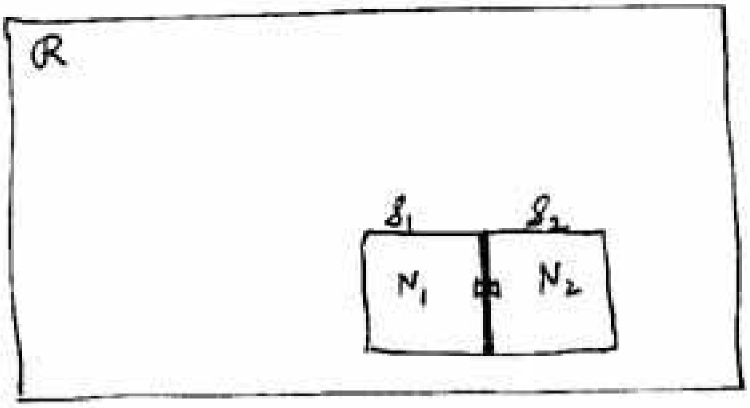
CHEMICAL POTENTIAL

Today we switch to get another ensemble - the grand canonical.

Put another way, we're going to consider 2 systems in equilibrium with a reservoir and allow them to exchange BOTH energy AND particles!



S_1 & S_2 Exchange energy via | thermal contact

and particles via the valve ⋈

* We can think of the combined systems S_1 & S_2 as like our old friend S from the R-S system!

▷ What was the principle we used there, at constant temperature τ and volume V? We had that the Helmholtz free energy F was minimized.

$\Rightarrow$ $F = U - \tau\sigma$ is minimized for $S_1 + S_2$ for fixed $N = N_1 + N_2$.

For constant volume,
what's the analog of maximizing the degeneracy/entropy?

We can treat $S_1 + S_2$
just like our friend of recent times
the system at constant N and V
- because $N = N_1 + N_2 =$ constant
even though N_1 & N_2 can change

* We minimized the Helmholtz Free Energy F
while allowing N_1 & N_2 to vary subject to $N_1 + N_2 = N$

$$dF = 0$$
$$= d(F_1 + F_2)$$

$$= \left(\frac{\partial F_1}{\partial N_1}\right)_{V_1,\tau} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{V_2,\tau} dN_2$$

But $dN_1 = -dN_2$ so

$$dF = 0 \Rightarrow \left(\frac{\partial F_1}{\partial N_1}\right)_{V_1,\tau} = \left(\frac{\partial F_2}{\partial N_2}\right)_{V_2,\tau}$$

$$\Rightarrow \boxed{\mu(\tau, V, N) \equiv \left(\frac{\partial F}{\partial N}\right)_{V,\tau}}$$ CHEMICAL POTENTIAL

μ's are equal for systems in equilibrium.

Just like for temperature,
if $\mu_1 > \mu_2$ then particles will follow the gradient and will carry N and U to the other system.

* Equilibrium conditions are therefore

$$\boxed{\tau_1 = \tau_2 \quad \text{AND} \quad \mu_1 = \mu_2}$$

The name for the thermodynamic ensemble of relevance here is the GRAND CANONICAL ensemble.

* Notice that we are slightly cheating when we pretend that N is a continuous variable.
As with any other statistical approximation when the # of particles is large, however, this is a VERY Good Approx when N is large.

* Each system's μ is computed by varying ITS F w.r.t. ITS N., holding all other variables fixed.

Example for say 3 gases in a box, with 3 different N_i's,
these systems each have a μ_i:

$$\mu_i = \left(\frac{\partial F_i}{\partial N_i}\right)_{N_{j\neq i},\, V,\, \tau \ldots}$$

what IS the chemical potential physically?

* We had a good sense for the temperature τ because we have been since we were little.

But what is μ?

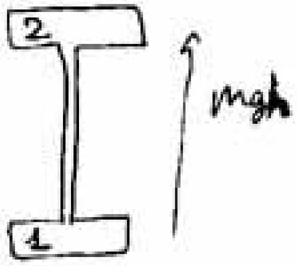
* The following thought experiment helps a lot.

Suppose that $\mathcal{S}_1$ and $\mathcal{S}_2$ have different μ's initially

e.g. $\mu_{2i} > \mu_{1i}$, or $\mu_{2i} = \mu_{1i} + \underbrace{(\mu_2 - \mu_1)_i}_{\Delta\mu > 0}$

Then miagine
taking N_1 particles from 1 to 2,

e.g.



In this case there is real potential energy differing between the states, or what KK call an "energy step" Here, the step is $N_1 mgh$

The Helmholtz free energy F is given by $F = U - \tau\sigma$ and so if we change the particles height then $\Delta F = \Delta N_1 mg\, h$

If we arrange for $\left\{ \begin{array}{c} \Delta\mu = mgh \\ \text{precisely} \end{array} \right\}$, then $\mu_{1\text{final}} = \mu_{1i} + \Delta\mu = \mu_2$

So the difference in chemical potential between two systems really acts just like a step increase in potential energy.

In particular, you need extra "oomph" to go *up* the potential gradient.

(⇒ the normal behaviour is to follow the μ gradient *down*)

E.g. also electrons at ⊕ versus ⊖ terminals of a battery.

We, like KK, will make a distinction between a truly external effect like mgh and an internal origin for μ.

After all, $\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau, V, \ldots}$

and often F does depend on N without any "external interference" ☺

* Consider our friend the Ideal Gas.

We had for N particles $Z_N = \frac{Z_1^N}{N!}$ where the partition fn for 1 particle was $Z_1 = n_Q(\tau) V = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}} V$

Using our other old friend Stirling

$$\log N! \approx N \log N - N$$

we had

$$F = -\tau \left[N \log Z_1 - N \log N + N \right]$$

so

$$\left(\frac{\partial F}{\partial N}\right)_{\tau, V} = -\tau \log Z_1 + \tau \frac{\partial}{\partial N}\left(N \log N - N\right)$$

$$= -\tau \log Z_1 + \tau \left\{ N \cdot \frac{1}{N} + \log N - 1 \right\}$$

$$= -\tau \log Z_1 + \tau \log N$$

$$= \tau \log\left(\frac{N}{Z_1}\right)$$

ie. $\mu = \tau \log\left(\frac{N}{V n_Q(\tau)}\right)$ with $n_Q(\tau) = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$

or $\boxed{\mu = \tau \log\left(\frac{n}{n_Q(\tau)}\right)}$

This is the intrinsic chemical potential for an ideal gas.

* If we were now to add the external chemical potential coming from the gravity "oomph" effect

$$\boxed{\mu = \mu_{int} + \mu_{ext}}$$

we'll get $\mu(h) = \tau \log\left(\frac{n(h)}{n_Q(\tau)}\right) + Mgh$

* In equilibrium,

μ should not depend on h

-if it did, particles would move around to "make it so"!

-think of the air as lots of little pancake systems on top of each other...

$$\Rightarrow \quad Mgh + \tau \log\left(\frac{n(h)}{n_Q(\tau, M)}\right) = \text{constant}$$

Let $n(h) = n_0$ at $h=0$. Then $(\text{constant}) = \tau \log\left(\frac{n_0}{n_Q(\tau)}\right)$

and so

$$\exp\left(\frac{Mgh}{\tau}\right) \cdot \frac{n(h)}{n_Q} = \frac{n_0}{n_Q}$$

i.e. $\boxed{n(h) = n_0 e^{-Mgh/\tau}}$

* This assumes that τ is constant as you go up which is definitely NOT a good approx. for the real atmosphere. But this situation can be realized under contolled lab conditions.

* Note: different concentrations (densities of particles) at different heights - so the pressures must also be different!

The ideal gas law we derived said that $pV = N\tau$ so

$$p = n\tau$$

and so

$$p(h) = p(0)\, e^{-Mgh/\tau}$$

The quantity $\left(\frac{Mg}{\tau}\right)^{-1}$ is called the scale height; it's the height at which p and n die off by $\frac{1}{e}$.

* Note that scale height $H \equiv \frac{\tau}{Mg}$ scales inversely with M – lighter particles extend further up than heavy ones.

* Also, $H \propto \frac{1}{g}$ so weaker gravity is also resulting in particles going further up.

This (plus external forces from stuff like solar wind) is why the Moon no longer has an atmosphere if it ever had one...

// I like to think of this ↑
as a metaphor for why small countries
like NZ can't "hang onto their people" ☺
= "brain drain" – we're OUT THERE though 😀

Recall last time we

considered 2 systems

able to exchange both energy and particles

$$N_1 + N_2 = N \quad \text{constant}$$

→ definition of chemical potential

$$\boxed{\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau, V, \ldots}}$$

We also learned that $\mu = \underset{\uparrow}{\mu_{int} + \mu_{ext}}$

potential energy arising from external things like gravity or EM fields

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Now we'll derive a few more things about μ some of which we'll need in the next few lectures.

① μ and σ

Let's look at σ, the entropy. We will study this because to find the Gibbs factor, the equivalent of the Boltzmann factor for systems which exchange U and N, we'll need it... and the things that vary are U and N ⇒ Let's look at $\sigma(U, N)$

Let's consider entropy as a fn of $\left\langle \begin{array}{l} U \\ N \end{array}\right.$

$$\sigma(U,N)_{\tau,V}$$

i.e. $\sigma = \sigma(U,N)$ and τ, V constant.

Then

$$d\sigma = \left(\frac{\partial\sigma}{\partial U}\right)_{N,\tau,N} dU + \left(\frac{\partial\sigma}{\partial N}\right)_{U,\tau,V} dN$$

$$\Rightarrow \left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V} = \left(\frac{\partial\sigma}{\partial U}\right)_{N,\tau,V} \left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \left(\frac{\partial\sigma}{\partial N}\right)_{U,\tau,V}$$

$$= \frac{1}{\tau}\left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \left(\frac{\partial\sigma}{\partial N}\right)_{U,\tau,V}$$

↖ This is NOT the same as $\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V}$ - because U is <u>also</u> held fixed here!

Now consider $\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$

But

$F = U - \tau\sigma$

So at constant τ, V

$$\left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} - \tau\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V}$$

So

$$\boxed{\mu = -\tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,\tau,V}}$$

Now for a full variation of $\sigma(U,V,N)$

$$d\sigma = \left(\frac{\partial\sigma}{\partial U}\right)_{V,N} dU + \left(\frac{\partial\sigma}{\partial V}\right)_{U,N} dV + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} dN$$

Using $\mu = -\tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,\tau,V}$

and $\left(\frac{\partial\sigma}{\partial U}\right)_{V,N} = \frac{1}{\tau}$

and another relation from earlier in the course

$$p = \tau\left(\frac{\partial\sigma}{\partial V}\right)_{U,N}$$

we have

$$d\sigma = \frac{dU}{\tau} + p\,dV - \frac{\mu dN}{\tau}$$

$$\Rightarrow \boxed{dU = \tau d\sigma - p dV + \mu dN}$$

$$\underbrace{\tau d\sigma}_{\text{"heat"}} \qquad \underbrace{- p dV + \mu dN}_{\text{"work"}}$$

KK call this the thermodynamic identity

(I call it the 1st law!) ☺