

## 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  $\mu$  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?

$$\underline{N=1}$$

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

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

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

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

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

↑  
vibrations  
rotations

$N > 1$  particles:

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

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

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

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

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

2. QM tells us about indistinguishability

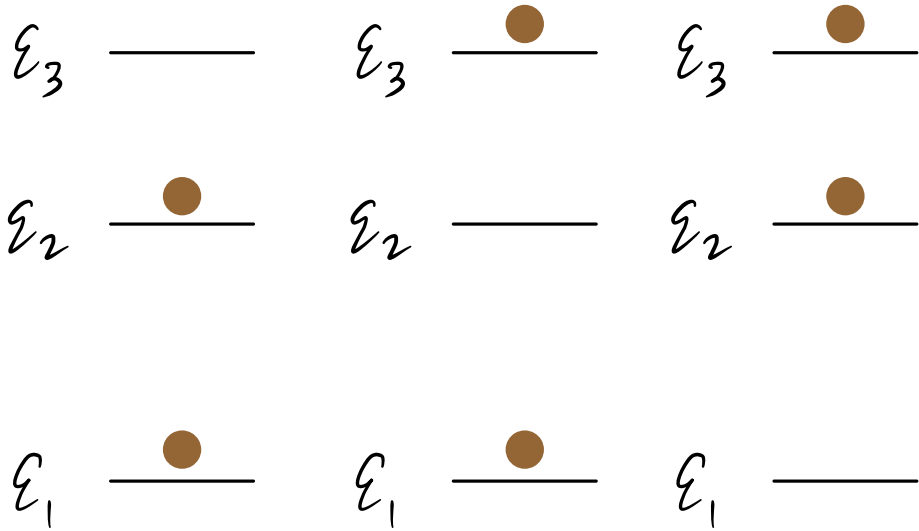
$$\Psi(\vec{r}_1, \vec{r}_2) = \pm \Psi(\vec{r}_2, \vec{r}_1)$$

Boson

Fermion

2 particles, 3 single-particle states

"Fermi-Dirac"

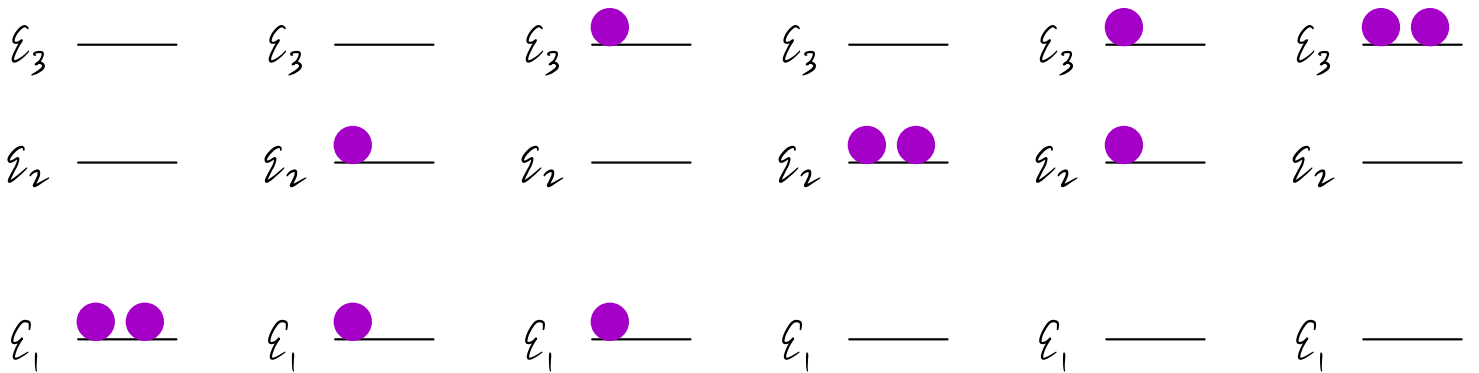


$$Q_{FD} = e^{-\beta(\epsilon_1 + \epsilon_2)} + e^{-\beta(\epsilon_1 + \epsilon_3)} + e^{-\beta(\epsilon_2 + \epsilon_3)}$$

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

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

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.

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

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

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

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

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

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  $V$

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

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

↑  
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.)