Theo. 4. Statistical Physics.

Lecture 20.

Felix Yu.

January 15, 2024.

Last time: Gibbs paradox + indistinguishably

Canonical Ensemble.

Today: Two-level system + ideal gas in canonical ensemble.

From last time, we considered the canonical ensemble, with a system coupled to a (very large) reservoir such that heat energy is exchanged at const. T but no work is performed. As expected, the probability of a microstate of energy $\mathcal{E}$ depends on the Helmholtz free Energy,

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

with $F \equiv E - TS$.

We now apply the canonical ensemble formalism to the two-level system + ideal gas.

Summary:

Ensemble	Macrostate	$p(\mu)$	Normalization
Microcanonical	$(E, \vec{x})$	$\delta_\Delta(\mathcal{H}(\mu) - E)/\Omega$	$S(E, \vec{x}) = k_B \ln \Omega$
Canonical	$(T, \vec{x})$	$\exp(-\beta \mathcal{H}(\mu))/Z$	$F(T, \vec{x}) = -k_B T \ln Z$

Keep in mind that in a canonical ensemble, all microstates have the same temperature, not E.

Two-level system:

N impurities again, macrostate $M \equiv (T, N)$.

Hamiltonian $\mathcal{H} = \epsilon \sum_{i=1}^{N} n_i$.

Microstates $\mu \equiv \{n_i\}$,

$$p(\{n_i\}) = \frac{1}{Z} \exp\left[-\beta\epsilon \sum_{i=1}^{N} n_i\right]$$

with $Z = \overset{\text{multiparticle}}{\text{partition function}}$

$$= \sum_{\{n_i\}} \exp\left[-\beta\epsilon \sum_{i=1}^{N} n_i\right]$$

$$= \left(\sum_{n_1=0}^{1} e^{-\beta\epsilon n_1}\right) \cdots \left(\sum_{n_N=0}^{1} e^{-\beta\epsilon n_N}\right)$$

$$= \left(1 + \exp(-\beta\epsilon)\right)^N$$

The free energy is $F(T,N) = -k_B T \ln Z$

$$= -N k_B T \ln\left(1 + \exp\left(-\frac{\epsilon}{k_B T}\right)\right)$$

The entropy is $S(T,N) = -\left.\frac{\partial F}{\partial T}\right|_N$

$$= N k_B \cancel{T} \ln\left(1 + \exp\left(-\frac{\epsilon}{k_B T}\right)\right) + N k_B T \left(\frac{\epsilon}{k_B T^2}\right) \frac{e^{-\epsilon/(k_B T)}}{1 + e^{-\epsilon/(k_B T)}}$$

$$= -\frac{F}{T} + \frac{N\epsilon}{T} \frac{e^{-\epsilon/(k_B T)}}{1 + e^{-\epsilon/(k_B T)}}$$

We can also calculate the internal energy

$$E = F + TS = \frac{N\epsilon}{\left(1 + \exp\left(\epsilon/(k_B T)\right)\right)}$$

or via $E = \frac{-\partial \ln Z}{\partial \beta} = \frac{N\epsilon \exp(-\beta\epsilon)}{1 + \exp(-\beta\epsilon)}$

Since joint probability is a product of each site,
$p = \prod_i p_i$, the excitations of different impurities are independent, with unconditional probabilities

$$p_i(n_i) = \frac{e^{-\beta \epsilon n_i}}{1+e^{-\beta\epsilon}}.$$

Ideal gas:

Macrostate: $M = (T, V, N)$

Microstates: $\mu = \{\vec{p}_i, \vec{q}_i\}$

$$p = (\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \begin{cases} 1 & \text{for } \{q_i\} \in \text{box} \\ 0 & \text{otherwise} \end{cases}$$

The partition function is sum over all Boltzmann factors of microstates with temp. T. ~~weighted by~~ .

Here we integrate over phase space & include $\frac{1}{N!}$ for identical particles:

$$Z(T,V,N) = \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3\vec{q}_i \; d^3\vec{p}_i}{h^3} \exp\left(-\beta \sum_{i=1} \frac{p_i^2}{2m}\right)$$

↳ h Planck's const. for dimensions.

cf. Kardar, p. 114–115.

$$= \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$$

cf. Blundell & Blundell, Sec. 21.2

$$= \frac{1}{N!} \left(\frac{V}{\lambda(T)^3}\right)^N$$

with $\lambda(T) \equiv \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal wavelength.

This ~~quantum~~ length scale controls the onset of QM effects.

A related variable is the quantum concentration,

$$n_Q = \frac{1}{(\lambda(T))^3}.$$

We have free energy

$$F = -k_B T \ln Z = -N k_B T \ln V + N k_B T \ln N - N k_B T - \frac{3N}{2} k_B T \ln\left(\frac{2\pi m k_B T}{h^2}\right)$$

$$= -N k_B T \left[\ln\left(\frac{Ve}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

Recall $dF = -S\,dT - P\,dV + \mu\,dN$

This lets us calculate E, for example:

$$-S = \left.\frac{\partial F}{\partial T}\right|_{V,N} = -N k_B\left[\ln\frac{Ve}{N} + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] - N k_B T \frac{3}{2T}$$

$$= \frac{F-E}{T}.$$

$$\Rightarrow E = \frac{3}{2} N k_B T.$$

We also see $P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} \Rightarrow PV = N k_B T.$

And $\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \frac{F}{N} + k_B T = \frac{E - TS + PV}{N} = k_B T \ln(n\lambda^3)$

cf. Kardas, p.113.

☆ Note that the canonical & microcanonical ensemble describe exactly the same physics in the thermodynamic limit $N \to \infty$.

This is because for $N \to \infty$, the canonical energy probability is so sharply peaked around the average energy that the ensemble behaves like a microcanonical ensemble.

We now remark on a conceptual clarification. The partition function can be used as a system-wide tool, summing over N particles, for example, but it can also be helpful to understand individual particles. The confusion usually stems from ~~is~~ trying to interpret macroscopic thermodynamic coordinates when $N \to$ small (like T, P, etc.) or even when $N \Rightarrow 1$. But nonetheless, we can still use the tools of stat. phys. to analyze ~~par~~ single particle partition functions or few-particle partition fcns. We have seen, already in the HW, the analysis of a two-level system with one site/ particle.

Key: $$Z = \sum_\alpha e^{-\beta E_\alpha}$$ for one particle with accessible energy levels E_α.

Example: Single particle quantum harmonic oscillator.

$$Z_1 = \sum_\alpha \exp(-\beta E_\alpha)$$

$$E_\alpha = (n+\tfrac{1}{2})\hbar\omega \quad \text{for } \alpha = n = 0, 1, 2, \ldots$$

$$Z = \sum_{n=0}^{\infty} \exp(-\beta(n+\tfrac{1}{2})\hbar\omega)$$

$$= \exp(-\beta\tfrac{1}{2}\hbar\omega) \sum_{n=0}^{\infty} \exp(-n\beta\hbar\omega)$$

Geometric series

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}.$$

Next time: Grand canonical ensemble.