Reading assignment. Schroeder, section **3.2**.

0.1 Temperature

0.1.1 Review of our current picture

Now that we've seen a real example of entropy in action, it would be wise to review our current worldview, which is so closely centered on entropy.

- Equilibrium of macroscopic systems is a statistical effect—the most probable macrostate is the one we see, simply because it is so overwhelmingly more probable than others that differ from it in any substantial way. (How many times have I said this?)

- To discover the value of some macroscopic parameter that characterizes the macrostates of a pair of systems as they come to equilibrium, find the value of the parameter that yields the most probable macrostate.

- Macrostate probabilities are determined by summing the probabilities of the corresponding microstates. Assuming all microstates are equally probable, only the numbers of microstates, the multiplicities of the macrostates, are needed in order to characterize the relative probabilities of macrostates. This gives $\Omega(\text{parameter})$.

- Entropy is defined in terms of the macrostate multiplicity:

$$S = k \ln \Omega \,. \tag{1}$$

- Maximization of macrostate probability in equilibrium implies maximization of entropy in equilibrium:

$$\max_{\text{parameter}} \Omega(\text{parameter}) \Rightarrow \max_{\text{parameter}} S(\text{parameter}) = S_{\text{equilibrium}} \,. \tag{2}$$

  This is the second law of thermodynamics.

- Equilibrium values of macroscopic variables follow from the equilibrium value of the entropy. So far, we've found

$$\left(\frac{\partial S(U,V,N)}{\partial U}\right)_{V,N} = \frac{1}{T} \tag{3}$$

  for the ideal gas.

0.1.2 Temperature—the definition

We'll just take the expression we found for the ideal gas as our definition of temperature:

$$\left(\frac{\partial S(U,\dots)}{\partial U}\right)_{\dots} = \frac{1}{T}\,. \tag{4}$$

Really, we should call this derivative the *coldness* of the system, since it behaves inversely to temperature.

It's worth noting the dimensional implications of this equation: it implies that the product TS has dimensions of energy. But recall that for the ideal gas, the energy is proportional to kT, so this dimensional analysis explains why we multiplied the logarithm of the multiplicity by Boltzmann's constant when we defined entropy: it endows the temperature with the correct conventional units.

0.1.3 A graphical view of temperature

The definition of temperature expresses the coldness as the slope of the $S(U)$ curve when other macroscopic variables (e.g., V and N) are held fixed. Since this is the inverse temperature, this suggests that the slope becomes large as $T \to 0$ and decreases monotonically to zero as $T \to \infty$. So the entropy of a *single system* generally looks like this:

FIGURE: $S(U)$ graph for single system.

This isn't guaranteed, of course, since U may not be proportional to T, but this is the kind of general trend we expect for systems for which there is no upper bound to the energy. There are some oddball systems, and one of our toy systems, the two-state paramagnet is one, for which there is a maximum energy. At least in the case of the paramagnet, it's possible to employ devious experimental trickery to increase the energy beyond half the maximum, which corresponds to infinite temperature. In that region, the $S(U)$ curve is a decreasing function of U, so the temperature is negative. Still other systems can actually have increasing slope with energy. We'll concentrate on more normal systems for now.

For a pair of systems in thermal contact, it is the total entropy, the sum of the entropies of the subsystems, that is maximized in equilibrium, so that must actually have a maximum within the accessible range of values of the parameter characterizing the division of energy between them. Schroeder has a very instructive figure that displays both the total entropy and the subsystem entropies for a pair of relatively small Einstein crystals:

FIGURE: Schroeder's 3.1 (p. 87) or similar

Recall that we showed the equilibrium condition for thermal contact to be:

$$\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2}\,, \tag{5}$$

where U_1, the energy of the first subsystem, is taken as the parameter. This says the slopes of the two $S_i(U_i)$ curves must be equal in equilibrium. Since both curves have monotonically decreasing slopes, there is only one point where they can be equal, which is comforting since it means the equilibrium state has a unique value of the parameter. The point where those slopes are equal coincides with the maximum of the total entropy, as our derivation of the equilibrium condition showed.

There's another important point to be gleaned from Schroeder's wonderful figure. Since the slopes of the $S_i(U_i)$ curves decrease monotonically, for any given value of U_A, or q_A, the subsystem with the larger slope (greater coldness) will gain energy at the expense of the other system, as the total entropy approaches its maximum. This means that energy flows from the hotter system to the colder one, until their temperatures (or coldnesses) become equal at equilibrium.

Now, Schroeder's figure represents two nonidentical subsystems, so the two subsystem entropy curves must be drawn in opposite directions in order to have the equality of the slopes occur at the same point on the abscissa. Thus, without looking at the quantitative details it's a little difficult to see graphically why the slopes of the single-system entropies become equal exactly at the point where the total entropy is maximized. We've shown that algebraically, but we can also see it graphically. To do so in a simplified case, consider two identical systems to be placed in thermal contact. Since they are identical, their $S(U)$ curves are identical and can be plotted on the same graph. We'll suppose they initially have different energies, so their initial states are represented by different points on the $S(U)$ graph:

FIGURE: Single-system $S(U)$ graph for both systems, with initial points

The total energy U_{tot} is twice the average of the energies of the two systems, and remains so after thermal contact is established. The total entropy S_{tot} is twice the average of the entropies.

After thermal contact is established, energy flows from the hotter system to the colder one, and the points representing the states of the systems move along the $S(U)$ curve toward the midpoint, where their energies will each equal the average of their initial energies. As they do so, the average of their entropies, half S_{tot} increases, reaching a maximum (for the fixed U_{tot}) at equilibrium, when the two points coalesce and their slopes become equal.

The property of these $S(U)$ curves that made this graphical argument work is their convexity, as seen from above. That means the curve is everywhere above the midpoint of any line connecting distinct points on the curve, and it is that property that enabled us to visualize clearly the increase in total entropy as the systems approached thermal equilibrium.