Theo. 4. Statistical Physics.
Lecture 13. Rewrite.
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Last time: H-theorem + proof.
Molecular chaos + irreversibility.
Today: Calculating entropy, return to 2nd Law
Extensivity.

Recall from last time, we constructed

$$H(t) = \int d^3\vec{p}\, d^3\vec{q}\; f_1(\vec{p},\vec{q},t) \ln\left(f_1(\vec{p},\vec{q},t)\right)$$

and showed that $\frac{dH}{dt} \leq 0$ for f_1 satisfying the Boltzmann eqn.

We were studying the Boltzmann eqn. because we wanted to understand how systems time-evolve toward equilibrium. This study is too detailed & involved to carry on further, unfortunately, because we would need to enter the realm of hydrodynamics. The reason is because we need to consider complete dynamics in 6D phase space (3D coordinates and 3D momentum), where the most general structure allows for tensorial differential eqns. As an aside, the Navier-Stokes eqn. is the most famous eqn. in hydrodynamics, which is a PDE that expresses momentum balance & conservation of mass for Newtonian fluids.

Without doing detailed calculations, though, an intuitive understanding of how *equilibrium can be reached is given by noticing that the fastest timescales cause local equilibrium in a small volume of phase space. Then the next set of interactions work at the interface of these local volumes to make larger patches of equilibrium. (You can also analyze the local growth of entropy which follows the time constants in the time domain.). An analogy is studying crowd behavior is a cramped volume when there are limited exits. First, there is general chaos & only people immediately next to exits will leave. But soon enough, there are pockets / channels that organize and groups of people move with a well-defined group velocity as streams.

We will not carry further the study of how systems approach thermal equilibrium, but we will instead pivot back to the question of constructing an expression for entropy.

Recall we had $S_B - S_A \equiv \int_A^B \frac{dQ_{rev}}{T}$.

and the second law of thermodynamics said any isolated system has $\frac{dS}{dt} \geq 0$. This definition is not entirely practical because we would need a dQ_{rev} for every possible movement in thermodynamic coordinate space. Instead, we should have a state fcn. expression for S = entropy, since it should be calculable directly.

We can try, as an ansatz, the Boltzmann entropy, $S_B = -k_B H(t)$. Unfortunately, this definition fails because it violates the mathematical requirement of extensivity. Also violates 3rd law.

Let us reintroduce extensive & intensive variables.

Mathematically, an extensive S fits into a general total differential energy as

$$dE = T\,dS + \vec{J}\cdot d\vec{x} + \vec{\mu}\cdot d\vec{N}$$

Here, $\vec{N} = \{N_1, N_2, N_3, \ldots\}$ lists the number of particles of each species, and $\vec{\mu} = \{\mu_1, \mu_2, \ldots\}$ is the chemical potential that measures the work necessary to add additional particles to the system: $\delta W = \vec{\mu}\cdot d\vec{N}$

Some examples: $2H_2 + O_2 \to 2H_2O$

Number conservation can be violated in interactions like chemical reactions. Another standard example are photons, which can be radiated in any electromagnetic interaction process.

Extensive $S, \vec{x}, \vec{N}$ means

$$E(\lambda S, \lambda\vec{x}, \lambda\vec{N}) = \lambda E(S, \vec{x}, \vec{N})$$

where λ is a rescaling const.

We can perform a $\frac{d}{d\lambda}$ of both sides:

$$d(\lambda E) = \frac{\partial E}{\partial(\lambda S)}\, d(\lambda S) + \frac{\partial E}{\partial(\lambda\vec{x})}\cdot d(\lambda\vec{x}) + \frac{\partial E}{\partial(\lambda\vec{N})}\cdot d(\lambda\vec{N})$$

We match $d\lambda$ terms & set $\lambda = 1$. (See, for example, Blundell & Blundell, eq. 22.44.)

We get $E = \left(\frac{\partial E}{\partial S}\right)\Big|_{\vec{x},\vec{N}\text{ fixed}} S + \sum_i \frac{\partial E}{\partial x_i}\Big|_{S,x_i\neq x_j,\vec{N}} x_i + \sum_\alpha \frac{\partial E}{\partial N_\alpha}\Big|_{S,\vec{x},N_\beta\neq N_\alpha} N_\alpha$

We recognize that $\frac{\partial E}{\partial S}\Big|_{\vec{x},\vec{N}} = T$, $\frac{\partial E}{\partial x_i}\Big|_{S,x_j\neq x_i,\vec{N}} = \vec{J}_i$,

and $\frac{\partial E}{\partial N_\alpha}\Big|_{S,\vec{x},N_\beta\neq N_\alpha} = \mu_\alpha$, because $dE = T\,dS + \vec{J}\cdot d\vec{x} + \vec{\mu}\cdot d\vec{N}$,

so fixed $\vec{x}$ + $\vec{N}$ sets $T = \frac{\partial E}{\partial S}$, etc.

Therefore, $E = TS + \vec{J}\cdot\vec{x} + \vec{\mu}\cdot\vec{N}$.

We can see that the properly extensive variables $(S,\vec{x},\vec{N})$ thus forces the intensive variables to obey the constraint

"Gibbs-Duhem" relation

$$S\,dT + \vec{x}\cdot d\vec{J} + \vec{N}\cdot d\vec{\mu} = 0$$

[We can derive this by performing a total derivative on $E = TS + \vec{J}\cdot\vec{x} + \vec{\mu}\cdot\vec{N}$ and then saturating dE by the extensive relation.]

Next time: discuss improper extensivity of Boltzmann entropy, third law of thermodynamics, Shannon entropy.