Theo. 4. Statistical Physics. (16)

Lecture 19.

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Last time: Non-interacting classical systems from stat. phys.
Two-level systems
Ideal gas.

Today: Gibbs paradox and indistinguishably
Canonical Ensemble
Single & multiparticle partition function

From last time, we studied the stat. mech. of a non-interacting system with total energy E in a volume V and arrived at the ideal gas and the familiar Maxwell-Boltzmann distribution.

based on $\Omega(E,V,N) = V^N \frac{2\pi^{3N/2}}{(3N/2-1)!} (2mE)^{(3N-1)/2} \Delta_R$,

with $\Delta_R = \sqrt{\frac{2m}{E}} \Delta E$ the thickness of the shell in momentum space for the uncertainty in energy ΔE, we have the entropy

$$S = k_B \ln \Omega \cong N k_B \ln\left[V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right]$$

This is <u>problematic</u>, though, because S is not extensive.

For $(E, V, N) \to (\lambda E, \lambda V, \lambda N)$, then $S \to$

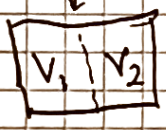
$$S' = \lambda N k_B \ln\left[\lambda V \left(\frac{4\pi e m \lambda E}{3\lambda N} \right)^{3/2} \right]$$

$$S' = \lambda N k_B \ln\left[\lambda V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right] = \lambda S + \lambda N k_B \ln \lambda$$

so we have an extra term $\lambda N k_B \ln \lambda$.

To understand this "mixing entropy" in more detail, consider two distinct gases at temp T in confined volumes V_1 & V_2. At a given time, the two volumes are joined into $V = V_1 + V_2$,

remove partition



and we have the initial entropy

$$S_i = S_1 + S_2 = N_1 k_B \left(\ln\left(\frac{V_1}{N_1}\right) + \sigma_1\right) + N_2 k_B \left(\ln\left(\frac{V_2}{N_2}\right) + \sigma_2\right)$$

$$\text{and } \sigma_1 = \ln\left(\frac{4\pi e m_1}{3}\frac{E_1}{N_1}\right)^{3/2} \text{ & } \sigma_2 = \ln\left(\frac{4\pi e m_2}{3}\frac{E_2}{N_2}\right)^{3/2}$$

We can simplify $\frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3 k_B T}{2}$ for monatomic gas.

$$\sigma_i(T) = \frac{3}{2}\ln\left(2\pi e m_i k_B T\right)$$

The temperature is unchanged: $\frac{3}{2} k_B T_f = \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T$

$$S_f = N_1 k_B \ln\left(\frac{V_1 + V_2}{N_1}\right) + N k_B \ln\left(\frac{V_1 + V_2}{N}\right) + k_B\left(N_1\sigma_1 + N_2\sigma_2\right)$$

$$\Delta S_{mix} = N_1 k_B \ln\frac{V}{V_1} + N_2 k_B \ln\frac{V}{V_2}$$

$$= -N k_B\left[\frac{N_1}{N}\ln\frac{V_1}{V} + \frac{N_2}{N}\ln\frac{V_2}{V}\right]$$

This leads to an interesting thought experiment:

$\Rightarrow$ Bigger S, irreversible process.

$\Rightarrow$ No change in S? Can always reinsert the partition, reversible.

What is the issue? In the first case, the particles are distinguishable, while they are indistinguishable in the second case. The logical flaw in evaluating $\Omega(E,V,N)$ is thus because the phase space is <u>overcounted</u> by $N!$ permutations.

The correct $\Omega(E,V,N) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N/2-1)!} (2mE)^{(3N-1)/2} \Delta_R$.

$\Rightarrow S = k_B \ln \Omega = k_B [N \ln V - N \ln N + N \ln e] + N k_B \sigma$

$= N k_B \left[\ln \frac{eV}{N} + \sigma \right]$ which is properly extensive.

The $\Delta S_{mix} = -N k_B \left[\frac{N_1}{N} \ln \frac{V_1}{V} + \frac{N_2}{N} \ln \frac{V_2}{V} \right]$

If the gases are identical, $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1+V_2}$

$\Rightarrow \Delta S_{mix} = (N_1+N_2) k_B \ln \frac{V_1+V_2}{N_1+N_2} - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2}$

$= 0.$

Coordinate volumes: $\frac{V^{N_1+N_2}}{N_1! N_2!}$ for distinct particles &

$\frac{V^{N_1+N_2}}{(N_1+N_2)!}$ for identical particles.

Remark: In classical mechanics, distinguishability is artificial. This is only justified from bosonic & fermionic wavefcns. & particle exchange in QM. Also fixes the phase space quantization by h = Planck's constant:

$$d\Gamma_N = \frac{1}{h^{3N} N!} \prod_{i=1}^{N} d^3\vec{q}_i \, d^3\vec{p}_i$$

Factor $\frac{1}{N!}$ Not applicable in two-level system since sites are labeled by index.

Next, we want to study the canonical ensemble, when a system is coupled to a reservoir at const. T, which allows heat exchange to the system but not work energy.

As a consequence of coupling the system to the reservoir, the system macrostates are labeled by T and $\vec{x}$, not E & $\vec{x}$ since internal energy is not conserved. Clearly, fundamentally, the system ⊕ reservoir is itself a microcanonical ensemble, except $E_{sys} \ll E_{tot}$. From this perspective,

$$p(\mu_S \otimes \mu_R) = \frac{1}{\Omega_{S\oplus R}(E_{tot})} \begin{cases} 1 & H_S(\mu_S) + H_R(\mu_R) = E_{tot} \\ 0 & \text{otherwise} \end{cases}$$

The unconditional probability for microstates of S is $p(\mu_S) = \sum_{\{\mu_R\}} p(\mu_S \otimes \mu_R)$.

[Recall unconditional probability is integrated/summed over all other variables/states.]

Sum is then over $E_{tot} - H_S(\mu_S)$.

$$\Rightarrow p(\mu_S) = \frac{\Omega_R(E_{tot} - H_S(\mu_S))}{\Omega_{S\oplus R}(E_{tot})} \propto \exp\left(\frac{1}{k_B} S_R(E_{tot} - H_S(\mu_S))\right)$$

(asg. of entropy)

We can approximate $S_R(E_{tot} - H_S(\mu_S)) \approx S_R(E_{tot}) - H_S(\mu_S)\frac{\partial S_R}{\partial E_R}$

$$= S_R(E_{tot}) - \frac{H_S(\mu_S)}{T}$$

Now, drop subscript S.

Normalized probabilities are

$$p_{(T,\vec{x})}(\mu) = \frac{\exp(-\beta H(\mu))}{Z(T,\vec{x})}, \quad \beta \equiv \frac{1}{k_B T}$$

with $Z(T,\vec{x}) = \sum_{\{\mu\}} \exp(-\beta H(\mu)) \equiv$ partition function

Recall that a probabilistic proportionality only requires normalization in order to become a proper probability.

Given the system energy is not fixed, we can study the expectation value of energy / Hamiltonian.

This requires change of variables from $p(\mu)$ to [redacted]

$$p(\mathcal{E}) = \sum_{\{\mu\}} p(\mu)\,\delta(\mathcal{H}(\mu)-\mathcal{E}) = \frac{e^{-\beta\mathcal{E}}}{\mathcal{Z}} \sum_{\{\mu\}} \delta(\mathcal{H}(\mu)-\mathcal{E})$$

The sum just counts the number of microstates of appropriate energy $\mathcal{E}$,

$$p(\mathcal{E}) = \frac{\Omega(\mathcal{E})\, e^{-\beta\mathcal{E}}}{\mathcal{Z}} = \frac{1}{\mathcal{Z}} \exp\left[\frac{S(\mathcal{E})}{k_B} - \frac{\mathcal{E}}{k_B T}\right]$$

$$= \frac{1}{\mathcal{Z}} \exp\left[\frac{-1}{k_B T}\left(\mathcal{E} - TS\right)\right]$$

Recall: $\mathcal{E} - TS \equiv F$ = Helmholtz Free Energy.

The probability $p(\mathcal{E})$ is sharply peaked at a most probable energy E^*, which minimizes $F(\mathcal{E})$.

Thus, $\mathcal{Z} = \sum_{\{\mu\}} e^{-\beta\mathcal{H}(\mu)} = \sum_{\mathcal{E}} e^{-\beta F(\mathcal{E})} \approx e^{-\beta F(E^*)}$

Thus, average energy is

$$\langle \mathcal{H} \rangle = \sum_{\mu} \mathcal{H}(\mu)\, \frac{e^{-\beta\mathcal{H}(\mu)}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial\beta} \sum_{\mu} e^{-\beta\mathcal{H}} = -\frac{\partial \ln \mathcal{Z}}{\partial\beta}$$

Recall: in thermodynamic potentials,

$$E = F + TS = F - T\left.\frac{\partial F}{\partial T}\right|_{\vec{x}}$$

$$= -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

$$= \frac{\partial(\beta F)}{\partial\beta}$$

Thus, we identify $F(T,\vec{x}) = -k_B T \ln \mathcal{Z}(T,\vec{x})$

and recognize that cumulants of $\mathcal{H}$ are generated by $\ln \mathcal{Z}$: $\langle \mathcal{H} \rangle_c = \frac{1}{\mathcal{Z}} \sum_{\mu} \mathcal{H}\, e^{-\beta\mathcal{H}} = \frac{-1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial\beta} = -\frac{\partial \ln \mathcal{Z}}{\partial\beta}$.

Also, $\langle H^2\rangle_c = \langle H^2\rangle - \langle H\rangle^2$

$$= \frac{1}{Z}\sum_\mu H^2 e^{-\beta H} - \frac{1}{Z^2}\left(\sum_\mu H e^{-\beta H}\right)^2$$

$$= \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$= -\frac{\partial \langle H\rangle}{\partial \beta}$$

In general, n^{th} cumulant of H is

$$\langle H^n\rangle_c = (-1)^n \frac{\partial^n \ln Z}{\partial \beta^n}.$$

$$\Rightarrow \langle H^2\rangle_c = -\frac{\partial \langle H\rangle}{\partial (1/k_B T)} = k_B T^2 \left.\frac{\partial \langle H\rangle}{\partial T}\right|_{\vec{x}}$$

$$= k_B T^2 C_{\vec{x}}.$$

This lets us ensure the diff. between the avg. energy $\langle H\rangle$ and most probable energy E^* vanishes as $\frac{1}{\sqrt{N}}$.

The PDF for energy is

$$p(E) = \frac{1}{Z} e^{-\beta F(E)} \approx \exp\left(-\frac{(E-\langle H\rangle)^2}{2 k_B T^2 C_{\vec{x}}}\right) \frac{1}{\sqrt{2\pi k_B T^2 C_{\vec{x}}}}$$

Finally, entropy of canonical ensemble is

$$S = -k_B \langle \ln p(\mu)\rangle$$

$$= -k_B \langle (-\beta H - \ln Z)\rangle = \frac{E-F}{T}.$$

Next time: Reexamine two-level system & ideal gas with canonical ensemble.