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Thermal

Physics

7 Quantum Statistics

7.1 The Gibbs Factor

In deriving the Boltzmann factor in Section 6.1, I allowed the small system and the reservoir to exchange energy, but not particles. Often, however, it is useful to consider a system that *can* exchange particles with its environment (see Figure 7.1). Let me now modify the previous derivation to allow for this possibility.

As in Section 6.1, we can write the ratio of probabilities for two different microstates as

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{[S_R(s_2)-S_R(s_1)]/k}. \tag{7.1}$$

The exponent now contains the change in the entropy of the reservoir as the system goes from state 1 to state 2. This is an infinitesimal change from the reservoir's viewpoint, so we can invoke the thermodynamic identity:

$$dS_R = \frac{1}{T}\big(dU_R + P\,dV_R - \mu\,dN_R\big). \tag{7.2}$$

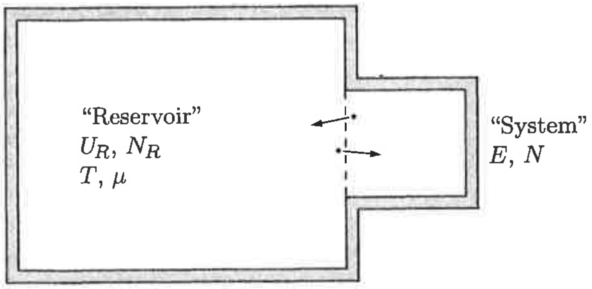

Figure 7.1. A system in thermal and diffusive contact with a much larger reservoir, whose temperature and chemical potential are effectively constant.

Since any energy, volume, or particles gained by the reservoir must be lost by the system, each of the changes on the right-hand side can be written as minus the same change for the system.

As in Section 6.1, I'll throw away the $P\,dV$ term; this term is often zero, or at least very small compared to the others. This time, however, I'll keep the $\mu\,dN$ term. Then the change in entropy can be written

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T}\big[E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)\big]. \tag{7.3}$$

On the right-hand side both E and N refer to the small system, hence the overall minus sign. Plugging this expression into equation 7.1 gives

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{-[E(s_2)-\mu N(s_2)]/kT}}{e^{-[E(s_1)-\mu N(s_1)]/kT}}. \tag{7.4}$$

As before, the ratio of probabilities is a ratio of simple exponential factors, each of which is a function of the temperature of the reservoir and the energy of the corresponding microstate. Now, however, the factor depends also on the number of particles in the system for state s. This new exponential factor is called a **Gibbs factor**:

$$\text{Gibbs factor} = e^{-[E(s)-\mu N(s)]/kT}. \tag{7.5}$$

If we want an absolute probability instead of a ratio of probabilities, again we have to slip a constant of proportionality in front of the exponential:

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}}\, e^{-[E(s)-\mu N(s)]/kT}. \tag{7.6}$$

The quantity $\mathcal{Z}$ is called the **grand partition function*** or the **Gibbs sum**. By requiring that the sum of the probabilities of all states equal 1, you can easily show that

$$\mathcal{Z} = \sum_s e^{-[E(s)-\mu N(s)]/kT}, \tag{7.7}$$

where the sum runs over all possible states (including all possible values of N).

If more than one type of particle can be present in the system, then the $\mu\,dN$ term in equation 7.2 becomes a sum over species of $\mu_i\,dN_i$, and each subsequent equation is modified in a similar way. For instance, if there are two types of particles, the Gibbs factor becomes

$$\text{Gibbs factor} = e^{-[E(s)-\mu_A N_A(s)-\mu_B N_B(s)]/kT} \qquad \text{(two species)}. \tag{7.8}$$

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*In analogy with the terms "microcanonical" and "canonical" used to describe the methods of Chapters 2–3 and 6, the approach used here is called **grand canonical**. A hypothetical set of systems with probabilities assigned according to equation 7.6 is called a **grand canonical ensemble**.

An Example: Carbon Monoxide Poisoning

A good example of a system to illustrate the use of Gibbs factors is an adsorption site on a hemoglobin molecule, which carries oxygen in the blood. A single hemoglobin molecule has four adsorption sites, each consisting of an Fe^{2+} ion surrounded by various other atoms. Each site can carry one O_2 molecule. For simplicity I'll take the system to be just one of the four sites, and pretend that it is completely independent of the other three.* Then if oxygen is the only molecule that can occupy the site, the system has just two possible states: unoccupied and occupied (see Figure 7.2). I'll take the energies of these two states to be 0 and ϵ, with $\epsilon = -0.7$ eV.†

The grand partition function for this single-site system has just two terms:

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT}. \tag{7.9}$$

The chemical potential μ is relatively high in the lungs, where oxygen is abundant, but is much lower in the cells where the oxygen is used. Let's consider the situation near the lungs. There the blood is in approximate diffusive equilibrium with the atmosphere, an ideal gas in which the partial pressure of oxygen is about 0.2 atm. The chemical potential can therefore be calculated from equation 6.93:

$$\mu = -kT \ln\left(\frac{VZ_{\text{int}}}{Nv_Q}\right) \approx -0.6 \text{ eV} \tag{7.10}$$

at body temperature, 310 K. Plugging in these numbers gives for the second Gibbs factor

$$e^{-(\epsilon-\mu)/kT} \approx e^{(0.1\,\text{eV})/kT} \approx 40. \tag{7.11}$$

The probability of any given site being occupied is therefore

$$\mathcal{P}(\text{occupied by } O_2) = \frac{40}{1+40} = 98\%. \tag{7.12}$$

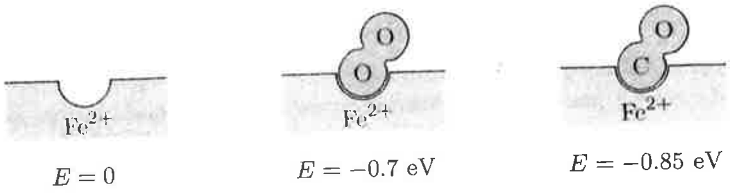

Figure 7.2. A single heme site can be unoccupied, occupied by oxygen, or occupied by carbon monoxide. (The energy values are only approximate.)

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*The assumption of independent sites is quite accurate for myoglobin, a related protein that binds oxygen in muscles, which has only one adsorption site per molecule. A more accurate model of hemoglobin is presented in Problem 7.2.

†Biochemists *never* express energies in electron-volts. In fact, they rarely talk about individual bond energies at all (perhaps because these energies can vary so much under different conditions). I've chosen the ϵ values in this section to yield results that are in rough agreement with experimental measurements.

Suppose, however, that there is also some carbon monoxide present, which can also be adsorbed into the heme site. Now there are three states available to the site: unoccupied, occupied by O_2, and occupied by CO. The grand partition function is

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} + e^{-(\epsilon'-\mu')/kT}, \tag{7.13}$$

where ϵ' is the negative energy of a bound CO molecule and μ' is the chemical potential of CO in the environment. On the one hand, CO will never be as abundant as oxygen. If it is 100 times less abundant, then its chemical potential is lower by *roughly* $kT \ln 100 = 0.12$ eV, so μ' is roughly -0.72 eV. On the other hand, CO is more tightly bound to the site than oxygen, with $\epsilon' \approx -0.85$ eV. Plugging in these numbers gives for the third Gibbs factor

$$e^{-(\epsilon'-\mu')/kT} \approx e^{(0.13\,\mathrm{eV})/kT} \approx 120. \tag{7.14}$$

The probability of the site being occupied by an *oxygen* molecule therefore drops to

$$\mathcal{P}(\text{occupied by } O_2) = \frac{40}{1+40+120} = 25\%. \tag{7.15}$$

Problem 7.1. Near the cells where oxygen is used, its chemical potential is significantly lower than near the lungs. Even though there is no gaseous oxygen near these cells, it is customary to express the abundance of oxygen in terms of the partial pressure of gaseous oxygen that *would* be in equilibrium with the blood. Using the independent-site model just presented, with only oxygen present, calculate and plot the fraction of occupied heme sites as a function of the partial pressure of oxygen. This curve is called the **Langmuir adsorption isotherm** ("isotherm" because it's for a fixed temperature). Experiments show that adsorption by *myoglobin* follows the shape of this curve quite accurately.

Problem 7.2. In a real hemoglobin molecule, the tendency of oxygen to bind to a heme site increases as the other three heme sites become occupied. To model this effect in a simple way, imagine that a hemoglobin molecule has just two sites, either or both of which can be occupied. This system has four possible states (with only oxygen present). Take the energy of the unoccupied state to be zero, the energies of the two singly occupied states to be -0.55 eV, and the energy of the doubly occupied state to be -1.3 eV (so the change in energy upon binding the *second* oxygen is -0.75 eV). As in the previous problem, calculate and plot the fraction of occupied sites as a function of the effective partial pressure of oxygen. Compare to the graph from the previous problem (for independent sites). Can you think of why this behavior is preferable for the function of hemoglobin?

Problem 7.3. Consider a system consisting of a single hydrogen atom/ion, which has two possible states: unoccupied (i.e., no electron present) and occupied (i.e., one electron present, in the ground state). Calculate the ratio of the probabilities of these two states, to obtain the Saha equation, already derived in Section 5.6. Treat the electrons as a monatomic ideal gas, for the purpose of determining μ. Neglect the fact that an electron has two independent spin states.

Problem 7.4. Repeat the previous problem, taking into account the two independent spin states of the electron. Now the system has two "occupied" states, one with the electron in each spin configuration. However, the chemical potential of the electron gas is also slightly different. Show that the ratio of probabilities is the same as before: The spin degeneracy cancels out of the Saha equation.

Problem 7.5. Consider a system consisting of a single impurity atom/ion in a semiconductor. Suppose that the impurity atom has one "extra" electron compared to the neighboring atoms, as would a phosphorus atom occupying a lattice site in a silicon crystal. The extra electron is then easily removed, leaving behind a positively charged ion. The ionized electron is called a **conduction electron**, because it is free to move through the material; the impurity atom is called a **donor**, because it can "donate" a conduction electron. This system is analogous to the hydrogen atom considered in the previous two problems except that the ionization energy is much less, mainly due to the screening of the ionic charge by the dielectric behavior of the medium.

(a) Write down a formula for the probability of a single donor atom being ionized. Do not neglect the fact that the electron, if present, can have two independent spin states. Express your formula in terms of the temperature, the ionization energy I, and the chemical potential of the "gas" of ionized electrons.

(b) Assuming that the conduction electrons behave like an ordinary ideal gas (with two spin states per particle), write their chemical potential in terms of the number of conduction electrons per unit volume, N_c/V.

(c) Now assume that every conduction electron comes from an ionized donor atom. In this case the number of conduction electrons is equal to the number of donors that are ionized. Use this condition to derive a quadratic equation for N_c in terms of the number of donor atoms (N_d), eliminating μ. Solve for N_c using the quadratic formula. (Hint: It's helpful to introduce some abbreviations for dimensionless quantities. Try $x = N_c/N_d$, $t = kT/I$, and so on.)

(d) For phosphorus in silicon, the ionization energy is 0.044 eV. Suppose that there are 10^{17} P atoms per cubic centimeter. Using these numbers, calculate and plot the fraction of ionized donors as a function of temperature. Discuss the results.

Problem 7.6. Show that when a system is in thermal and diffusive equilibrium with a reservoir, the average number of particles in the system is

$$\overline{N} = \frac{kT}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu},$$

where the partial derivative is taken at fixed temperature and volume. Show also that the mean *square* number of particles is

$$\overline{N^2} = \frac{(kT)^2}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}.$$

Use these results to show that the standard deviation of N is

$$\sigma_N = \sqrt{kT(\partial \overline{N}/\partial \mu)},$$

in analogy with Problem 6.18. Finally, apply this formula to an ideal gas, to obtain a simple expression for σ_N in terms of $\overline{N}$. Discuss your result briefly.

Problem 7.7. In Section 6.5 I derived the useful relation $F = -kT \ln Z$ between the Helmholtz free energy and the ordinary partition function. Use an analogous argument to prove that

$$\Phi = -kT \ln \mathcal{Z},$$

where $\mathcal{Z}$ is the grand partition function and Φ is the grand free energy introduced in Problem 5.23.

7.2 Bosons and Fermions

The most important application of Gibbs factors is to **quantum statistics**, the study of dense systems in which two or more identical particles have a reasonable chance of wanting to occupy the same single-particle state. In this situation, my derivation (in Section 6.6) of the partition function for a system of N indistinguishable, noninteracting particles,

$$Z = \frac{1}{N!} Z_1^N, \tag{7.16}$$

breaks down. The problem is that the counting factor of $N!$, the number of ways of interchanging the particles among their various states, is correct only if the particles are always in *different* states. (In this section I'll use the word "state" to mean a single-particle state. For the state of the system as a whole I'll always say "system state.")

To better understand this issue, let's consider a very simple example: a system containing two noninteracting particles, either of which can occupy any of five states (see Figure 7.3). Imagine that all five of these states have energy zero, so every Boltzmann factor equals 1 (and therefore Z is the same as Ω).

If the two particles are *distinguishable*, then each has five available states and the total number of *system* states is $Z = 5 \times 5 = 25$. If the two particles are *indistinguishable*, equation 7.16 would predict $Z = 5^2/2 = 12.5$, and this can't be right, since Z must (for this system) be an integer.

So let's count the system states more carefully. Since the particles are indistinguishable, all that matters is the number of particles in any given state. I can therefore represent any system state by a sequence of five integers, each representing the number of particles in a particular state. For instance, 01100 would represent the system state in which the second and third states each contain one particle,

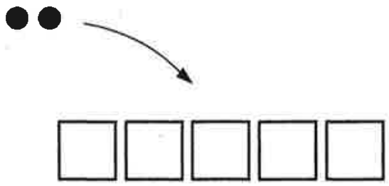

Figure 7.3. A simple model of five single-particle states, with two particles that can occupy these states.