

Lecture 14

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?

$N=1$

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

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

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

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

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

↑
vibrations
rotations

$N > 1$ particles:

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

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

$$= g^N \quad ? \quad \text{Careful Indistinguishability?}$$

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

1. $\sum_{\substack{\text{particle} \\ 1's \ \nu}}$ is discretized — good for counting
2. QM tells us about indistinguishability

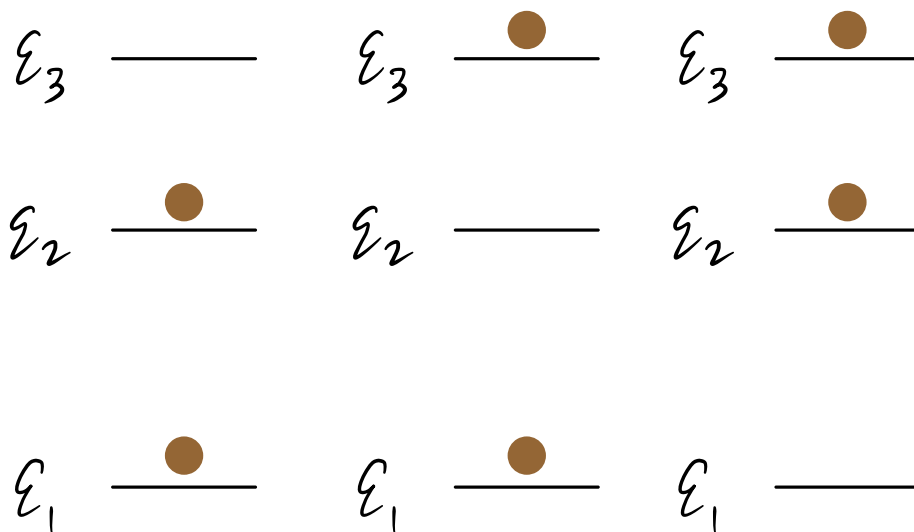
$$\Psi(\vec{r}_1, \vec{r}_2) = \pm \Psi(\vec{r}_2, \vec{r}_1)$$

Boson

Fermion

2 particles, 3 single-particle states

"Fermi-Dirac"

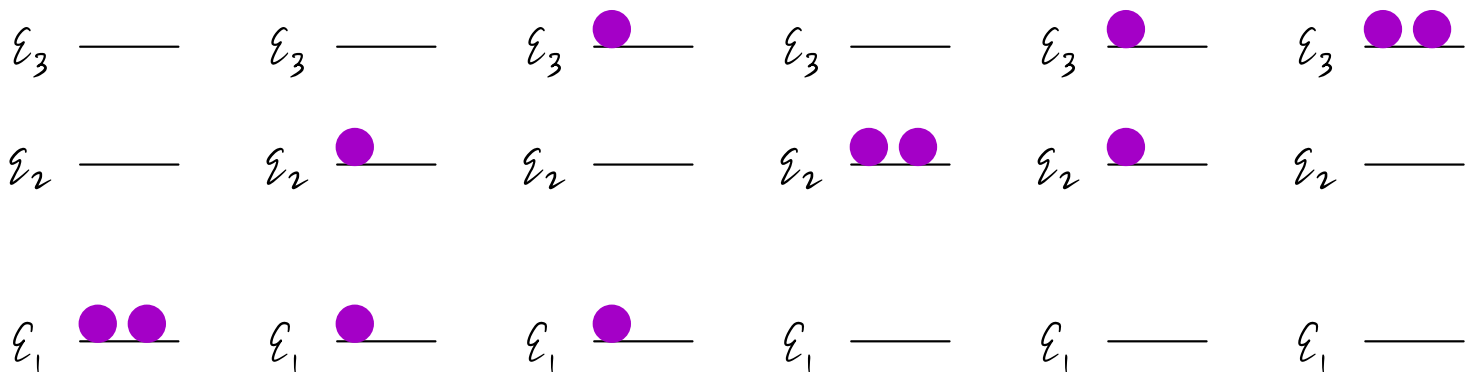


$$Q_{FD} = e^{-\beta(\epsilon_1 + \epsilon_2)} + e^{-\beta(\epsilon_1 + \epsilon_3)} + e^{-\beta(\epsilon_2 + \epsilon_3)}$$

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

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

"Bose-Einstein"



$$Q_{BE} = e^{-\beta(\epsilon_1 + \epsilon_2)} + e^{-\beta(\epsilon_1 + \epsilon_3)} + e^{-\beta(\epsilon_2 + \epsilon_3)} \\ + e^{-2\beta\epsilon_1} + e^{-2\beta\epsilon_2} + e^{-2\beta\epsilon_3}$$

m states, 2 Bosons... How many extra? m more than FD.
 $\frac{m^2 + m}{2}$ terms

"Maxwell-Boltzmann" - Classical Limit

Suppose $k_B T \gg \epsilon$ (quantized energies smeared out)
 # of states $\rightarrow m \gg 1$

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

First treat ● and ● as if they are distinguishable



$$Q = (e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3})^2$$

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

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

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

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

Let's start with $g_{\text{internal}} = \sum_v e^{-\beta E(v)}$

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.

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

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

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

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

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

de Broglie
wavelength

$$\begin{aligned} Q(N, V, T) &= \frac{1}{N!} (g_{\text{translations}} g_{\text{internal}})^N \\ &= \frac{1}{N!} \left(\frac{V}{\lambda(T)^3} g_{\text{int}}(T) \right)^N \end{aligned}$$

Recall,

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

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

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

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

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

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

$\uparrow$
Ideal gas law

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

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

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

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

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

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

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

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

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

Notice that the essential 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 decorrelated from fluctuations in particle 2's state.

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