Lecture 13

Recall from last lectures...

Remember, the conditions for being in equilibrium in a coexistence region is that each phase must have equal chemical potential for all components

We used a lattice model to find how μ depends on T and p for an ideal gas ...

$$\mu(T, p) = \mu^{(0)}(T) + k_B T \ln\left(\frac{p}{p_0}\right)$$

[Problem Set 4 #3]

Let's see this another way...

What is the canonical partition function for a non-interacting gas of N particles?

$\underline{N=1}$

$$q(V,T) = \sum_{\nu} e^{-\beta E(\nu)} = \sum_{\substack{\text{translations}\\ t}} \sum_{\substack{\text{internal}\\ \text{states } i}} e^{-\beta E(t,i)}$$

Do translations interact (affect the energy) with internal degrees of freedom?

Nope, so $E(t,i) = E(t) + E(i)$

$$\Rightarrow \quad q(V,T) = \sum_{\substack{\text{translations}\\ t}} e^{-\beta E(t)} \sum_{\substack{\text{internal}\\ \text{states } i}} e^{-\beta E(i)}$$

$$= q_{\text{translations}}(V,T) * q_{\text{internal}}(T)$$

vibrations
rotations

$N > 1$ particles:

$$Q(N,V,T) = \sum_{\nu} e^{-\beta E(\nu)}$$

$$= \underbrace{\left(\sum_{\substack{\text{particle} \\ \text{1's } \nu}} e^{-\beta E_1(\nu)} \right)}_{q} \underbrace{\left(\sum_{\substack{\text{particle} \\ \text{2's } \nu}} e^{-\beta E_2(\nu)} \right)}_{q} \cdots$$

$= q^N$? Careful Indistinguishability?

Shockingly, this can be easier to think abaut in a quantum mechanical setting.

1. $\sum_{\substack{\text{particle} \\ \text{1's } \nu}}$ is discretized – good for counting

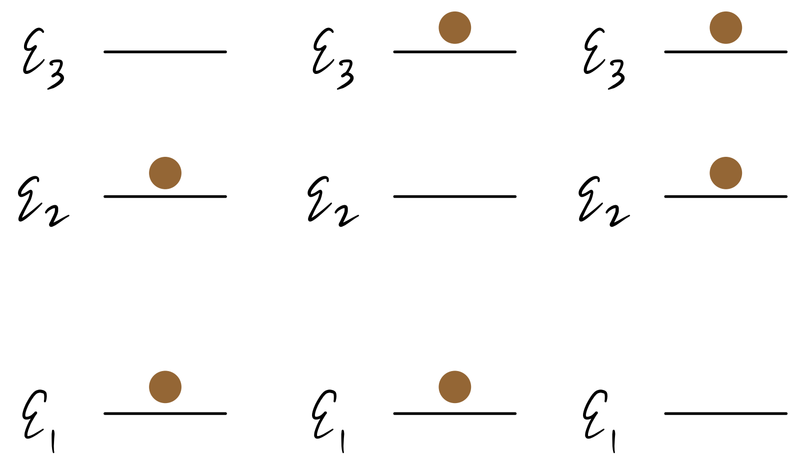
2. QM tells us about indistinguishability

$$\psi(\vec{r}_1, \vec{r}_2) = \pm \psi(\vec{r}_2, \vec{r}_1)$$

Boson Fermion

2 particles, 3 single-particle states

"Fermi-Dirac"

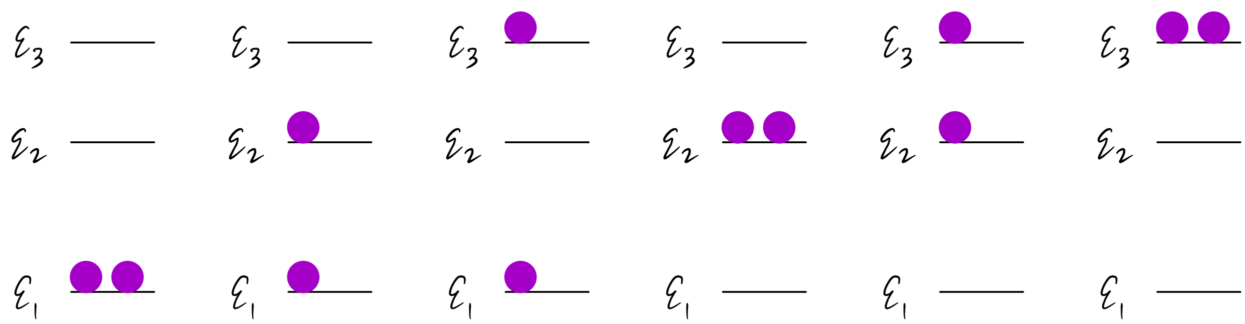


$$Q_{FD} = e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} + e^{-\beta(\varepsilon_2+\varepsilon_3)}$$

m states, 2 Fermions ... $\binom{m}{2} = \dfrac{m!}{2!\,(m-2)!}$

$$= \frac{m^2-m}{2} \text{ terms}$$

"Bose-Einstein"



$$Q_{BE} = e^{-\beta(\varepsilon_1 + \varepsilon_2)} + e^{-\beta(\varepsilon_1 + \varepsilon_3)} + e^{-\beta(\varepsilon_2 + \varepsilon_3)}$$
$$+ e^{-2\beta\varepsilon_1} + e^{-2\beta\varepsilon_2} + e^{-2\beta\varepsilon_3}$$

m states, 2 Bosons... How many extra? m more than FD.

$\frac{m^2+m}{2}$ terms

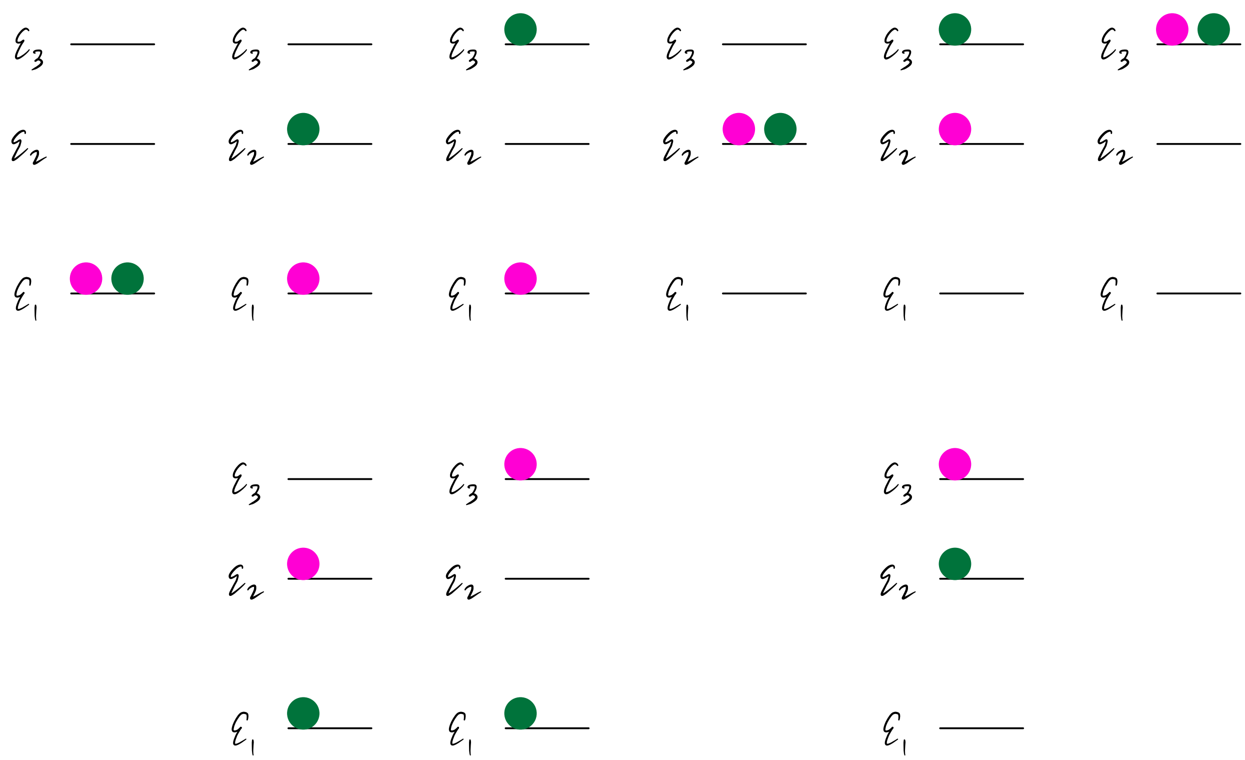
"Maxwell-Boltzmann" – Classical Limit

Suppose $k_BT \gg \varepsilon$ (quantized energies smeared out)

\# of states $\rightarrow$ $m \gg 1$

$$\Rightarrow \quad Q_{FD} = Q_{BE} = \#\text{ of terms} \approx \frac{m^2}{2}$$

First treat ● and ● as if they are distinguishable



$$Q = \left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_3}\right)^2$$

m states, 2 classical particles ... m^2 terms

Second, divide by $N!$ to avoid overcounting.

$$\Rightarrow \quad Q(N,V,T) = \frac{1}{N!}\left(q_{\text{translations}}\, q_{\text{internal}}\right)^N$$

How do q_{internal} and $q_{\text{translations}}$ depend on N?
on V?
on T?

Let's start with $q_{\text{internal}} = \sum_{\nu} e^{-\beta E(\nu)}$

Summing over quantum numbers that define bond stretches, electronic excited states, etc.

$\beta \Rightarrow T$ dependence (details depend on bonding), but

No N dependence. No V dependence.

$$q_{\text{translations}} = \sum_{\substack{\text{regions}\\ \text{of space}}} e^{-\beta E(\text{spatial region})}$$

Due to translational symmetry, E does not depend on the location in space.

$q_{\text{translations}} = 1 * \left(\begin{smallmatrix}\text{how many} \\ \text{regions of space}\end{smallmatrix}\right) \propto V$

It turns out this proportionality has to do with quantum mechanics — a Planck cell.

$$q_{\text{translations}} = \frac{V}{\lambda^3}, \text{ where } \lambda = \left(\frac{h}{\sqrt{2\pi m k_B T}}\right)$$

de Broglie wavelength

$$Q(N,V,T) = \frac{1}{N!}\left(q_{\text{translations}}\, q_{\text{internal}}\right)^N$$

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

Recall,

$$-\beta A = \ln Q(N,V,T) = N \ln q - \ln N!$$

$$\approx N \ln \frac{V}{\lambda(T)^3} + N \ln q_{\text{int}}(T) - N \ln N + N$$

$$= -(N \ln N - N) + N \ln \frac{V\, q_{\text{int}}(T)}{\lambda(T)^3}$$

By taking partial derivatives of $\ln Q$, we re-derive the properties of an ideal gas...

Recall $A = E - TS$

$$\Rightarrow dA = -SdT - pdV + \mu dN$$

First, differentiate with respect to V

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = -p \quad \Rightarrow \left(\frac{\partial(-\beta A)}{\partial V}\right)_{T,N} = \beta p$$

$$\Rightarrow \beta p = \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = \frac{N}{V} \quad \Rightarrow \boxed{\beta p = \rho}$$

Ideal gas law

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = -\langle E\rangle = N\frac{\partial}{\partial\beta}\ln\left(\frac{q_{int}(T)}{\lambda(T)^3}\right)$$

$$= N * \text{function of } T$$

$$\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} = -\beta\mu = -(\ln N + 1 - 1) + \ln\frac{V\, q_{int}(T)}{\lambda(T)^3}$$

$$= \ln\frac{V\, q_{int}(T)}{N\lambda(T)^3}$$

$$\Rightarrow \quad \beta\mu = \ln\frac{N\lambda(T)^3}{V\, q_{int}(T)}$$

Plugging in $\frac{N}{V} = \beta p$ (Ideal gas law)...

$$\beta\mu = \ln\frac{\beta p\lambda(T)^3}{q_{int}(T)} = \ln\frac{p}{p_0} + \ln p_0 + \ln\frac{\beta\lambda(T)^3}{q_{int}(T)}$$

$$= \ln\frac{p}{p_0} + \ln\frac{p_0\beta\lambda(T)^3}{q_{int}(T)}$$

$\mu^{(0)}(T)$ defines a standard state at pressure p_0.

Notice that the <u>essential</u> feature leading to these ideal forms was the factorization of the partition function into a product of single-particle partition functions. Fluctuations in particle 1's state are <u>decorrelated</u> from fluctuations in particle 2's state.

Decorrelated fluctuations are the essence of ideal systems (ideal gases, ideal solutions, etc.)