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. $T_1$, $V_1$, $N_1$
2. $T_2$, $V_2$, $N_2$

Now bring 1 and 2 into different 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 optimum way (and fluctuations $\delta N_1/N_1$, $\delta N_2/N_2$ are small for a large value of $N$).

\[ \frac{\text{chemical potential}}{\text{temperature}} \text{ governs flow of particles as temperature governs flow of heat.} \]

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 $T$) seeks most probable configuration by minimizing

\[ F = U - TS \] (Minimizing $F$ determines optimal way of dividing available energy between system and reservoir)

\[ F = F_1(T, V, N_1) + F_2(T, V, N_2) \]

Most probable configuration minimizes total $F$

\[ dF = 0 = \left( \frac{\partial F_1}{\partial N_1} \right) \delta V dN_1 + \left( \frac{\partial F_2}{\partial N_2} \right) \delta V dN_2 \]
and \( \Delta N_2 = - \Delta N_1 \implies \frac{\partial F_i}{\partial N_i} |_{\xi, V_1} = - \frac{\partial F_i}{\partial N_2} |_{\xi, V_2} \)

in diffusive equilibrium. We define the chemical potential

\[
\mu = \left( \frac{\partial F}{\partial N} \right)_{\xi, V}
\]

and the condition for diffusive equilibrium is

\[
\mu_1 = \mu_2
\]

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 chemical potential.

**Example:** Ideal Gas (in classical regime)

Recall (chapter 3)

\[
e^{-\frac{F}{kT}} = Z_N = \frac{1}{N!} (Z_1)^N \quad \text{where} \quad Z_1 = n_0 V, \quad \text{and} \quad n_0 = \left( \frac{m_0 e^2}{2 \pi \hbar^2} \right)
\]

Chemical potential is cost in free energy of adding one more particle. \( N \) is really discrete, but can be treated as continuous for \( N \gg 1 \).
\[ F = -T \ln Z_N = -T(N \log Z_i - \log N!) \]

\[ \mu(T,V,N) = F(T,V,N) - F(T,V,N-1) \]

\[ = -T \left[ \log Z_i - \log \frac{N!}{(N-1)!} \right] = T \log \left( \frac{N}{Z_i} \right) \]

and \[ Z_i = N Q V \Rightarrow \mu = T \log \left( \frac{N}{Q N} \right) \]

We may also use ideal gas law (Chapter 3)

\[ pV = N \kappa \quad \text{or} \quad p = \frac{N \kappa}{V} \]

\[ \Rightarrow \mu = T \log \left( \frac{p}{\kappa N} \right) \]

So \( \mu \) increases as \( n \) or \( p \) increase at fixed \( T \). This makes sense.

Ideal gases will flow from high to low concentration (or pressure).

For \( n < Q \), \( \mu > 0 \). This means energy cost of adding a particle is more than compensated by entropy gain.

For \( n > Q \), \( \mu < 0 \). This means energy cost is more important.

**Thermodynamic Identity**

We define \( \mu \) by \( \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} \), \( F = F(T,V,N) \).

We can also relate \( \mu \) directly to entropy \( S(U,V,N) \).
\[ d\delta = (\frac{\partial \delta}{\partial U})_{V,N} dU + (\frac{\partial \delta}{\partial V})_{U,N} dV + (\frac{\partial \delta}{\partial N})_{U,V} dN \]

Thus:
\[ (\frac{\partial \delta}{\partial N})_{U,V} = (\frac{\partial \delta}{\partial U})_{U,N} (\frac{\partial U}{\partial N})_{U,V} + (\frac{\partial \delta}{\partial N})_{U,V} \]

\[ \Rightarrow (\frac{\partial \delta}{\partial N})_{U,V} = (\frac{\partial \delta}{\partial N})_{U,V} - \frac{1}{\tau} (\frac{\partial U}{\partial N})_{U,V} \]

But \( F = U - \tau E \)

\[ \Rightarrow (\frac{\partial F}{\partial N})_{U,V} = (\frac{\partial U}{\partial N})_{U,V} - \tau (\frac{\partial \delta}{\partial N})_{U,V} = -\tau (\frac{\partial \delta}{\partial N})_{U,V} \]

Thus:
\[ (\frac{\partial \delta}{\partial N})_{U,V} = -\frac{\mu}{\tau} \]

(an alternative def. of \( \mu \))

Now we have:
\[ d\delta = \frac{1}{\tau} dU + \frac{p}{\tau} dV - \frac{\mu}{\tau} dN \]

or:
\[ dU = \tau d\delta - p dV + \mu dN \]

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

i.e. \( \mu = (\frac{\partial U}{\partial N})_{U,V} \) is yet another expansion for \( \mu \)
Internal and External Chemical Potential

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

Recall that
\[ \text{d}(F_1 + F_2) = (\mu_1 - \mu_2) \text{d}N \]
(with \( T_1 = T_2, V_1, V_2 \) fixed)

so \( \mu_1 - \mu_2 \) gives the cost in free energy of taking a particle from 1 and putting it in 2.

Thus \( \mu_1 = \mu_2 \) in defensive equilibrium.

We will want to consider situations 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 unequal pressure and density.

We have
\[ U = U_{\text{ext}} + U_{\text{int}} \]
\[ \text{grad. pot. energy} \quad \text{kinetic energy} \]

\[ F = U - T S \]
\[ \Rightarrow \mu_1 - \mu_2 = \Delta \mu_{\text{total}} = \Delta \mu_{\text{int}} + \Delta \mu_{\text{ext}} \]

More generally, \( \mu_{\text{ext}} = \text{pot. energy cost due to ext. influence} \)
\( \mu_{\text{int}} = \text{free energy cost in absence of ext. influence} \)
Another example:

Electron gases in two metals, maintained at potential difference $\Delta V$ by battery $\Rightarrow$ Next $= \frac{\Delta V}{e}$ (electron charge)

So $\Delta n_{total} = 0 \Rightarrow \Delta n_{int} = -\Delta n_{next}$

Isothermal Model of Atmosphere

Suppose atmosphere as an ideal gas (good approx.) with $T$ independent of height $\neq$ (not so good)

The pressure is $p = n \frac{m}{V} \Rightarrow \frac{p}{T} = \text{constant}

Diffusion equilibrium $\Rightarrow n = y$ independent of $y$

On $\frac{dn}{dy} = 0$ determines $n(y)$

$\frac{1}{T} \frac{dn}{dy} + mg = \frac{dn}{dy} = -\frac{mg}{T} dy$

(Heavier atoms fall faster, lighter ones slower)

This $e^{-mg/y/T}$ behavior is easy to anticipate.

For the Boltzmann factor when we compare states for a single atom, $\frac{m_g}{g} = \frac{m_g}{g} \left(\frac{3k_B T}{2m_g}\right)^{1/2}$ which gives $\frac{m_g}{g} \approx 3700 \text{ m/s}$
**Gibbs factor and Gibbs sum**

Recall: \[ R \]

**Boltzmann factor** \[ P(\varepsilon) \propto e^{-\varepsilon/kT} \]

gives probability of occupancy of given microscopic state \( s \).

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

\[
P(N_1, \varepsilon_1) = \frac{g_R(N_0 - N_1, \varepsilon_0 - \varepsilon_1)}{g_R(N_0 - N_2, \varepsilon_0 - \varepsilon_2)}
\]

Here \( g \) is multiplicity of \( R \), \( N_0, \varepsilon_0 \) total number, energy shared by \( I \) and \( R \)

\[
= \exp \left[ \beta_R(N_0 - N_1, \varepsilon_0 - \varepsilon_1) - \beta_R(N_0 - N_2, \varepsilon_0 - \varepsilon_2) \right]
\]

\[
= \exp \left[ -(N_1 - N_2) \left( \frac{\partial \varepsilon}{\partial N} \right)_U - (\varepsilon_1 - \varepsilon_2) \left( \frac{\partial \varepsilon}{\partial \varepsilon} \right)_N \right]
\]

Here \( \varepsilon \) is energy of reservoir. We expand log \( g \) because \( \mu, T \) 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.

\[
\exp \left[ (N_1 \mu - \varepsilon_1)/\tau \right] \frac{\text{Gibbs factor}}{\text{Gibbs factor}}
\]
We normalize this distribution by dividing by the Gibbs sum of the system

\[ Z = \sum_{\text{states}} \exp\left(\frac{N\mu - e_i}{\beta}\right) \]

and

\[ P(N,e) = \frac{1}{Z} \exp\left(\frac{N\mu - e}{\beta}\right) \]

Then

\[ \sum_{\text{states}} P(\text{is}) = 1 \]

and expectation values are

\[ \langle X \rangle = \sum_{\text{states}} X(\text{is}) P(\text{is}) \]

\[ \langle N \rangle = \frac{1}{Z} \sum_{\text{states}} N(e)(\frac{\mu - e}{\beta}) = \frac{1}{2} \frac{(e - \mu)}{\beta} \]

\[ = \frac{1}{2} (\beta \mu \ln \beta) \]

(Analogous to \( U = -\frac{e^2}{2\varepsilon} \log Z \) — indeed

\[ U = \langle e \rangle = -\frac{1}{2\varepsilon} \log \beta \mu \)

— we may adjust \( \mu \) to get desired \( N \). If \( \beta \)

so large — fluctuations in \( N \) will be small.

\[ \text{Example: Impurity in a semiconductor} \]

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

This is not mere energetic controlled by ionization potential \( I \). For whether atom wants to ionize depends on how many electrons are already in conduction band.
May think of impurity atom as a (small) system in equilibrium (thermal and diffusive) with large reservoir (exchange energy and electrons with semiconductor).

States of atom:
- ionized: \( \varepsilon = 0 \) \( N = 0 \)
- neutral, \( + \) : \( \varepsilon = I \) \( N = 1 \)
- neutral, \( - \) : \( \varepsilon = -I \) \( N = 1 \)

Gibbs sum:
\[
\beta = 2 + 2e^{(\mu + I)/\tau}
\]

Gibbs factor:
\[
P_{\text{ionized}} = P(N = 0, \varepsilon = 0) = \frac{1}{\beta} = \frac{1}{2 + 2e^{(\mu + I)/\tau}}
\]

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) \( (\text{if } \mu + I > 0) \)

Chemical potential \( \mu \) characterizes availability of conduction electrons:
- \( \mu \) large and positive: many electrons already in band \( P_{\text{ion}} \to 0 \)
- \( \mu \) large and negative: no electrons \( P_{\text{ion}} \to 1 \) (many places for electron to go.)
Further idealization: conduction band is an ideal gas, with
\[ \mu = 2 \log \left( \frac{n}{n_0} \right) \quad e^{\mu/\tau} = \frac{n}{n_0} \]

Then
\[ P_{\text{im}} = \frac{n}{1 + 2 \frac{n}{n_0} e^{\mu/\tau}} \]

\[ n \to 0 \Rightarrow P_{\text{im}} = 1 \]
\[ \frac{n}{n_0} \to \infty \Rightarrow P_{\text{im}} = 0 \quad \text{(continuum limit)} \]

In practice, semiconductors have \( n/n_0 \ll 1 \), and impurities tend to ionize ("doped semiconductor", e.g. Li in Si).