

Chapter 5. Chemical potential and Gibbs distribution

1 Chemical potential

So far we have only considered systems in contact that are allowed to exchange “heat”, *i.e.* systems in thermal contact with one another. In this chapter we consider systems that can also exchange particles with one another, *i.e.* systems that are in *diffusive* contact.

Consider 2 systems $\mathcal{S}_1$ and $\mathcal{S}_2$ that are in diffusive contact with one another and in thermal contact with a 3rd system, a reservoir at temperature τ . We have shown that the Helmholtz free energy for the combined system $\mathcal{S}_1 + \mathcal{S}_2$ will be a minimum when it is in equilibrium with the reservoir. We must therefore minimise

$$F = F_1 + F_2$$

with respect to the distribution of the particles between $\mathcal{S}_1$ and $\mathcal{S}_2$ to find the equilibrium state of this combined system. The total number of particles in the system is fixed, so that

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

in equilibrium, *i.e.*

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

The quantity

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

is known as the *chemical potential*, so that our equilibrium condition is that

$$\mu_1 = \mu_2.$$

Inspecting the expression for dF , we see that when $\mu_1 > \mu_2$ moving particles from $\mathcal{S}_1$ to $\mathcal{S}_2$ decreases F , taking the system closer to equilibrium. Thus, particles tend to flow from systems of high chemical potential to systems of lower chemical potential. μ is the (Helmholtz) free energy “per particle” in a system.

If several chemical species are present within a system, then there is chemical potential associated with each distinct species, *e.g.*

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{\tau, V, N_1, N_2, \dots}$$

is the chemical potential for species j .

1.1 Example: the ideal gas

In chapter 3 we showed that the Helmholtz free energy of an ideal monatomic gas is

$$F = -N\tau \ln(n_Q V) + N\tau \ln N - N\tau,$$

so that

$$\mu = -\tau \ln(n_Q V) + \tau \ln N = \tau \ln \left(\frac{n}{n_Q} \right),$$

where $n = N/V$ is the particle concentration (or number density) and

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

is the quantum concentration. We can also use the ideal gas law, $p = n\tau$ to rewrite this as

$$\mu = \tau \ln \left(\frac{p}{\tau n_Q} \right).$$

Note that a gas is only classical when $n \ll n_Q$, so that the chemical potential of an ideal gas is always negative.

2 Internal and total chemical potential

We consider diffusive equilibrium in the presence of an external force. Again consider $\mathcal{S}_1$ and $\mathcal{S}_2$, in thermal but not diffusive equilibrium. Take the case when $\mu_2 > \mu_1$ and arrange the external force so that the particles in $\mathcal{S}_1$ are raised in potential by $\mu_2 - \mu_1$ relative to those in $\mathcal{S}_2$. (Possible candidates for the external force are gravity or an electric field.) This adds the quantity $N_1(\mu_2 - \mu_1)$ to the free energy of $\mathcal{S}_1$ without altering the free energy of $\mathcal{S}_2$, so that now $\mu_1 = \mu_2$ and the 2 systems are in diffusive equilibrium. This leads to a simple physical interpretation for the chemical potential —

- *Chemical potential is equivalent to a true potential energy: the difference in chemical potential between 2 systems is equal to the potential barrier that will bring the 2 systems into diffusive equilibrium.*

This provides a means for measuring (differences in) the chemical potential — simply by establishing what potential barrier is required to halt particle exchange between 2 systems. It is important to remember that only differences in chemical potential are physically significant. The zero of chemical potential depends on our definition of the zero of energy.

We are also able to use the notion of the *total chemical potential* for a system as the sum of 2 parts:

$$\mu = \mu_{\text{tot}} = \mu_{\text{ext}} + \mu_{\text{int}},$$

where μ_{ext} is the potential due to the presence of external forces, and μ_{int} is the *internal chemical potential*, the chemical potential in the absence of external forces. These concepts tend to get confused when applied in practice, particularly in the fields of electrochemistry and semiconductors, where the term chemical potential is usually applied to the internal chemical potential.

2.1 Example: the atmosphere

Consider the atmosphere as a sequence of layers of gas in thermal and diffusive equilibrium with one another. (Thermal equilibrium in the atmosphere is approximate — disturbed by weather.) The gravitational potential of an atom is Mgh , so that the total chemical potential in the atmosphere at height h is

$$\mu = \tau \ln \left(\frac{n}{n_Q} \right) + Mgh,$$

and this must be independent of height in equilibrium. Thus,

$$n(h) = n(0) \exp \left(-\frac{Mgh}{\tau} \right),$$

or, using the ideal gas law,

$$p(h) = p(0) \exp\left(-\frac{Mgh}{\tau}\right).$$

We can characterise an atmosphere by its pressure scale-height, the height over which the pressure falls by a factor of $1/e \simeq 0.37$, *i.e.* τ/Mg . The Earth's atmosphere is dominated by N_2 with a molecular weight of 28 amu $\simeq 4.65 \times 10^{-26}$ kg, so that it has a scale height of about 8.8 km when the temperature is $T = 290$ K. Kittel & Kroemer has a graph showing that atmospheric pressure is quite exponential between about 10 and 40 km in altitude. The temperature at these altitudes is about 227 K.

Note that the different constituents of the atmosphere would have differing scale-heights in true equilibrium. The different constituents do fall off at differing rates.

2.2 Example: mobile magnetic particles in a magnetic field

Consider a system of N identical particles with magnetic moment m . These are the usual 2 state magnets, so that they either have spin $\uparrow$ or $\downarrow$, with corresponding energies $-mB$ and mB respectively. We segregate the particles into those with spin up and those with spin down, so that

$$\mu_{\text{tot}}(\uparrow) = \tau \ln\left(\frac{n_{\uparrow}}{n_Q}\right) - mB \quad \text{and} \quad \mu_{\text{tot}}(\downarrow) = \tau \ln\left(\frac{n_{\downarrow}}{n_Q}\right) + mB,$$

where the external contribution to μ is $\pm mB$.

If the magnetic field varies over the volume of the system, then we may treat it (as we did the atmosphere) as a number of smaller systems over which the field is uniform. In equilibrium the chemical potential must be uniform over the whole system (if the particles can diffuse around in the system). Also, if there is exchange between the 2 groups of spins, then in equilibrium we must also have $\mu_{\text{tot}}(\uparrow) = \mu_{\text{tot}}(\downarrow)$ (not discussed in K&K). We therefore get

$$n_{\uparrow}(B) = \frac{1}{2}n(0) \exp\left(\frac{mB}{\tau}\right) \quad \text{and} \quad n_{\downarrow}(B) = \frac{1}{2}n(0) \exp\left(\frac{-mB}{\tau}\right),$$

where $n(0)$ is the total concentration where $B = 0$.

The total concentration of particles at some point in the system is then

$$n(B) = n_{\uparrow}(B) + n_{\downarrow}(B) = n(0) \cosh\left(\frac{mB}{\tau}\right).$$

Notice that the particles tend to congregate towards regions of high B . The form of the result applies to fine ferromagnetic particles in suspension in a colloidal solution. This property is used in the study of magnetic field structure and for finding cracks.

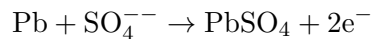
The ideal gas form for μ_{int} applies generally as long as the particles do not interact and their concentration is low. In general in this case

$$\mu_{\text{int}} = \tau \ln n + \text{constant},$$

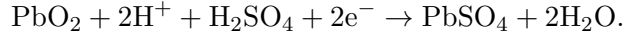
and the constant does not depend on the concentration of the particles.

2.3 Example: batteries

A lead-acid battery consists of 2 Pb electrodes immerses in dilute sulfuric acid. One of the electrodes is coated in PbO_2 . A sequence of chemical reactions take place near to the electrodes, with the nett effect near the negative electrode of



and near the positive electrode of



The former reaction makes the chemical potential $\mu(\text{SO}_4^{--})$ of the sulfate ions at the surface of the negative electrode lower than in the bulk electrolyte and so draws these ions to the negative electrode. Similarly, H^+ is drawn to the surface of the positive electrode.

If the battery terminals are not connected the buildup of charge on the electrodes produces an electric potential which balances the internal chemical potentials of the ions and stops the flow of ions. Electrically connecting the terminals of the battery allows an external current to discharge the electrodes, so that the ions keep flowing. (Internal electron currents in the battery are negligible.) Charging sets up the opposite reactions at each electrode by reversing the signs of the total chemical potentials for the respective ions.

Measuring electrostatic potentials relative to the electrolyte, the equilibrium (zero current) potential on the negative electrode is given by

$$-2q\Delta V_- = \Delta\mu(\text{SO}_4^{--})$$

and that on the positive electrode by

$$q\Delta V_+ = \Delta\mu(\text{H}^+).$$

These 2 potentials are known as the *half-cell potentials*. They are -0.4 V and 1.6 V respectively. The total electrostatic potential across one cell of the battery is then

$$\Delta V = \Delta V_+ - \Delta V_- = 2.0 \text{ V},$$

the *open-circuit voltage* of one lead-acid cell.

3 Chemical potential and entropy

We can derive an expression for the chemical potential as a derivative of the entropy. There are 2 steps to the process, first we use the expression $F = U - \tau\sigma$ to write

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

Next we must find an expression for the derivatives on the right, with σ regarded as a function of (U, V, N) . We could use Jacobians (try this as an exercise), but we will follow the “constructive” approach taken in K&K. Regarding σ as $\sigma(U, V, N)$, we have

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

and we combine these expression to get

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

The principal difference between these two expressions for μ is that the first gives $\mu(\tau, V, N)$, while the new expression most naturally gives $\mu(U, V, N)$. We can also show that

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

This table summarises the various ways that we can express the intensive variables in terms of the other thermodynamic variables.

	$\sigma(U, V, N)$	$U(\sigma, V, N)$	$F(\tau, V, N)$
τ	$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_{V, N}$	$\tau = \left(\frac{\partial U}{\partial \sigma} \right)_{V, N}$	
p	$\frac{p}{\tau} = \left(\frac{\partial \sigma}{\partial V} \right)_{U, N}$	$p = - \left(\frac{\partial U}{\partial V} \right)_{\sigma, N}$	$p = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N}$
μ	$\mu = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U, V}$	$\mu = \left(\frac{\partial U}{\partial N} \right)_{\sigma, V}$	$\mu = \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$

3.1 Thermodynamic identity

We can use the result just derived for μ to improve our expression of the thermodynamic identity. We now have

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

Rearranging into the form most representative of the 1st law,

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

which now allows for variations of the particle number too.

4 Gibbs factor and Gibbs sum

We showed before that for a system in thermal contact with a reservoir the probability that the system will be in the state s is

$$P(s) \propto \exp \left(-\frac{\epsilon_s}{\tau} \right).$$

We will now derive a similar result for systems in thermal and diffusive contact with a reservoir.

Consider a system $\mathcal{S}$ in thermal and diffusive contact with a reservoir $\mathcal{R}$. The combined system is isolated so that it has fixed total energy U_0 and a fixed number of particles N_0 . As before, we can use the fundamental hypothesis — that all states of the system are equally likely — to deduce that the probability that $\mathcal{S}$ has N particles and is in the state s is just

$$P(N, s) = \frac{g_{\mathcal{R}}(N_0 - N, U_0 - \epsilon_s)}{\sum_{N', s'} g_{\mathcal{R}}(N_0 - N', U_0 - \epsilon_{N', s'})}.$$

(Note that the accessible states of the system generally depend on the number of particles within it.) The denominator in this expression is the same for all N and s , so that we can ignore it for the purpose of argument and write

$$P(N, s) \propto g_{\mathcal{R}}(N_0 - N, U_0 - \epsilon_s).$$

The next step, again, is to expand $g_{\mathcal{R}}$ under the assumption that, since $\mathcal{R} \gg \mathcal{S}$, then $N_0 \gg N$ and $U_0 \gg U$. We actually expand $\sigma_{\mathcal{R}} = \ln g_{\mathcal{R}}$ because it is a much better behaved function of its arguments. Hence use

$$\sigma_{\mathcal{R}}(N_0 - N, U_0 - \epsilon_s) \simeq \sigma_{\mathcal{R}}(N_0, U_0) - N \left(\frac{\partial \sigma_{\mathcal{R}}}{\partial N} \right)_U - \epsilon_s \left(\frac{\partial \sigma_{\mathcal{R}}}{\partial U} \right)_N,$$

where the derivatives are evaluated at $N = N_0$ and $U = U_0$, so that

$$\sigma_{\mathcal{R}}(N_0 - N, U_0 - \epsilon_s) \simeq \sigma_{\mathcal{R}}(N_0, U_0) + \frac{N\mu}{\tau} - \frac{\epsilon_s}{\tau},$$

which gives

$$P(N, s) \propto \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right).$$

This is called the *Gibbs factor*.

As with the Boltzmann factor, the normalization which we need to turn the Gibbs factor into a probability is intrinsically interesting. This is

$$\mathcal{Z}(\mu, \tau) = \sum_{N=0}^{\infty} \sum_s \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right) = \sum_{\text{ASN}} \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right),$$

and is known as the *Gibbs sum*, *grand sum* or the *grand canonical partition function*. Remember that the states accessible to a system (s) will always depend on the number of particles N in the system. Note that the system may contain no particles (of the given type), so that the pertinent term(s) must be included in the sum.

We may write, for a system at temperature τ and with chemical potential μ , that

$$P(N, s) = \frac{1}{\mathcal{Z}} \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right).$$

We can use this to determine the average value of any parameter for a system in thermal and diffusive contact with a reservoir (at temperature τ and chemical potential μ). The average of $X(N, s)$ is

$$\langle X \rangle = \sum_{\text{ASN}} X(N, s) P(N, s) = \frac{1}{\mathcal{Z}} \sum_{\text{ASN}} X(N, s) \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right).$$

One of the simplest examples is the mean number of particles:

$$\begin{aligned} \langle N \rangle &= \frac{1}{\mathcal{Z}} \sum_{\text{ASN}} N \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right) \\ &= \frac{\tau}{\mathcal{Z}} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)_{\tau, V} = \tau \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_{\tau, V}. \end{aligned} \quad (1)$$

Notation: beware that N is frequently used to represent $\langle N \rangle$. We will follow this convention where there is no ambiguity over which quantity is being referred to.

Another notation that we will use is

$$\lambda = \exp\left(\frac{\mu}{\tau}\right),$$

where λ is known as the *absolute activity*, so that the Gibbs sum is

$$\mathcal{Z} = \sum_{\text{ASN}} \lambda^N \exp\left(-\frac{\epsilon_s}{\tau}\right).$$

We also have

$$\langle N \rangle = \lambda \left(\frac{\partial \ln \mathcal{Z}}{\partial \lambda} \right)_{\tau, V} = \left(\frac{\partial \ln \mathcal{Z}}{\partial \ln \lambda} \right)_{\tau, V}.$$

For the ideal gas

$$\lambda = \frac{n}{n_Q}.$$

It is a little more complicated to write the average energy for a system in thermal and diffusive contact with a reservoir in terms of $\mathcal{Z}$. We have

$$\langle N\mu - \epsilon \rangle = \langle N \rangle \mu - U = \left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_{\mu, V}.$$

Using the expression we already have for $\langle N \rangle$, we then have

$$U = \left(\frac{\mu}{\beta} \left(\frac{\partial}{\partial \mu} \right)_{\tau, V} - \left(\frac{\partial}{\partial \beta} \right)_{\mu, V} \right) \ln \mathcal{Z}.$$

4.1 Example: zero/one particle systems

A heme molecule is a typical example of a system that may contain 0 or 1 particles (O_2 molecules). If the energy of the adsorbed O_2 molecule is ϵ more than when it is free, then the grand canonical partition function for this system is

$$\mathcal{Z} = 1 + \lambda \exp \left(-\frac{\epsilon}{\tau} \right).$$

Kittel & Kroemer use the examples of the heme group in myoglobin. Haemoglobin has 4 heme groups in one molecule.

We can deduce the mean occupation of myoglobin in the presence of O_2 if we assume that the chemical potential of the O_2 is given by the ideal gas result

$$\lambda = \frac{n}{n_Q} = \frac{p}{\tau n_Q}.$$

The occupied fraction is then

$$f = \frac{\lambda \exp \left(-\frac{\epsilon}{\tau} \right)}{1 + \lambda \exp \left(-\frac{\epsilon}{\tau} \right)} = \frac{p}{n_Q \tau \exp \left(\frac{\epsilon}{\tau} \right) + p} = \frac{p}{p_0 + p},$$

where

$$p_0 = n_Q \tau \exp \left(\frac{\epsilon}{\tau} \right),$$

so that it depends on τ but not p . This result is known as the *Langmuir adsorption isotherm* when applied to the adsorption of gases onto solid surfaces.

Experiment have confirmed this result for myoglobin, but it does not apply to haemoglobin due to the effect of the interaction between the 4 O_2 molecules on this molecule. The O_2 uptake of haemoglobin is more gradual, and better suited to its use in transporting O_2 in the blood.

The initial form for the occupation fraction f is just the Fermi-Dirac distribution.

4.2 Example: donor impurities in semiconductors

Electron donors are one of the two major classes of dopants used in making semiconductor devices. When they are incorporated into a semiconductor crystal lattice in small quantities they are easily ionized, donating an electron to the conduction bands of the lattice. At low concentration the electrons act as an ideal gas.

A single donor atom may be regarded as a system in thermal and diffusive equilibrium with the rest of the lattice. We will treat the donor as having a single electron with ionization energy

I. The donor atom then has 3 possible states: ionized; spin up or spin down. With energy measured relative to the conduction electrons, these give the grand canonical partition function

$$\mathcal{Z} = 1 + 2 \exp \left(\frac{\mu + I}{\tau} \right).$$

The probability that the donor atom is ionized is then

$$P(\text{ionized}) = \frac{1}{1 + 2 \exp \left(\frac{\mu + I}{\tau} \right)}.$$

The probability that the donor electron is bound is simply the complementary probability

$$P(\text{neutral}) = 1 - P(\text{ionized}).$$

5 Problems, Chapter 5

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