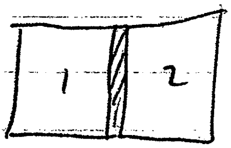
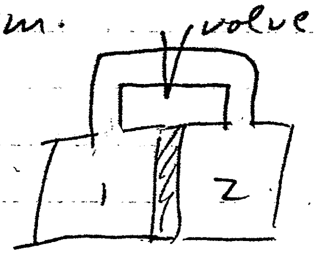
5. Chemical Potential and Gibbs Distribution

Read: chapter 5

("chemical" potential concept very useful in discussing e.g. how chemical reaction rates depend on concentrations, etc. But concept is much more general, and not particularly "chemical" "potential" – in sense of potential energy.)



Recall: concept of temperature is useful if we consider two systems brought into thermal contact – allowed to exchange energy. Then combined system seeks most probable configuration, and so energy (heat) flows from hot system to cold system.



Now generalize this idea. Suppose 1, 2 are already in thermal equilibrium

① τ, V_1, N_1

② τ, V_2, N_2

Now bring ① and ② into *diffusive* contact – open a valve so that they are connected by a permeable membrane. Now particles can flow from ① to ②, so

N_1 and N_2 can change, but with $N = N_1 + N_2$ held fixed (conservation of total number of particles). So combined system will seek most probable configuration by dividing N between ① and ② in optimal way (and fluctuations $\delta N_1/N_1$, $\delta N_2/N_2$ are small for a large value of N)

chemical potential governs flow of particles as *temperature* governs flow of heat. In diffusive equilibrium, $\mu_1 = \mu_2$. When the valve opens, particles flow from higher chem. potential to lower chem. potential.

Recall that a system in thermal contact with reservoir (temperature τ) seeks most probable configuration by minimizing

$$F = U - \tau \sigma$$

(Minimizing F determines optimal way of dividing available energy between system and reservoir)

Combined system

$$F = F_1(\tau, V_1, N_1) + F_2(\tau, V_2, N_2)$$

Most probable configuration minimizes total F

$$dF = 0 = \left(\frac{\partial F_1}{\partial N_1}\right)_{\tau, V_1} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau, V_2} dN_2$$

and $dN_2 = -dN_1 \Rightarrow$

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

in diffusive equilibrium. So we define chemical potential

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

and condition for diffusive equilibrium is

$$\boxed{\mu_1 = \mu_2}$$

If $\mu_1 \neq \mu_2$ and valve is opened, particles will flow. Which way?

$$dF = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_1 - \mu_2) dN_1$$

So, to lower F, flow is from higher to lower chem. potential

<u>Example</u>: <u>Ideal Gas</u> (in classical regime)

Recall (chapter 3)

$$e^{-F/\tau} = Z_N = \frac{1}{N!}(Z_1)^N \quad \text{where } Z_1 = n_Q V, \text{ and}$$

$$n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$$

= quantum concentration"

Chemical potential is cost in free energy of adding one more particle. (N is really discrete, but can be treated as continuous for $N \gg 1$.)

So $F = -\tau \ln Z_N = -\tau(N \log Z_1 - \log N!)$

$$\mu(\tau,V,N) = F(\tau,V,N) - F(\tau,V,N-1)$$

$$= -\tau\left[\log Z_1 - \log\frac{N!}{(N-1)!}\right] = \tau \log(N/Z_1)$$

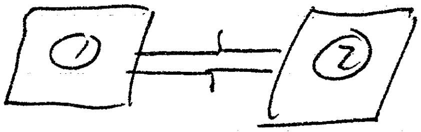
and $Z_1 = n_Q V \Longrightarrow \boxed{\mu = \tau \log(n/n_Q)}$

We may also use ideal gas law (chapter 3)

$$pV = N\tau \quad \text{or} \quad p = n\tau$$

$$\Rightarrow \boxed{\mu = \tau \log(p/\tau n_Q)}$$

So μ increases as n or p increase at fixed τ. That makes sense. Ideal gas will flow from high to low concentration (or pressure)



For $n < n_Q$, $\mu < 0$. This means energy cost of adding a particle is more than compensated by entropy gain

For $n > n_Q$, $\mu > 0$. This means that energy cost is more important

Caution: this formula is not correct for a high density gas!

Thermodynamic Identity

We define μ by $\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$, $F = F(\tau,V,N)$

We can also relate μ directly to entropy $\sigma(U,V,N)$

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

Thus

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

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

But $F = U - \tau\sigma$

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

Thus — $\boxed{\left(\frac{\partial \sigma}{\partial N}\right)_{U,V} = -\mu/\tau}$ (an alternative def. of μ)

Now we have

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV - \mu/\tau \, dN$$

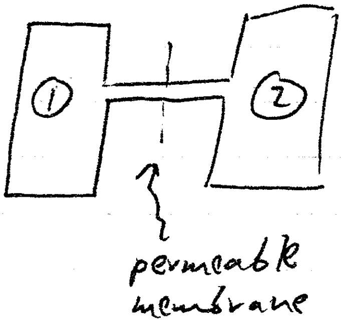
or $\boxed{dU = \tau d\sigma - p dV + \mu dN}$

"Thermodynamic identity" satisfied by $U(\sigma, V, N)$

i.e. $\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$ is yet another expression for μ

Internal and External Chemical Potential

(This distinction is the key to most applications of chemical potential.)

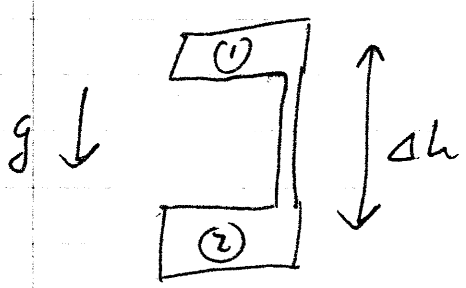


Recall that
$$d(F_1+F_2) = (\mu_1-\mu_2)\,dN_1$$
(with $\tau_1=\tau_2$, V_1, V_2 fixed)

So $\mu_1-\mu_2$ gives the cost in free energy of taking one particle from ① and putting it in ②

Thus $\mu_1=\mu_2$ in diffusive equilibrium.

We will want to consider situation in which "external" conditions on ① and ② are different



E.g. at different heights in earth's gravitational field

Ideal gases will then be at <u>unequal</u> pressure and density

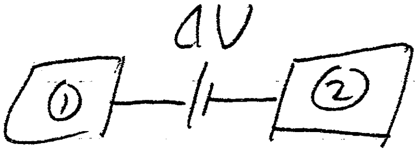
we have $U = \underset{\text{grav. pot. energy}}{U_{ext}} + \underset{\text{kinetic energy}}{U_{int}}$

$F = U - \tau\sigma$

$$\Rightarrow \mu_1-\mu_2 = \Delta\mu_{total} = \Delta\mu_{int} + \overset{mg\,\Delta h}{\Delta\mu_{ext}}$$

More generally μ_{ext} = pot. energy cost due to ext. influence
μ_{int} = free energy cost in absence of ext influence

Another example:



electron gases in two metals, maintained at pot. difference ΔV by a battery $\Rightarrow$

$$\mu_{ext} = e\,\Delta V$$

(electron charge)

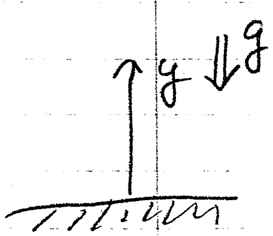
So $\Delta\mu_{total} = 0 \Rightarrow \boxed{\Delta\mu_{int} = -\Delta\mu_{ext}}$

- in thermal and diffusive equilibrium.

Isothermal Model of Atmosphere

Suppose atmosphere is an ideal gas (good approx) with τ independent of height (not so good)

[How hard to breathe at top of Mt. Everest?]



$$\mu = \mu_{ideal} + mgy$$

$$= \underbrace{\tau \log(n/n_Q)}_{(internal)} + \underbrace{mgy}_{(external)}$$

Diffusive equilibrium $\Rightarrow \mu = y$-independent

or $\frac{d\mu}{dy} = 0$ determines $n(y)$

or just solve
$\mu = \mu_0 = $ constant
$\tau \log(n/n_Q) = -mgy + $ const

$$= \tau/n \frac{dn}{dy} + mg \Rightarrow \frac{dn}{n} = \frac{-mg}{\tau} dy$$

(Heavier atoms fall off faster, lighter ones slower)

$$\Rightarrow \boxed{n(y) = n(0)\, e^{-(mg/\tau)y}}$$

This $e^{-mgy/\tau}$ behavior is easy to anticipate, just the Boltzmann factor when we compare states for a single atom.

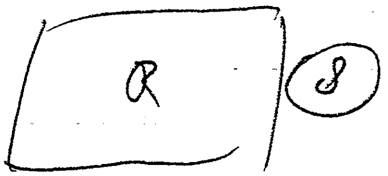
$$\frac{mg}{\tau}y = \left(\frac{300°K}{T}\right)\left(\frac{y}{1Km}\right)\frac{1}{8.0}$$

MT everest 8700 m)

Fall off by $\frac{1}{e}$ at 8 K

Gibbs factor and Gibbs sum

Recall:



For small system in thermal contact with large reservoir

Boltzman factor $P(\epsilon) \propto e^{-\epsilon/\tau}$

gives probability of occupancy of given microscopic state of S.

Now: generalize to system in thermal and diffusive contact with reservoir. Same logic as before

$$\frac{P(N_1,\epsilon_1)}{P(N_2,\epsilon_2)} = \frac{g_R(N_0-N_1,\ U_0-\epsilon_1)}{g_R(N_0-N_2,\ U_0-\epsilon_2)}$$

Here g is multiplicity of R, N_0, U_0 total number, energy shared by S and R

$$= \exp\left[\sigma_R(N_0-N_1,\ U_0-\epsilon_1) - \sigma_R(N_0-N_2,\ U_0-\epsilon_2)\right]$$

$$\cong \exp\left[-(N_1-N_2)\left(\frac{\partial\sigma}{\partial N}\right)_U - (\epsilon_1-\epsilon_2)\left(\frac{\partial\sigma}{\partial U}\right)_N\right]$$

Here σ is entropy of reservoir. We expand log g because μ, τ of reservoir are equal to those of system in thermal and diffusive equilibrium, and can be taken to be constant for a sufficiently large reservoir.

$$= \frac{\exp\left[(N_1\mu-\epsilon_1)/\tau\right]}{\exp\left[(N_2\mu-\epsilon_2)/\tau\right]}$$

Gibbs factor

We normalize this distribution by dividing by the Gibbs sum of the system

$$\mathcal{Z} = \sum_{\text{states } s} \exp[(N_s\mu - \epsilon_s)/\tau]$$

and $P(N,\epsilon) = \frac{1}{\mathcal{Z}} \exp(N\mu - \epsilon)/\tau$

Then $\sum_s P(s) = 1$

and expectation values are $\langle X\rangle = \sum_s X(s)P(s)$

E.g. $\langle N\rangle = \frac{1}{\mathcal{Z}} \sum N e^{(N\mu-\epsilon)/\tau} = \tau/_{\mathcal{Z}}\left(\frac{\partial}{\partial\mu}\mathcal{Z}\right)_\tau$

$$= \tau\left(\frac{\partial}{\partial\mu}\ln\mathcal{Z}\right)_\tau$$

(Analogous to $U = \tau^2 \frac{\partial}{\partial\tau}\log Z$ — indeed

$$U = \langle\epsilon\rangle = \tau^2\left(\frac{\partial}{\partial\tau}\log\mathcal{Z}\right)_\mu \quad)$$

— we may adjust μ to get desired N. If $\mathcal{S}$ is large — fluctuations in N will be small

<u>Example:</u> <u>Impurity in a semiconductor</u>

When we put impurity atom in semiconductor, will it want to ionize — giving up electron to conduction "band" of semiconductor

This is not mere energetics controlled by ionization potential I — for whether atom wants to ionize depends on how many electrons are <u>already</u> in conduction band

(5.10)

May think of impurity atom as a (small) system in equilibrium (thermal and diffusive) with large reservoir. (Can exchange energy and electrons with semiconductor)

States of atom:

ionized	$\epsilon = 0$	$N = 0$
neutral, ↑	$\epsilon = -I$	$N = 1$
neutral, ↓	$\epsilon = -I$	$N = 1$

Gibbs sum:

$$\mathcal{Z} = 1 + 2e^{(\mu+I)/\tau}$$

Gibbs factor!

$$P_{\text{ionized}} = P(N=0, \epsilon=0) = \frac{1}{\mathcal{Z}} = \frac{1}{1 + 2\exp[(\mu+I)/\tau]}$$

Limits: $\tau \to \infty \Rightarrow P_{\text{ion}} = \frac{1}{3}$
(all 3 states equally likely)

$\tau \to 0 \Rightarrow P_{\text{ion}} = 0$
(no ionization) (if $\mu + I > 0$)

chemical potential μ characterizes availability of conduction electrons

μ large + positive: many electrons already in band
$P_{\text{ion}} \to 0$

μ large and negative: no electrons
$P_{\text{ion}} \to 1$ (many places for electron to go.)

e.g.
Further idealization: conduction band is an ideal gas, with

$$\mu = \tau \log(n/n_Q) \qquad e^{\mu/\tau} = \frac{n}{n_Q}$$

Then
$$P_{ion} = \frac{1}{1 + 2\,\frac{n}{n_Q}\,e^{I/\tau}}$$

$$n \to 0 \Rightarrow P_{ion} = 1$$

$$n/n_Q \to \infty \Rightarrow P_{ion} = 0$$ (Caution: not the right formula at high density)

In practice, semiconductors have $n/n_Q \ll 1$, and impurities tend to ionize
("doped semiconductor" - e.g. P in Si)