d^3p_2 \, d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2| \left[f_2(\vec{p}_1{}', \vec{q}_1{}', \vec{p}_2{}', \vec{b}, -; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \right]$$

Change variables $d^2\vec{b} = d^2\Omega \left|\frac{d\sigma}{d\Omega}\right|$, with $\frac{d\sigma}{d\Omega}$ the differential cross section

Cons. of momentum + energy then fix $\vec{p}_1{}'$ + $\vec{p}_2{}'$.

We use <u>assumption</u> <u>of</u> <u>molecular</u> <u>chaos</u> to obtain the Boltzmann equation,

$$f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) = f_1(\vec{p}_1, \vec{q}_1, t) \, f_1(\vec{p}_2, \vec{q}_1, t)$$

Boltzmann eqn. $\Rightarrow$

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{q}_1} \right] f_1$$

$$= -\int d^3\vec{p}_2 \, d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1, \vec{q}_1, t) f_1(\vec{p}_2, \vec{q}_1, t) - f_1(\vec{p}_1{}', \vec{q}_1, t) f_1(\vec{p}_2{}', \vec{q}_1, t) \right]$$

In words: Boltzmann equation.

LHS streaming of single particle in ext. potential U.

RHS prob. of finding particle of $\vec{p}_1$ at $\vec{q}$:

reduced by prob. of having particle $\vec{p}_2$, integrated by $\int d^3\vec{p}_2$

added by prob. of having $\vec{p}_1{}' + \vec{p}_2{}'$.

Weighted by $\left| \frac{d\sigma}{d\Omega} \right|$, flux prop. to $|\vec{v}_1 - \vec{v}_2|$,

This is a technical result, but now we come to the thrust of the calculation: <u>the H theorem</u>.

If $f_1(\vec{p}, \vec{q}, t)$ satisfies the Boltzmann eqn., then $\frac{dH}{dt} \leq 0$, where $H(t) = \int d^3\vec{p}\, d^3\vec{q}\; f_1(\vec{p}, \vec{q}, t) \ln f_1(\vec{p}, \vec{q}, t)$

So $H(t)$ can be thought of as the information content of the one-particle PDF, $I[p_1] = \langle \ln p_1 \rangle$.

This opens up the concept of information entropy as related to probability, and we will focus on the H-theorem & entropy next time.