Theo. 4. Statistical Physics

Lecture 12.

Felix Yu

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Last time: BBGKY hierarchy

Boltzmann equation.

Today: H-theorem + proof.

Molecular chaos + irreversibility

From the end of last time, we constructed the Boltzmann eqn.

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

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

This time-evolution of f_1, the one-particle PDF, obeys a ~~surprising~~ surprising result: the H-theorem.

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

Pf: $$\frac{dH}{dt} = \int d^3\vec{p}_1\, d^3\vec{q}_1\, \frac{\partial f_1}{\partial t}(\ln f_1 + 1)$$

$$= \int d^3\vec{p}_1\, d^3\vec{q}_1\, \ln f_1 \frac{\partial f_1}{\partial t} + \int dV_1\, f_1$$

$\int dV_1 f_1 = N\int d\Gamma\, \rho = N$ is time-independent

So $$\frac{dH}{dt} = \int d^3\vec{p}_1\, d^3\vec{q}_1\, \ln f_1 \left(\frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\vec{p}_1}{m} \cdot \frac{\partial f}{\partial \vec{q}_1} \right)$$

$$- \int d^3\vec{p}_1\, d^3\vec{q}_1\, d^3\vec{p}_2\, d^2\sigma\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1, \vec{q}_1) f_1(\vec{p}_2, \vec{q}_1) - f_1(\vec{p}_1{}', \vec{q}_1) f_1(\vec{p}_2{}', \vec{q}_1) \right] \ln f_1(\vec{p}_1, \vec{q}_1)$$

with $d^2\sigma = d^2\vec{b} = d^2\Omega \left| \frac{d\sigma}{d\Omega} \right|$ as shorthand.

First, streaming terms are 0 by IBP.

$$\int d^3\vec{p}_1\, d^3\vec{q}_1\, \ln f_1\, \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial f}{\partial \vec{p}_1} = - \int d^3\vec{p}_1\, d^3\vec{q}_1\, f_1 \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{1}{f_1} \frac{\partial f_1}{\partial \vec{p}_1}$$

use $\frac{\partial}{\partial \vec{p}_1} \ln f_1 = \frac{1}{f_1} \frac{\partial f_1}{\partial \vec{p}_1}$

$$= \int d^3\vec{p}_1\, d^3\vec{q}_1\, f_1 \frac{\partial}{\partial \vec{p}_2} \cdot \underbrace{\frac{\partial U}{\partial \vec{q}_1}}_{\text{no dep. on } \vec{p}_1} = 0$$

Next, $$\int d^3\vec{p}_1\, d^3\vec{q}_1\, \ln f_1\, \frac{\vec{p}_1}{m} \cdot \frac{\partial f_1}{\partial \vec{q}_1}$$

$$= - \int d^3\vec{p}_1\, d^3\vec{q}_1\, f_1 \frac{\vec{p}_1}{m} \frac{1}{f_1} \frac{\partial f_1}{\partial \vec{q}_1}$$

$$= \int d^3\vec{p}_1\, d^3\vec{q}_1\, f_1 \frac{\partial}{\partial \vec{q}_1} \frac{\vec{p}_1}{m} = 0$$

Collision term on RHS integrates over dummy variables $\vec{p}_1$ + $\vec{p}_2$. Can swap labels $1 \leftrightarrow 2$ without affecting total integral, so average the two expressions. (symmetrize)

(i) $$\frac{dH}{dt} = -\frac{1}{2} \int d^3\vec{q}\, d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\sigma\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}) f_1(\vec{p}_2) - f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right] \ln \left(f_1(\vec{p}_1) f_1(\vec{p}_2) \right)$$

suppressing q + t arguments in f_1.

Now, change from $(\vec{p}_1, \vec{p}_2, \vec{b})$ coordinates to $(\vec{p}_1{}', \vec{p}_2{}', \vec{b}')$ coordinates of final state variables. We know the Jacobian is unity by time-reversal symmetry (every collision has an inverse by reversing momenta of products).

We get
$$\frac{dH}{dt} = -\frac{1}{2}\int d^3\vec{q}\; d^3\vec{p}_1{}'\; d^3\vec{p}_2{}'\; d^2\vec{b}'\; |\vec{v}_1{}' - \vec{v}_2{}'| \left[f_1(\vec{p}_1) f_1(\vec{p}_2) - f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right] \ln\left(f_1(\vec{p}_1) f_1(\vec{p}_2) \right)$$
where we use $|\vec{v}_1 - \vec{v}_2| = |\vec{v}_1{}' - \vec{v}_2{}'|$ for elastic collisions.

Since $(\vec{p}_1{}', \vec{p}_2{}', \vec{b}')$ are new dummy variables, we ~~symmetrize~~ relabel again

(ii) $$\frac{dH}{dt} = -\frac{1}{2}\int d^3\vec{q}\; d^3\vec{p}_1\; d^3\vec{p}_2\; d^2\vec{b}\; |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \ln\left(f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right)$$

Now, symmetrize (i) & (ii) and average,

$$\frac{dH}{dt} = -\frac{1}{4}\int d^3\vec{q}\; d^3\vec{p}_1\; d^3\vec{p}_2\; d^2\vec{b}\; |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1) f_1(\vec{p}_2) - f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right] \times \left[\ln\left(f_1(\vec{p}_1) f_1(\vec{p}_2) \right) - \ln\left(f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right) \right]$$

Now, if $f_{11} f_{12} - f_{11'} f_{12'} > 0$, then
$\ln f_{11} f_{12} - \ln f_{11'} f_{12'} > 0$ and ~~both~~ the product $[\ldots][\ln \ldots]$ is pos.

If $f_{11} f_{12} - f_{11'} f_{12'} < 0$, then
$\ln f_{11} f_{12} - \ln f_{11'} f_{12'} < 0$ and the product $[\ldots][\ln \ldots]$ is again pos.

Thus the integrand is always positive and the H theorem is proven; $\frac{dH}{dt} \leq 0$.

Why is this surprising?

We have, somewhere, introduced an arrow of time even though all the microscopic physics obeys time-reversal symmetry.

This came because of the assumption of molecular chaos before the collisions,

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

instead of after. We therefore treat two-body densities before and after the collision differently. Perfect time-reversal symmetry implies there are subtle correlations in the assumption of molecular chaos that are ignored.

Note that irreversibility emerges even in classical time-evolution. Collisions tend to correlate coordinates. Given $H(t)$ measures information, the loss of information is carried by the inevitable coarse-graining of a measurement apparatus. For two immiscible fluids, as they interact, the coarse-grained nature of a measurement will only be able to determine the composition of each component at a probabilistic level.

We now relate $H(t)$ back to the second law of thermodynamics & the concept of entropy and the question of how systems approach equilibrium.

A necessary condition in equilibrium is that $\frac{dH}{dt}=0$,

so H does <u>not</u> decrease anymore with time.

This requires $f_1(\vec{p}_1,\vec{q}_1)\, f_1(\vec{p}_2,\vec{q}_1) - f_1(\vec{p}_1{}',\vec{q}_1) f_1(\vec{p}_2{}',\vec{q}_1)=0$

This is for <u>each</u> point $\vec{q}$!

$$\Rightarrow \quad \ln f_1(\vec{p}_1,\vec{q}) + \ln f_1(\vec{p}_2,\vec{q}) = \ln f_1(\vec{p}_1{}',\vec{q}) + \ln f_1(\vec{p}_2{}',\vec{q})$$

This is exactly like a conservation law for a collision. We can use a "form factor" decomposition to thus reexpress f_1 as a linear function of known conserved quantities in 2-to-2 scattering:

particle number, kinetic energy, and three comp. of total momenta

$$\Rightarrow \quad \ln f_1 = a(\vec{q}) - \vec{\alpha}(\vec{q})\cdot\vec{p} - \beta(\vec{q})\left(\frac{\vec{p}^{\,2}}{2m}\right)$$

Can include potential energy $U(\vec{q})$ by redefining $a(\vec{q})$, $\alpha(\vec{q})$, $\beta(\vec{q})$:

$$f_1 \equiv \mathcal{N}(\vec{q}) \exp\left(-\alpha(\vec{q})\cdot\vec{p} - \beta(\vec{q})\left(\frac{p^2}{2m} + U(\vec{q})\right)\right)$$

Such a distribution describes local equilibrium. Over time, it evolves away from collisions unless $\{H_1, f_1\}=0$ which thus constrains (sufficient condition) f_1 to depend only on H_1. This is easily satisfied if

$$\mathcal{N}(\vec{q}) \equiv \mathcal{N}_1,\ \beta(\vec{q}) \equiv \beta_1, \text{ and } \vec{\alpha}=0.$$

Easy to normalize, e.g. in a box of volume V.

$$f_1(\vec{p}, \vec{q}) = n\left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left(-\beta \frac{(\vec{p}-\vec{p}_0)^2}{2m}\right)$$

$$\vec{p}_0 = \langle \vec{p} \rangle = \frac{m\vec{\alpha}}{\beta}, \quad n = \frac{N}{V}.$$

Can identify $\beta = \frac{1}{k_B T}$.

The Boltzmann equation is central to understanding thermal evolution & effects of collisions on number densities, steady state behavior, etc. !

Next time:

Boltzmann entropy, violation of extensivity,
Third law of thermodynamics.
Shannon entropy