

- (a) Find an expression for the entropy of this system in terms of N and N_R , the number of links pointing to the right.
- (b) Write down a formula for L in terms of N and N_R .
- (c) For a one-dimensional system such as this, the length L is analogous to the volume V of a three-dimensional system. Similarly, the pressure P is replaced by the tension force F . Taking F to be positive when the rubber band is pulling inward, write down and explain the appropriate thermodynamic identity for this system.
- (d) Using the thermodynamic identity, you can now express the tension force F in terms of a partial derivative of the entropy. From this expression, compute the tension in terms of L , T , N , and ℓ .
- (e) Show that when $L \ll N\ell$, the tension force is directly proportional to L (Hooke's law).
- (f) Discuss the dependence of the tension force on temperature. If you increase the temperature of a rubber band, does it tend to expand or contract? Does this behavior make sense?
- (g) Suppose that you hold a relaxed rubber band in both hands and suddenly stretch it. Would you expect its temperature to increase or decrease? Explain. Test your prediction with a real rubber band (preferably a fairly heavy one with lots of stretch), using your lips or forehead as a thermometer. (Hint: The entropy you computed in part (a) is not the total entropy of the rubber band. There is additional entropy associated with the vibrational energy of the molecules; this entropy depends on U but is approximately independent of L .)

3.5 Diffusive Equilibrium and Chemical Potential

When two systems are in *thermal* equilibrium, their temperatures are the same. When they're in *mechanical* equilibrium, their pressures are the same. What quantity is the same when they're in *diffusive* equilibrium?

We can find out by applying the same logic as in the previous section. Consider two systems, A and B , that are free to exchange both energy and particles, as shown in Figure 3.18. (The volumes of the systems could also vary, but I'll take these to be fixed for simplicity.) I've drawn a system of two interacting gases, but it could just as well be a gas interacting with a liquid or solid, or even two solids in which atoms gradually migrate around. I'm assuming, though, that both systems are made of the same *species* of particles, for instance, H_2O molecules.

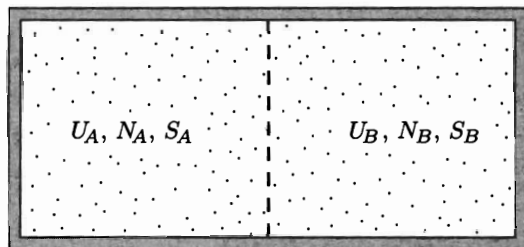


Figure 3.18. Two systems that can exchange both energy and particles.

NS!

NS!

Assuming that the total energy and total number of particles are fixed, the total entropy of this system is a function of U_A and N_A . At equilibrium, the total entropy is a maximum, so

$$\left(\frac{\partial S_{\text{total}}}{\partial U_A}\right)_{N_A, V_A} = 0 \quad \text{and} \quad \left(\frac{\partial S_{\text{total}}}{\partial N_A}\right)_{U_A, V_A} = 0. \quad (3.52)$$

(If the volumes of the systems are allowed to vary, then $\partial S_{\text{total}}/\partial V_A = 0$ as well.) Again, the first condition says that the two systems must be at the same temperature. The second condition is new, but is entirely analogous to the condition on volume from the previous section. Following the same reasoning as there, we can conclude

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad \text{at equilibrium,} \quad (3.53)$$

where the partial derivatives are taken at fixed energy and volume. We're free to multiply this equation through by a factor of T , the temperature, since the systems are also in thermal equilibrium. By convention, we also multiply by -1 :

$$-T \frac{\partial S_A}{\partial N_A} = -T \frac{\partial S_B}{\partial N_B} \quad \text{at equilibrium.} \quad (3.54)$$

The quantity $-T(\partial S/\partial N)$ is much less familiar to most of us than temperature or pressure, but it's still extremely important. It is called the **chemical potential**, denoted μ :

$$\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U, V}. \quad (3.55)$$

This is the quantity that's the same for both systems when they're in diffusive equilibrium:

$$\mu_A = \mu_B \quad \text{at equilibrium.} \quad (3.56)$$

If the two systems are *not* in equilibrium, then the one with the larger value of $\partial S/\partial N$ will tend to gain particles, since it will thereby gain more entropy than the other loses. However, because of the minus sign in definition 3.55, this system has the *smaller* value of μ . Conclusion: Particles tend to flow from the system with higher μ into the system with lower μ (see Figure 3.19).

NB.

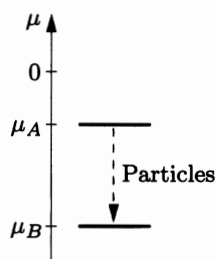


Figure 3.19. Particles tend to flow toward lower values of the chemical potential, even if both values are negative.

It's not hard to generalize the thermodynamic identity to include processes in which N changes. If we imagine changing U by dU , V by dV , and N by dN , then, by the same logic as in the previous section, the total change in the entropy is

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \\ &= \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN. \end{aligned} \quad (3.57)$$

Solving for dU as before, we obtain

$$dU = T dS - P dV + \mu dN. \quad (3.58)$$

Just as the $-P dV$ term is usually associated with mechanical work, the μdN term is sometimes referred to as "chemical work."

This generalized thermodynamic identity is a great way to remember the various partial-derivative formulas for T , P , and μ , and to generate other similar formulas. Notice that four quantities are changing in this equation: U , S , V , and N . Now just imagine a process in which any two of these are fixed. For instance, in a process with fixed U and V ,

$$0 = T dS + \mu dN, \quad \text{that is,} \quad \mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}. \quad (3.59)$$

Similarly, in a process with fixed S and V ,

$$dU = \mu dN, \quad \text{that is,} \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \quad (3.60)$$

This last result is another useful formula for the chemical potential. It tells us directly that μ has units of energy; specifically, μ is the amount by which a system's energy changes, when you add one particle and keep the entropy and volume fixed. Normally, to hold the entropy (or multiplicity) fixed, you must remove some energy as you add a particle, so μ is negative. However, if you have to give the particle some potential energy (gravitational, if the system lives on a mountain top, or chemical, if the system is a solid crystal) to get it into the system, this energy also contributes to μ . In Chapter 7 we'll see an example where you have to give a particle *kinetic* energy just to get it into a system.

Now let's look at some examples. First consider a very small Einstein solid, with three oscillators and three units of energy. The multiplicity is 10, so the entropy is $k \ln 10$. Now suppose we add one more oscillator (thinking of each oscillator as a "particle"). If we leave all three units of energy in the system, the multiplicity increases to 20 and the entropy increases to $k \ln 20$. To hold the entropy fixed, we need to remove one unit of energy, as shown in Figure 3.20. Thus the chemical potential of this system is

$$\mu = \left(\frac{\Delta U}{\Delta N}\right)_S = \frac{-\epsilon}{1} = -\epsilon, \quad (3.61)$$

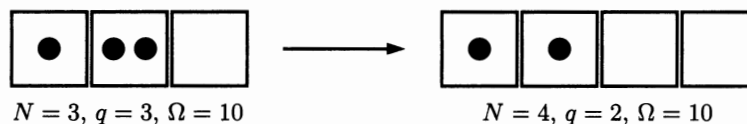


Figure 3.20. In order to add an oscillator (represented by a box) to this very small Einstein solid while holding the entropy (or multiplicity) fixed, we must remove one unit of energy (represented by a dot).

if ϵ is the size of a unit of energy. (Because the addition of one particle is not an infinitesimal change for such a small system, this example should be taken with a grain of salt. Strictly speaking, the derivative $\partial U/\partial N$ is not well defined. Besides, in a real solid crystal, adding an atom would entail adding three oscillators, not just one, and we would also have to add some negative potential energy to create the chemical bonds around the added atom.)

As a more realistic example, let's compute μ for a monatomic ideal gas. Here we need the full Sackur-Tetrode equation (2.49) for the entropy,

$$S = Nk \left[\ln \left(V \left(\frac{4\pi m U}{3h^2} \right)^{3/2} \right) - \ln N^{5/2} + \frac{5}{2} \right]. \quad (3.62)$$

Differentiating with respect to N gives

$$\begin{aligned} \mu &= -T \left\{ k \left[\ln \left(V \left(\frac{4\pi m U}{3h^2} \right)^{3/2} \right) - \ln N^{5/2} + \frac{5}{2} \right] - Nk \cdot \frac{5}{2} \frac{1}{N} \right\} \\ &= -kT \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right] \\ &= -kT \ln \left[\frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right]. \end{aligned} \quad (3.63)$$

(In the last line I used the relation $U = \frac{3}{2} NkT$.) At room temperature and atmospheric pressure, the volume per molecule, V/N , is $4.2 \times 10^{-26} \text{ m}^3$, while the quantity $(h^2/2\pi m k T)^{3/2}$ is much smaller. For helium, this quantity is $1.3 \times 10^{-31} \text{ m}^3$, so the argument of the logarithm is 3.3×10^5 , the logarithm itself is 12.7, and the chemical potential is

$$\mu = -0.32 \text{ eV} \quad \text{for helium at 300 K, } 10^5 \text{ N/m}^2. \quad (3.64)$$

If the concentration is increased while holding the temperature fixed, μ becomes less negative, indicating that the gas becomes more willing to give up particles to other nearby systems. More generally, increasing the density of particles in a system always increases its chemical potential.

Throughout this section, I've implicitly assumed that each system contains only one type of particle. If a system contains several types of particles (such as air, a mixture of nitrogen and oxygen molecules), then each species has its own chemical potential:

$$\mu_1 \equiv -T \left(\frac{\partial S}{\partial N_1} \right)_{U, V, N_2}, \quad \mu_2 \equiv -T \left(\frac{\partial S}{\partial N_2} \right)_{U, V, N_1}, \quad (3.65)$$

and so on for each species 1, 2, The generalized thermodynamic identity is then

$$dU = T dS - P dV + \sum_i \mu_i dN_i, \quad (3.66)$$

where the sum runs over all species, $i = 1, 2, \dots$. If two systems are in diffusive equilibrium, the chemical potentials must be separately equal for each species: $\mu_{1A} = \mu_{1B}$, $\mu_{2A} = \mu_{2B}$, and so on, where A and B are the two systems.

The chemical potential is a central concept in the study of equilibrium in chemical reactions and phase transformations. It also plays a central role in “quantum statistics,” the study of exotic, dense gases and other related systems. We’ll make use of it many times in Chapters 5 and 7.

One more comment: I should mention that chemists usually define the chemical potential in terms of *moles*, not individual particles:

$$\mu_{\text{chemistry}} \equiv -T \left(\frac{\partial S}{\partial n} \right)_{U,V}, \quad (3.67)$$

where $n = N/N_A$ is the number of moles of whatever type of particle is being considered. This means that their chemical potentials are always larger than ours by a factor of Avogadro’s number, N_A . To translate this section into chemistry conventions, just change every N to an n , except in the examples in equations 3.61 through 3.64, where every formula for μ should be multiplied by N_A .

Problem 3.35. In the text I showed that for an Einstein solid with three oscillators and three units of energy, the chemical potential is $\mu = -\epsilon$ (where ϵ is the size of an energy unit and we treat each oscillator as a “particle”). Suppose instead that the solid has three oscillators and *four* units of energy. How does the chemical potential then compare to $-\epsilon$? (Don’t try to get an actual *value* for the chemical potential; just explain whether it is more or less than $-\epsilon$.)

Problem 3.36. Consider an Einstein solid for which both N and q are much greater than 1. Think of each oscillator as a separate “particle.”

(a) Show that the chemical potential is

$$\mu = -kT \ln \left(\frac{N+q}{N} \right).$$

(b) Discuss this result in the limits $N \gg q$ and $N \ll q$, concentrating on the question of how much S increases when another particle carrying no energy is added to the system. Does the formula make intuitive sense?

Problem 3.37. Consider a monatomic ideal gas that lives at a height z above sea level, so each molecule has potential energy mgz in addition to its kinetic energy.

(a) Show that the chemical potential is the same as if the gas were at sea level, plus an additional term mgz :

$$\mu(z) = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + mgz.$$

(You can derive this result from either the definition $\mu = -T(\partial S/\partial N)_{U,V}$ or the formula $\mu = (\partial U/\partial N)_{S,V}$.)