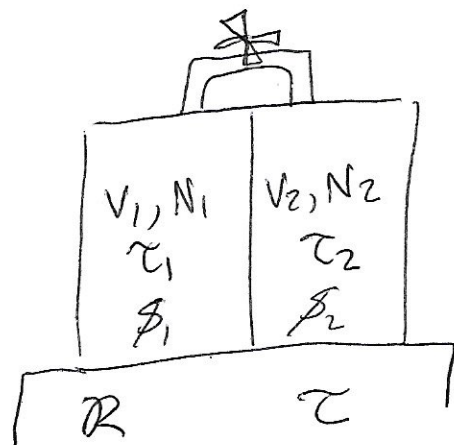


# Ch. 5: Chemical Potential and Gibbs Distribution

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(81)

We considered before two systems in thermal contact



Initially,  $\tau_1$  and  $\tau_2$  could be different, but in thermal contact energy can flow, so they become equal and the temperature achieved maximizes the entropy of the combined system.

$U = U_1 + U_2$ . If  $\tau_1 > \tau_2$ , heat flows from  $\beta_1$  to  $\beta_2$

Now, add the option of also exchanging particles, called diffusive contact

$N = N_1 + N_2$ . ~~the~~ ~~the~~  $\star$  In what situation would particles move from  $\beta_1$  to  $\beta_2$ ?

The Helmholtz free energy is always minimized,

$$F = F_1 + F_2 = U_1 + U_2 - \tau (\sigma_1 + \sigma_2) \quad \text{KK Eq. 5.1}$$

$$dF = 0$$

$\swarrow$   $dN$  is possible if  $N$  is large

$$\text{If } N \text{ can change, } \left( \frac{\partial F_1}{\partial N_1} \right) dN_1 + \left( \frac{\partial F_2}{\partial N_2} \right) dN_2 = 0 \quad \text{KK Eq. 5.2}$$

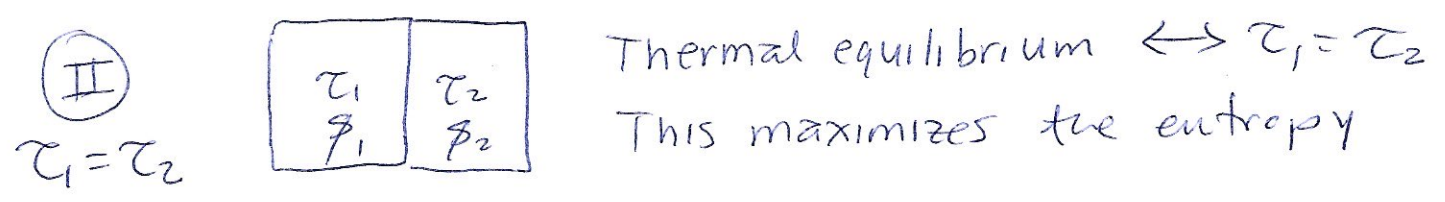
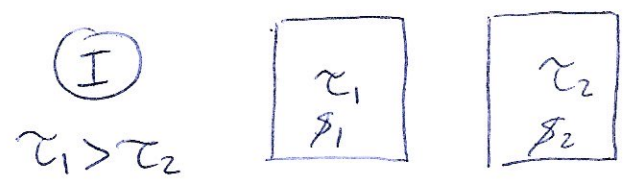
$$\text{Because } N = N_1 + N_2, \quad dN = dN_1 + dN_2 \Rightarrow dN_1 = -dN_2$$

$$\left( \frac{\partial F_1}{\partial N_1} \right) dN_1 - \left( \frac{\partial F_1}{\partial N_2} \right) dN_1 = 0 \quad \text{KK Eq. 5.3}$$

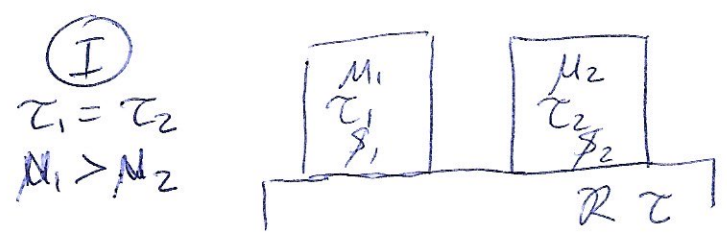
$\left(\frac{\partial F_1}{\partial N_1}\right) = \left(\frac{\partial F_2}{\partial N_2}\right)$  *compare to temp.*  
KK Eq. 5.4

The definition of chemical potential is  $\mu(\tau, V, N) \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau, V}$  *KK Eq. 5.5*  
In diffusive equilibrium,  $\boxed{\mu_1 = \mu_2}$  *KK Eq. 5.6*

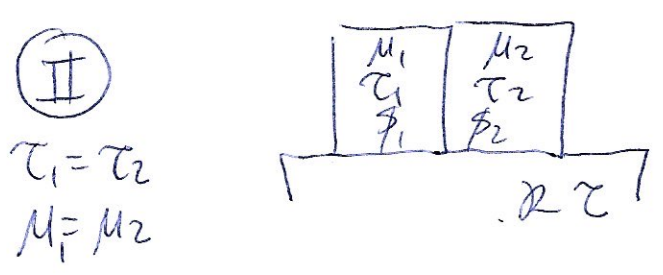
The temperature regulates the energy transfer



The chemical potential regulates the particle transfer



(particles move from higher to lower chemical potential)



Diffusive equilibrium  $\leftrightarrow \mu_1 = \mu_2$   
This minimizes the free energy

"The chemical potential is fully as important as temperature"  
*Makes you think about temperature in a somewhat different way.*  
KK pg. 120

Recall that the free energy of the ideal gas is

KK 3.70  $F = -\tau \ln Z = -\tau \ln Z_1^N + \tau \ln N!$

$$F = -\tau [N \ln Z_1 - \ln N!] \quad \text{KK Eq. 5.8}$$

Partition fn. of 1-particle ideal gas  $Z_1 = n_Q V = \left(\frac{M\tau}{2\pi\hbar}\right)^{3/2} V \quad \text{KK Eq. 5.9}$

So the chemical potential of the ideal gas is

$$\begin{aligned} \mu = \left(\frac{\partial F}{\partial N}\right)_{\tau, V} &= \frac{\partial}{\partial N} \left\{ -\tau [N \ln Z_1 - \ln N!] \right\} \\ &= -\tau \left[ \ln Z_1 - \frac{d}{dN} \ln N! \right] \quad \text{KK Eq. 5.10} \end{aligned}$$

if  $N$  is large, then we can take the derivative. Remember KK A12b

Stirling's approximation  $\ln N! = \frac{1}{2} \ln(2\pi) + \left(N + \frac{1}{2}\right) \ln N - N$  the better one

$$\frac{d}{dN} \left[ \cancel{\ln \sqrt{2\pi}} + \left(N + \frac{1}{2}\right) \ln N - N \right] = \frac{d}{dN} \left[ N \ln N + \frac{1}{2} \ln N - N \right]$$

$$N \frac{d}{dN} \ln N + \frac{dN}{dN} + \frac{1}{2} \frac{d}{dN} \ln N + \cancel{\ln(1/2)} - \frac{dN}{dN}$$

$$N \left( \frac{1}{N} + \ln N + \frac{1}{2N} \right) - 1$$

KK Eq. 5.11

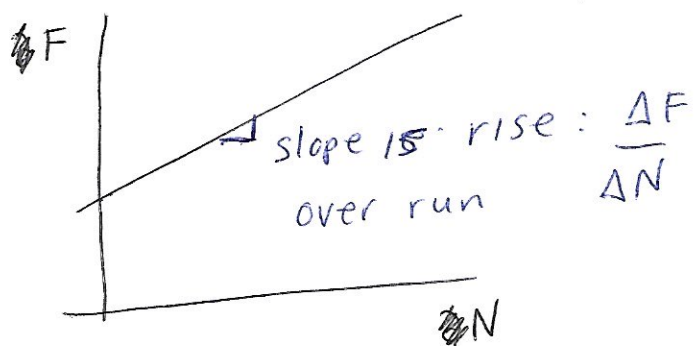
$$\frac{d}{dN} \ln N! = \ln N + \frac{1}{2N} \quad \text{since } N \text{ is large, } \frac{d}{dN} \ln N! \approx \ln N$$



$$\text{So } \mu = -\tau \left[ \ln z_1 - \ln N \right] = -\tau \ln \left( \frac{z_1}{N} \right) \quad (84)$$

$$\mu = \ln \left( \frac{N}{z_1} \right) = \ln \left( \frac{N}{n_Q V} \right) = \boxed{\ln \left( \frac{n}{n_Q} \right)} \quad \text{KK Eq. 5.12}$$

Another way, perhaps more elegant, is to notice that  $\mu \partial N = \partial F$ .  $\mu$  is the proportionality constant between the rate of change of the free energy and the number of particles: how does the free energy change when you add or remove a particle.



Let  $\Delta N = 1$ , then

$$\mu = F(N) - F(N-1)$$

$$\begin{aligned} \mu &= -\tau \left[ N \ln z_1 - \ln N! \right] + \tau \left[ (N-1) \ln z_1 - \ln (N-1)! \right] \\ &= -\tau \left[ \cancel{N \ln z_1} - \ln N! + \cancel{N \ln z_1} + \ln z_1 + \ln (N-1)! \right] \\ &= -\tau \left[ \ln z_1 - \ln N \right] = -\tau \ln \left( \frac{z_1}{N} \right) = \tau \ln \left( \frac{N}{z_1} \right) \end{aligned}$$

Again,  $\boxed{\mu = \tau \ln \left( \frac{n}{n_Q} \right)}$  for an ideal gas

Remember that  $PV = Nk_B T = N\tau$  KK Eq. 3.73 (85)

$$P = \frac{N\tau}{V} = n\tau \Rightarrow n = P/\tau$$

$$\mu = \tau \ln(P/\tau n_Q) \quad \text{KK Eq. 12b}$$

$$\mu = \tau \ln(n/n_Q) \quad \text{KK Eq. 12a}$$

This is a very interesting equation: particles move from high chemical potential to low chemical potential, so they will move from high pressure/high concentration to low pressure/concentration, e.g., they will fill space!

You can predict this by thinking about Newtonian mechanics. If you have a high density part and a low density part, collisions will be more likely in the high density part and particles will bounce preferentially towards low density areas. The equations above were derived just by "counting," but reproduces Newtonian expectations.

Notice that the units of  $\mu$  are energy. The chemical potential is very much a real potential and it can interact with other potentials. Magnetic, gravitational, electric, etc.

$$\mu = \mu_{tot} = \mu_{ext} + \mu_{int} \quad \text{inherent to the gas}$$

$\uparrow$  external potential, e.g., gravitational       $\uparrow$  internal chemical potential

$$\mu_1 = \mu_{1,ext} + \mu_{1,int} \quad \mu_2 = \mu_{2,ext} + \mu_{2,int}$$

In diffusive equilibrium,  $\mu_1 = \mu_2 \Rightarrow \mu_2 - \mu_1 = 0$

$$\mu_{2,ext} - \mu_{1,ext} + \mu_{2,int} - \mu_{1,int} = \Delta\mu_{ext} + \Delta\mu_{int} = 0$$

$$\Delta\mu_{ext} = -\Delta\mu_{int} \quad \text{KK Eq. 5.16}$$

$\uparrow$  there is an interplay between the chemical potential and the external potential.

Consider two layers of the atmosphere, one at height  $h$  and another one on the ground, the two layers are in diffusive and thermal equilibrium  $\mu_1 = \mu_2$ ,  $\tau_1 = \tau_2$

$$\mu_1 = \mu_2 \Rightarrow \Delta\mu_{ext} = -\Delta\mu_{int}$$

$\uparrow$   
 gravitational potential  
 $\approx Mgh$

where  $M$  is the particle mass  
and  $g$  is acceleration due to gravity

dependent variable  
concentration is a function of the height

$$Mgh - Mg(0) = -\left\{ \tau \ln \left[ \frac{n(h)}{n_0} \right] - \tau \ln \left[ \frac{n(0)}{n_0} \right] \right\}$$

$$-\frac{Mgh}{\tau} = \ln n(h) - \ln n_0 - \ln(0) + \ln n_0$$



$$-\frac{Mgh}{\tau} = \ln \left[ \frac{n(h)}{n(0)} \right] \Rightarrow \exp \left[ -\frac{Mgh}{\tau} \right] = \frac{n(h)}{n(0)} \quad (87)$$

$$n(h) = n(0) \exp \left[ -Mgh/\tau \right] \quad \leftarrow \begin{array}{l} \text{Boltzmann distribution} \\ \text{KK Eq. 5.18} \end{array} \quad \text{cool!}$$

Notice that  $n(h)$  is the concentration at arbitrary height

$$p(h) = p(0) \exp \left[ -Mgh/\tau \right]$$

Let the characteristic height  $h_c = \tau/Mg$ , then

$$p(h) = p(0) \exp \left[ -h/h_c \right]$$

$$\text{At } h_c, \quad p(h) = p(0) e^{-1} \Rightarrow \frac{p(h)}{p(0)} = e^{-1} = 0.37$$

concentration/density decreases to 37% at  $h_c$

so atmosphere closer to the ground if the particles are massive or the acceleration due to gravity is large

(remember  $g = G \frac{M_{\text{planet}}}{(r_{\text{planet}} + h)^2}$ ), farther away if high temp.

This, along with magnetic fields and solar wind, explains the composition and densities of atmospheres in mercury, venus, earth, mars.