Some notes to supplement Chapter 5 of the text

Recapitulation key points about the **chemical potential**. The chemical potential is the Gibbs free energy per particle or the Helmholtz free energy required to add a particle at constant temperature and volume. The difference in chemical potential is equal to a potential energy barrier that will bring the two systems to diffusive equilibrium.

As the book emphasizes it is often useful to think of the total chemical potential as being made up of two parts, external and internal. The external is the potential energy of the particle in an external field such as that of a mass in a gravitational field or of charge in an electric potential. The internal part is thermal in origin.

Therefore, \( \mu_{\text{tot}} = \mu_{\text{int}} + \mu_{\text{ext}} \) and this is Equation (15) on page 124.

Worth noting that the chemical potential of an ideal gas at temperature \( T \) and with density \( n = \frac{N}{V} \) is \( \mu = k_B T \ln \left( \frac{n}{n_Q} \right) \) where \( n_Q \) is the quantum concentration defined on page 73 of the text.

Please study the examples (1) electric potential for charged particles Example in Figure 5.3 and my discussion of two dissimilar metals (2) particles in a gravitational field (3) particles with magnetic moments in a mobile magnetic field (pp 127-129) and (4) particles in a rotating frame with a centrifugal potential (Problem 1 and see below) (5) read example on page 251 in Chapter 8.

4.1 In the rotating frame of reference there is an extra term in the potential energy \( U_{\text{eff}} = -\frac{1}{2}M\omega^2r^2 \) which gives rise to \( -\vec{\nabla}U_{\text{eff}} = \hat{r}M\omega^2r \) the centrifugal force. Thus the total chemical potential (following Kittel and Kroemer) of an ideal gas with number density \( n(r) \) at a distance \( r \) from the axis of rotation is

\[
\mu = k_B T \ln \left( \frac{n(r)}{n_Q} \right) - \frac{1}{2}M\omega^2r^2
\]

where the quantum concentration \( n_Q = \left( \frac{2\pi mk_BT}{\hbar^2} \right)^{3/2} \). Note that the chemical potential at position \( r \) is the ideal gas chemical potential corresponding to the density at \( r \) plus the external potential, in this case the centrifugal potential energy. In equilibrium there should be no gradient in the chemical potential and we have \( \mu(r) \) is independent of \( r \). Therefore, using \( \mu(r) = \mu(0) \) we obtain

\[
\mu(r) = k_B T \ln \left( \frac{n(r)}{n_Q} \right) - \frac{1}{2}M\omega^2r^2 = \mu(0) = k_B T \ln \left( \frac{n(0)}{n_Q} \right)
\]
Simplifying, we obtain
\[ \ln \left( \frac{n(r)}{n(0)} \right) = \frac{\beta M \omega^2}{2} r^2. \]  
(3)
Thus \[ n(r) = n(0) e^{\frac{M \omega^2 r^2}{2k_BT}}. \]

Centrifuges are an effective way of separating isotopes; if the difference in the masses of two isotopes is \( \Delta M = M_1 - M_2 > 0 \), the relative ratios of the heavy to light densities increases as \( r \) increases as \( e^{\Delta M \omega^2 r^2/2} \). This is one of the preferred methods of separating \( ^{235}\text{U} \) and \( ^{238}\text{U} \). The former is needed for fission while the latter is much more abundant (> 99%) in naturally occurring uranium ore. Uranium is converted into uranium hexafluoride \( UF_6 \) and cascades of gas centrifuges are used to enrich uranium ore, i.e., increase the \( ^{235}\text{U} \) concentration to around 3 to 5%. A gas diffusion process was used in the Manhattan project. The key difficulty is that the centrifuges have speeds 1–2 times the speed of sound (more than 100,000 RPM, I believe) and so the challenge lies in manufacturing centrifuges that are light and yet strong so that they do not fracture (Can you estimate the speed at which ordinary metal will fracture?) and even designing high-speed bearings. A German material scientist G. Zippe worked in the Soviet Union (where he was taken as a prisoner) and developed this method.

Useful results derived in class; the isothermal compressibility defined by \( \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,V} \) can be written in terms of \( v \equiv V/N \) and its inverse the number density \( n \equiv N/V \). We have
\[ \kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = \frac{1}{n} \left( \frac{\partial n}{\partial p} \right)_T. \]
Using one of these expressions eases the algebra. For example, write the ideal gas equation of state as \( p = nk_BT \) and find \( \kappa_T = \frac{1}{nk_BT} \). Check the units quickly.

**Neater derivation of the expression for the compressibility:** We start from the Gibbs-Duhem relation derived in the earlier notes on the web
\[ d\mu = -S \, dT + V \, dp \]
we divide by \( N \) and write it in the intensive form
\[ d\mu = -s \, dT + \frac{1}{n} \, dp \]  
(6)

\(^1\)Easy but useful algebra: since \( v = 1/n \) we have \( \ln n = - \ln v \) and thus
\[ -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right) = - \left( \frac{\partial (\ln v)}{\partial p} \right) = \left( \frac{\partial (\ln n)}{\partial p} \right) = \frac{1}{n} \left( \frac{\partial n}{\partial p} \right). \]
(4)
where \( s \equiv S/N \) is the entropy per particle. Note that this means that \( \mu \) is a function of \( T \) and \( p \) only. Divide the above equation by \( dn \) with \( dT = 0 \) and obtain

\[
\frac{n}{T} \left( \frac{\partial \mu}{\partial n} \right)_T = \left( \frac{\partial p}{\partial n} \right)_T.
\] (7)

This is interesting and gives one more view of the chemical potential: at fixed temperature its variation with density is related to the variation of pressure with density. Since \( \kappa_T = \frac{1}{n} \left( \frac{\partial n}{\partial p} \right)_T \) (See above) and Equation (7) we have the important relation

\[
\kappa_T = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_T.
\] (8)

This is useful in quantum many body theory and in thinking about the compressibility of electron fluids. The chemical potential can be controlled by applying a voltage.

We start from the definition of the grand potential

\[
\mathcal{Z} = \sum_{N} e^{N\beta \mu} Z_N(T, V)
\] (9)

where \( Z_N \) is the canonical partition function of the system with \( N \) particles. (It is convenient to write \( Z(T, V, N) \) as \( Z_N(T, V) \) since it can be abbreviated as \( Z_N \) when only the dependence on \( N \) is important.) The probability of finding the system in a state with \( N \) particles is

\[
P(N) = \frac{e^{\beta \mu N} Z_N(T, V)}{\mathcal{Z}}.
\] (10)

For completeness check that

\[
k_B T \frac{\partial \mathcal{Z}}{\partial \mu} = \sum_{N} N e^{N\beta \mu} Z_N(T, V)
\] (11)

\[
(k_B T)^2 \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \sum_{N} N^2 e^{N\beta \mu} Z_N(T, V)
\] (12)

These derivatives are evaluated at constant \( V \) and \( T \). Are you sure?

Thus we have (this is the standard way such identities are obtained and you have seen this before) dividing Equation (11) by \( \mathcal{Z} \)

\[
\langle N \rangle = \sum_{N} P(N) N = \frac{1}{\mathcal{Z}} k_B T \frac{\partial \mathcal{Z}}{\partial \mu} = k_B T \frac{\partial}{\partial \mu} \log \mathcal{Z}.
\] (13)

Taking another derivative with respect to \( \beta \mu \) of the above equation we have

\[
k_B T \frac{\partial}{\partial \mu} \langle N \rangle = (k_B T)^2 \frac{\partial}{\partial \mu} \left[ \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right] = (k_B T)^2 \left[ \frac{1}{\mathcal{Z}} \left( \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right) - \left( \frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right].
\] (14)
Using Equations (11) and (12) and the expression for $P(N)$ we identify the right-hand side as $\langle N^2 \rangle - \langle N \rangle^2$. We evaluate the variance\footnote{It is worth remembering that}

$$\sigma_N^2 = \langle (\Delta N)^2 \rangle = k_B T \frac{\partial}{\partial \mu} \langle N \rangle = V (k_B T) \frac{\partial}{\partial \mu} n$$

(16)

We look up the expression for the compressibility (Equation (8) and deduce

$$\langle (\Delta N)^2 \rangle = (k_B T) V n^2 \kappa T.$$  

(17)

Thus we obtain the

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle^2} = \frac{k_B T \kappa T}{V};$$ therefore, $\frac{\sigma_N}{\langle N \rangle} \propto \frac{1}{\sqrt{V}} \propto \frac{1}{\sqrt{N}}$. For large $N$ the variance is small compared to the mean value.

It is worth recalling that

$$\langle (\Delta E)^2 \rangle = k_B T^2 C_V$$

(18)

and comparing with Equation(17). The heat capacity, the response to temperature changes, is related to energy fluctuations; the compressibility is the response to changes in $V$ at fixed $N$ or changes in $N$ at fixed $V$ and is related to number fluctuations in the grand canonical ensemble. Later we will see that the magnetic susceptibility, the response to changes in the magnetic field, is related to magnetization fluctuations.

\footnote{Please expand the squared term and check the above result. One usually denotes $N - \langle N \rangle$ the deviation or fluctuation of the random variable $N$ from its mean value by $\Delta N$.}
For doing problems it is worth noting the following:

- If there are two parts to a system between which particles can be exchanged, say particles can either be in a vapor or be adsorbed on a solid surface then in equilibrium \( \mu \) or \( \lambda \equiv e^{\beta \mu} \) should be the same in the two parts.

- For calculations
  \[
  \mathcal{Z} = \lambda^0 Z_0 + \lambda^1 Z_1 + \lambda^2 Z_2 + \cdots
  \]
  and for most problems in this chapter we will deal with small numbers of particles. \( Z_k \) is the partition function of \( k \) particles, to wit, the sum of \( e^{-\beta \epsilon} \) over all energy levels of the \( k \)-particle system. You already know how to evaluate \( Z_k \) the canonical partition function and so \( \mathcal{Z} \) is not hard to evaluate.

- The probability that the number of particles is 1 is \( \lambda Z_1 \) and similarly for two particles, etc.

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Myoglobin is an oxygen-binding protein found in the muscle tissue of vertebrates in general and in almost all mammals. It is related to hemoglobin, which is the iron- and oxygen-binding protein in blood, specifically in the red blood cells. Myoglobin (abbreviated Mb) is the primary oxygen-carrying pigment of muscle tissues.

Myoglobin can bind one and only one oxygen molecule with a binding energy (this is of the order of \( 7 k_B T \) from experiment. I believe) \( \epsilon \equiv -\Delta \). Its grand partition function is

\[
\mathcal{Z} = 1 + \lambda e^{-\beta \epsilon}
\]

where we have used \( Z_0 = 1 \) and \( Z_1 = e^{-\beta \epsilon} \).

In equilibrium the chemical potential of the adsorbed or bound oxygen must equal the surrounding oxygen molecules in the medium. Using an ideal gas approximation for the suspended oxygen and the result that \( \lambda_{\text{ideal}} = \frac{n}{n_Q} = \frac{p}{k_B T n_Q} \) we have

\[
f = \frac{Z_1}{\mathcal{Z}} = \frac{\lambda e^{-\beta \epsilon}}{1 + \lambda e^{-\beta \epsilon}} = \frac{1}{1 + \frac{n_Q k_B T}{p} e^{\beta \epsilon}} = \frac{p}{p + p_0}
\]

where we have defined a pressure \( p_0 = k_B T n_Q e^{-\beta \Delta} \). See Figure 5.11 for experimental confirmation. These curves are called Langmuir isotherms and \( p_0 \) is the pressure at which the fraction equals 1/2.

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Oxygen binding at the four heme sites in hemoglobin occur cooperatively. Note that adsorption curve for hemoglobin in Figure 5.12 is different and this is due to interaction effects.
between the oxygen in the four subunits, referred to as cooperativity

Look at the curve in Figure 5.12. It is a switching curve that is characteristic of cooperative interactions. Typically drawn at \( T = 37^\circ C \) and a pH value of around 7.2. The oxygen saturation curve is the number of \( O_2 \) molecules bound divided by 4 times the number of Hemoglobin molecules. Argue that this curve implies that hemoglobin absorbs oxygen where the partial pressure of oxygen is highest as in the lungs and release it when it is the lowest as in muscles. In muscles the partial pressure of oxygen is of the order of 40 mm \( Hg \) (residual oxygen pressure in venous blood) and at this pressure the oxygenated fraction around 75%. This is somewhat surprising but it means that blood retains a large oxygen reserve that can be released in the case of increased demand as with muscular activity. Pretty clever!

Mutations in hemoglobin can cause sickle cell anemia and other diseases. Favorable mutations can decrease \( p_0 \) so that at high altitude creatures such as wild geese and some deer mice have greater ability to have a larger oxygen absorption at low pressures.

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**Adsorption problem:** A surface containing \( N_s \) adsorption sites is in equilibrium with a monatomic ideal gas. Atoms adsorbed on the surface have an energy \(-\Delta\) and no kinetic energy. Each adsorption site can accommodate at most one atom. Calculate the fraction of occupied adsorption sites as a function of the gas density \( n \), the temperature \( T \), and the binding energy \( \Delta \).

**Solution:** The grand partition function of the adsorbing surface is a product of the grand partition function for each of the sites since we will assume that they are non-interacting:

\[
\mathcal{Z}_1 = 1 + e^{\beta(\mu+\Delta)} \Rightarrow \mathcal{Z} = \left(1 + e^{\beta(\mu+\Delta)}\right)^{N_s}.
\]

(22)

Explain clearly why there is no delabelling factor \( 1/N! \). The fraction of occupied sites is given by

\[
\frac{\langle N \rangle}{N_s} = -\frac{1}{N_s} k_B T \left( \frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_T = \frac{e^{\beta \mu}}{(e^{\beta \mu} + e^{-\beta \Delta})}.
\]

(23)

Note that \( N_s \) cancels out so we could have worked with a single site as we did for myoglobin.

What \( \mu \) should we use? Since the adsorbed atoms are in equilibrium with respect to exchange with the atoms in the vapor we set \( \mu = \mu_{\text{ideal}} \).

\[
\text{Use } e^{\beta \mu_{\text{ideal}}} = \frac{n}{nQ}.
\]

Therefore, we have \( f = \frac{n}{n + nQ e^{-\beta \Delta}} \). Write \( nQ e^{-\beta \Delta} \) as \( n_0 \) and we find the Langmuir adsorption isotherm \( f = \frac{n}{n + n_0} \); one has different curves for different temperatures.
We assumed that the atom at an adsorption site has only one state. We could include spin and have two or more states. The atom could vibrate thus necessitating evaluation of an oscillator partition function.

The following was discussed in the lecture:

Consider two dissimilar metal plates connected by a wire both at fixed $T$ (in contact with a thermal reservoir) and $V$. Electrons (free in a metal) flow from one to the other (constraint $N_A$ and $N_B$ are fixed is removed) until when? Let $N_e$ electrons flow from $A$ to $B$. Minimize the appropriate (total) free energy (state your assumptions) with respect to $N_e$; do not forget to include the capacitive energy since the plates are charged. Expand the free energy of the two metals in powers of $N_e$ retaining the lowest non-trivial order term in $N_e$ before you minimize. Express the condition for equilibrium in terms of the voltage difference and the chemical potentials. See if it corresponds to the statement “The total chemical potential of the electrons (internal or intrinsic plus the external potentials) are equal.” Please pay attention to signs including that of the electron charge.