

The pressure can also be characterized by the slope of the tangent line:

$$P = -\frac{U_d(V_i) - U_\beta(V_f)}{V_i - V_f}. \quad (62)$$

This can be rearranged with final and initial quantities on opposite sides, yielding

$$U_\beta(V_f) + PV_f = U_d(V_i) + PV_i, \quad (63)$$

which is just the equality of the enthalpies of the two phases at the endpoints of the transition:

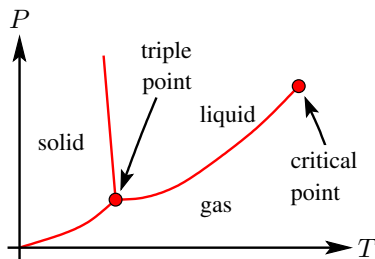
$$H_\beta(V_f) = H_d(V_i). \quad (64)$$

This is the condition for the coexistence of the two phases when the temperature and entropy play no role. That is the case here, where the energy *vs* volume curves were generated via calculations for  $T = 0$ .

More commonly, both pressure and temperature changes are considered, so that the Gibbs free energy plays a key role.

**HW Problem.** Schroeder problem 5.29, p. 172.

Also, in such cases, it is useful to map out the boundaries between the different phases in a *phase diagram* in the temperature-pressure plane. A convenient example is water, both because it is familiar and because it exhibits common general features. At low pressures, the phase diagram of water looks roughly like this:



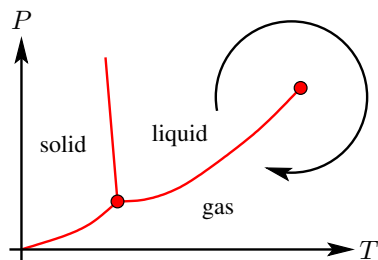
The temperatures and pressures of the triple point and critical point are

$$\begin{aligned} T_t &= 0.0098^\circ\text{C} & T_c &= 374^\circ\text{C} \\ P_t &= 6.12 \text{ mbar} & P_c &= 220.6 \text{ bar} . \end{aligned} \quad (65)$$

Some of the features of this phase diagram (taken to be typical) are:

- When a coexistence curve is encountered at fixed pressure, the temperature stops changing, while heat is added or removed. Generally, the volume changes during the transition. An analogous statement applies when a coexistence curve is encountered at given temperature.

- At a triple point, three phases coexist. Its pressure and temperature are unique, so it can serve as a standard.
- Beyond the critical point, the distinction between liquid and gas is lost. For temperatures above  $T_c$  or pressures above  $P_c$ , it's just a generic fluid. Near (within a fraction of a degree) the critical point, the fluid exhibits *critical opalescence*. It becomes milky white and opaque, scattering light strongly. The reason is that the uniformity that is generally characteristic of macroscopic equilibrium states disappears near the critical point. The fluid exhibits large, macroscopic fluctuations in density, which scatter light, leading to the milky appearance.
- The existence of an endpoint on the liquid-gas coexistence curve implies that it is possible to transform between the liquid and gas phases continuously:



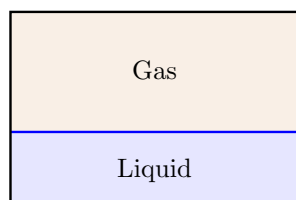
**Reading assignment.** Schroeder, section 6.1.

[EOC, Fri. 3/10/2006, #26]

At high pressures, above about one or two kilobars, water exhibits a number of additional solid phases having crystal structures different from that of familiar ice. Recall our discussion of silicon for a general idea of how solid-solid phase transitions can occur.

### 0.1.7 Phase coexistence curves

Consider a system containing two coexisting phases of a single substance, such as gas and liquid:

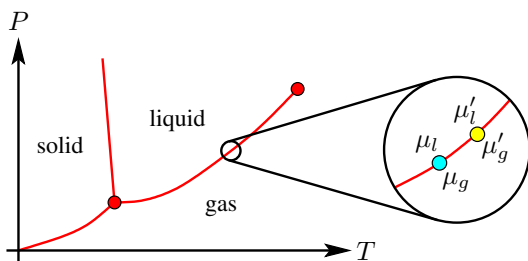


The two phases can be treated as subsystems in thermal, mechanical, and diffusive contact—they can exchange energy, volume, and particles. We've already seen that the conditions for equilibrium in such a case are:

$$T_g = T_l, \quad P_g = P_l, \quad \text{and} \quad \mu_g = \mu_l. \quad (66)$$

If any of those don't hold initially, then exchanges of the corresponding quantities will be biased in one direction until the equalities are established. These conditions are satisfied at all points on the coexistence curves, though the values of the temperature, pressure, and chemical potential vary from point to point on the curves.

Now consider two nearby points on the liquid-gas phase coexistence curve



On each side of the curve at each of the two points, we consider a state consisting entirely of liquid or entirely of gas. At each of the two points the pressures and temperatures of the gas and the liquid are equal, and so are the chemical potentials:

$$\mu_l = \mu_g \quad \text{and} \quad \mu_l' = \mu_g'. \quad (67)$$

Thus, the differences between the chemical potentials at the two points must be equal in the two phases:

$$\mu_l' - \mu_l = \mu_g' - \mu_g. \quad (68)$$

In the limit as the separation between the points goes to zero, the differences become infinitesimal:

$$d\mu_l = d\mu_g. \quad (69)$$

We showed recently that the chemical potential and the Gibbs free energy are closely related in a one-component system:

$$G = \mu N. \quad (70)$$

So the equality of the changes in the chemical potentials on the two sides of the curve implies equality of the changes in the Gibbs free energies:

$$dG_l = dG_g. \quad (71)$$

But we know that the total differential of  $G$  is

$$dG = -S dT + V dP + \mu dN, \quad (72)$$

so the equality of  $dG_l$  and  $dG_g$  implies that

$$-S_l dT + V_l dP = -S_g dT + V_g dP, \quad (73)$$

with  $dN = 0$ , since  $N$  is fixed. This can be rearranged to find the slope of the coexistence curve:

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}. \quad (74)$$

Now the entropy change is closely related to the heat transfer needed to accomplish the phase transformation:

$$Q = T \Delta S = L, \quad (75)$$

where  $L$  is the latent heat. Since we're treating  $Q$  and  $S$  as extensive quantities,  $L$  must represent one as well. Thus,  $L$  is the latent heat for the entire sample. We can use the latent heat to write the slope of the phase coexistence curve as:

$$\frac{dP}{dT} = \frac{L}{T(V_g - V_l)} = \frac{L}{T \Delta V}, \quad (76)$$

which is known as the *Clausius-Clapeyron equation*.

**HW Problem.** Schroeder problem 5.45, pp. 177, 178.

**HW Problem.** Schroeder problem 5.47, p. 179.

# Chapter 1

## Boltzmann Statistics

**Reading assignment.** Schroeder, section 6.2.

Our work on statistical mechanics has been focused principally on the understanding of the underlying probabilistic reason for macroscopic equilibrium of isolated systems and the justification that provides for the concepts and methods of thermodynamics. We have found that the statistical approach can easily be applied to a few simple systems to determine the entropy, from which we can obtain all the other important macroscopic properties of those systems.

We extended the thermodynamic formalism built upon that foundation by considering systems in contact with reservoirs that determine the equilibrium values of one or more of the intrinsic variables of the system, such as the temperature, pressure, or chemical potential. That extension was based upon the foundation established by our understanding of the central importance of probability, and therefore entropy, in determining the equilibrium state of a composite system consisting of the system of interest and the reservoir(s) to which is connected. The result was a collection of new formalisms based on appropriate thermodynamic potentials, each of which is obtained from the energy (or the entropy) of the system by Legendre transformation. Each of the potentials provides a basis for analyzing the thermodynamic behavior of a system with one or more of its intrinsic variables externally controlled. Derivatives of the potentials, like those of the entropy and the energy, are closely related to important thermodynamic quantities and/or materials properties, and the conditions for equilibrium of the system take the form of variational principles involving the potentials.

What is still missing in this picture is the appropriate statistical mechanical treatment of systems in contact with reservoirs. As we saw with the thermodynamics, a formalism directly targeted to the relevant type of reservoir contact helps to make the analysis simpler, avoiding the need to treat the reservoir itself as part of the system. The same is true in statistical mechanics, and our next goal is to begin to fill in the missing pieces of that

portion of thermal physics. We will find that the emerging formalism has tremendous power, enabling a substantial increase in the range of systems we can analyze.

Before embarking on that task, let's summarize in tabular form the essentials of the statistical and thermodynamic formalisms we have developed so far. This will make clear which pieces are still missing and suggest the relationships we can expect them to have with their thermodynamic kin.

Type of contact	State weight	Norm.	Massieu function	Thermodynamic potential
Isolated	1	$\Omega$	$S(U, V, N) = k \ln \Omega$	$U(S, V, N)$
Thermal			$S - \frac{1}{T}U$	$F = U - TS$
Mechanical			$S - \frac{P}{T}V$	$H = U + PV$
Therm. & Mech.			$S - \frac{1}{T}U - \frac{P}{T}V$	$G = U - TS + PV$
Diffusive			$S + \frac{\mu}{T}N$	$U - \mu N$
Therm. & Diff.			$S - \frac{1}{T}U + \frac{\mu}{T}N$	$\Phi = U - TS - \mu N$

The second and third columns are the basic ingredients of the statistical mechanics of the system, as the ratio of the weight in the second column to normalization constant in the third gives the probability of the state. For an isolated system, the states referred to are its accessible microstates, and the normalization constant  $\Omega$  is the sum of the weights of all the states, which is simply the number of microstates, since they are all assumed to have equal weight. That is,  $\Omega$  is the multiplicity of the macrostate with energy  $U$ . I've included in the thermodynamic columns, the fourth and fifth, both the Massieu functions, most of which we haven't used, and the corresponding thermodynamic potentials, most of which should be familiar by now. Clearly, we are missing the appropriate weights and normalization constants for the probability distributions of the states of systems in contact with reservoirs, and we will remedy that for the case of thermal contact in this chapter.

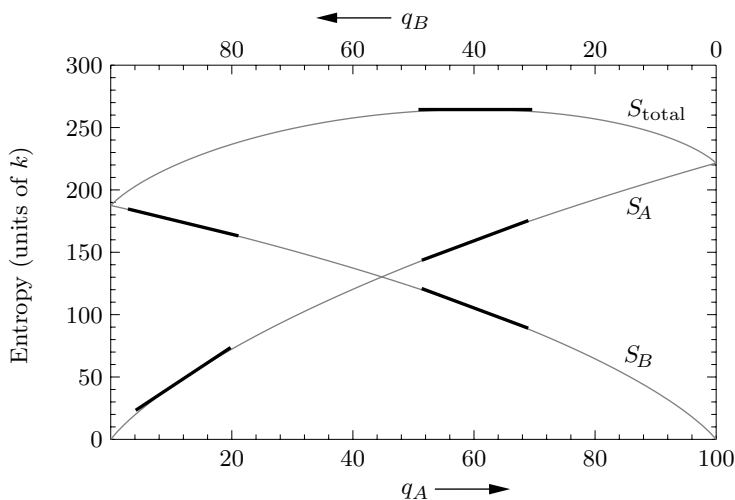
## 1.1 The Boltzmann factor

As we know, when a system is placed in thermal contact with a reservoir, exchanges of energy will be biased in such a way as to bring the temperature of the system into equality with that of the reservoir. Just as we developed a thermodynamic formalism for such a system that refers only to the variables of the system itself, we would like to develop a statistical formalism that refers only to the microstates of the system, ignoring those of the reservoir. It is only the temperature of the reservoir, its tendency to act as a source or sink of energy when in contact with a system, that should influence

the probabilities of the states of the system. Specifically, we expect that raising the temperature of the reservoir will increase the probabilities of higher-energy states of the system at the expense of lower-energy states.

To determine the probability distribution of the microstates of a system in thermal contact with a reservoir, we can make use of a strategy similar to the one we used to discover that the free energy  $F = U - TS$  determines the thermodynamics of such a system through the minimization of  $F$  in equilibrium. That is, we treat the combined system plus reservoir as an isolated system and apply the entropy-based formalism to the combined system.

Let's first think about the way in which the reservoir influences the probabilities of the states of the system. We've seen already that the overall multiplicity as a function of the division of energy between two macroscopic systems in thermal contact is strongly peaked at the point where the total entropy is maximized. We looked at a small-scale example of this long ago, when we examined Schroeder's Figure 3.1 (p. 87):



The situation depicted is the thermal contact between two Einstein crystals, system  $A$  having 300 oscillators and system  $B$  having 200 oscillators. The difference is small in this case, and the systems are individually quite small, but you can see that the entropy of the larger system is larger for any given energy than that of the smaller system, and the equilibrium state, in which the temperatures are equal, has greatest overall entropy, corresponding to its having greatest probability. The overall probability of any given division of energy, a macrostate of the combined system, is proportional to the product of the multiplicities of the corresponding macrostates of the individual systems. So the probability of any particular microstate of the smaller system is proportional to the multiplicity of the macrostate of the larger system when the latter has the remainder of the fixed total energy.

Thus, we can write the probability of the state  $n$  of the system, having

energy  $E_n$ , to within a normalization factor, as

$$\mathcal{P}_n \propto \Omega_R(U_{\text{tot}} - E_n), \quad (1.1)$$

where  $U_{\text{tot}}$  is the fixed total energy of the combined system plus reservoir, and  $\Omega_R(U_{\text{tot}} - E_n)$  is the multiplicity of the reservoir when its share of the energy is  $U_{\text{tot}} - E_n$ . We've suppressed the dependence of  $\Omega_R$  on the particle number  $N_R$  and the volume  $V_R$ . The first of these is rigorously fixed, since only thermal contact is allowed, and the volume can't change much, given that the amounts of energy exchanged with the system are very small compared to the total energy of the reservoir.

Because the entropy of the reservoir is related to its multiplicity by  $S_R = k \ln \Omega_R$ , we can write the multiplicity in terms of the entropy:

$$\Omega_R(U_{\text{tot}} - E_n) = e^{S_R(U_{\text{tot}} - E_n)/k}. \quad (1.2)$$

And, since the reservoir is much larger than the system, near the equilibrium state the energy  $U_{\text{tot}}$  is much greater than the system's energy  $E_n$ . This means it is a good approximation to expand the entropy of the reservoir in a Taylor series about the energy  $U_{\text{tot}}$  and truncate the result to the first-order term:

$$\begin{aligned} S_R(U_{\text{tot}} - E_n) &\approx S_R(U_{\text{tot}}) + \left[ \frac{\partial S(U_{\text{tot}})}{\partial U} \right]_{V,N} dU \\ &= S_R(U_{\text{tot}}) - \frac{1}{T} E_n. \end{aligned} \quad (1.3)$$

In the last line we used the definition of temperature in terms of  $\partial S/\partial U$ , together with the fact that the difference between the energy of interest and the reference energy  $U_{\text{tot}}$  is  $dU = -E_n$ .

When we insert this approximation for  $S_R$  back into the expression for the multiplicity of the reservoir, we find the probability for state  $n$  of the system to be

$$\mathcal{P}_n \propto e^{S_R(U_{\text{tot}})/k} e^{-E_n/kT}. \quad (1.4)$$

We can normalize the probability distribution by summing these values over all microstates of the system, then dividing each by that sum. The sum is

$$\begin{aligned} C &= \sum_n e^{S_R(U_{\text{tot}})/k} e^{-E_n/kT} \\ &= e^{S_R(U_{\text{tot}})/k} \sum_n e^{-E_n/kT} \\ &= e^{S_R(U_{\text{tot}})/k} Z, \end{aligned} \quad (1.5)$$

where we've denoted the sum of the exponentials by  $Z$ . The normalized probability of the  $n$ th state of the system is then

$$\mathcal{P}_n = \frac{e^{S_R(U_{\text{tot}})/k} e^{-E_n/kT}}{e^{S_R(U_{\text{tot}})/k} Z}, \quad (1.6)$$



which reduces immediately to

$$\mathcal{P}_n = \frac{e^{-E_n/kT}}{Z}. \quad (1.7)$$

The exponential  $e^{-E_n/kT}$  is called a *Boltzmann factor*, and the sum of the Boltzmann factors of all the microstates of the system

$$Z = \sum_n e^{-E_n/kT} \quad (1.8)$$

is called the *partition function* of the system.

[EOC, Mon. 3/13/2006, #27; HW08 closed, due Mon. 3/27/2006]

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