

1. **An ideal gas on a lattice.** In class we introduced Boltzmann's microscopic definition of entropy:

$$S_B = k_B \ln \Omega.$$

A more general expression for entropy due to Gibbs is:

$$S_G = -k_B \sum_{\nu} P(\nu) \ln P(\nu),$$

where  $\nu$  is a microstate and  $P(\nu)$  is the probability of that microstate.

(i) For an isolated system (with fixed energy  $E$ , number of molecules  $N$ , and volume  $V$ ) show that  $S_B$  and  $S_G$  are identical. Recall that in such a system, all allowed microstates are equally likely.

(ii) For the rest of this problem, consider a collection of  $N$  indistinguishable particles arranged on a lattice of  $M$  cells. Each cell can be occupied by at most one particle, and particles in different cells do not interact. Calculate the total number  $\Omega(M, N)$  of possible configurations for this system.

(iii) Assuming  $M$ ,  $N$ , and  $M - N$  are all very large, use Stirling's approximation to write the Boltzmann entropy per cell,  $S_B/M$ , as a function of  $f \equiv N/M$  alone.

(iv) The occupation state of one cell in this lattice system is not affected by that of any other cell. As a result, the total entropy can be written as  $S = M s_{\text{cell}}$ , where  $s_{\text{cell}}$  is the entropy of a single cell. Using Gibbs' definition of entropy, calculate  $s_{\text{cell}}$  in terms of  $p_1$  and  $p_0$ , the probabilities of finding a particular cell occupied or unoccupied, respectively.

(v) By expressing  $p_0$  and  $p_1$  in terms of  $f$ , the fraction of occupied cells, demonstrate that the Boltzmann and Gibbs lattice gas entropies are the same.

(vi) Show that for the low density lattice gas ( $f \ll 1$ ),

$$S \approx -k_B V [\rho \ln(\rho v) - \rho],$$

where  $v$  is the volume of a single lattice cell, and  $\rho = N/V = N/(Mv)$  is the density.

(vii) From macroscopic thermodynamics we know that

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN,$$

so

$$\frac{p}{T} = \left( \frac{\partial S}{\partial V} \right)_{E, N}.$$

Use the expression you just obtained for the entropy of a low density lattice gas to explicitly compute the partial derivative. Express your result as the familiar ideal gas law:  $pV = Nk_B T$ . (You may be more familiar with  $pV = nRT$ . Make sure you think through the distinction between the two forms if it's not immediately obvious to you.)

(viii) An ideal gas is one with particles which do not interact. Is the lattice gas model whose entropy you found in parts (iii) through (v) an ideal gas? In other words, are there any interactions between the particles? Explain how your answer does or does not agree with your derivation of an ideal gas law in (vii).

## 2. The climb up.

“[The Boltzmann distribution] is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived.” —Richard Feynman

In class we presented a reasonable but less than rigorous derivation of the Boltzmann distribution,

$$P(\nu) \propto e^{-\beta E(\nu)},$$

for microstates  $\nu$  of a system that can exchange energy with a very large bath. This result was obtained from the fundamental relationship

$$P(\nu) \propto \Omega_B(E_T - E(\nu))$$

through a Taylor expansion of  $\ln \Omega_B$ , where  $E_T$  denotes the total energy shared by system and bath, and  $\Omega_B(E_B)$  is the number of bath microstates with energy  $E_B$ . Here you will develop this argument a little more carefully (and perhaps a little more convincingly—you may have wondered, for example, why we were Taylor expanding  $\ln \Omega_B$  and not  $\Omega_B$ ).

We will assume that  $\Omega_B$  has a large deviation form,

$$\Omega_B = [\omega_B(\epsilon_B)]^{N_B},$$

where  $N_B$  is the number of molecules in the bath,  $\epsilon_B \equiv E_B/N_B$  is the corresponding energy per molecule, and  $\omega_B(\epsilon_B)$  is a smooth function that does not depend on the size of the bath. As in lecture the dependence of  $\Omega_B$  on  $E_B$  will be used to define a property  $\beta$  of the bath:

$$\beta \equiv \left( \frac{\partial \ln \Omega_B}{\partial E_B} \right)_{N_B, V_B}$$

(i) Show that  $\beta$  is insensitive to the extent of the bath. In particular, relate  $\beta$  to  $\omega_B$  and derivatives of  $\omega_B$  with respect to  $\epsilon_B$ . Explain why this relationship indicates independence of the bath's size. (As we will see in future lectures, this  $\beta$  is an inverse temperature, so it should be pleasing  $\beta$  doesn't depend on bath size. When I say to put a test tube in a 25° C water bath, I shouldn't have to specify if the bath is 1 liter or 2 liters in volume. Assuming the volume of the bath is very big compared to the system, I should be able to specify  $\beta$  alone.)

(ii) Show that

$$\left( \frac{\partial \Omega_B}{\partial E_B} \right)_{N_B, V_B} = \beta \Omega_B$$

(iii) Show that

$$\left( \frac{\partial^2 \Omega_B}{\partial E_B^2} \right)_{N_B, V_B} = \beta^2 \Omega_B + c.$$

Identify the quantity  $c$  and explain why it can be neglected in the limit  $N_B \rightarrow \infty$ .

(iv) Calculate

$$\left( \frac{\partial^n \Omega_B}{\partial E_B^n} \right)_{N_B, V_B}$$

for arbitrary (integer)  $n$ . Do not include any terms that are negligible in the limit  $N_B \rightarrow \infty$ .

(v) Consider the Taylor expansion

$$\begin{aligned}\Omega_B(E_T - E) &= \Omega_B(E_T) - E \left( \frac{\partial \Omega_B}{\partial E_B} \right)_{N_B, V_B} + \frac{1}{2} E^2 \left( \frac{\partial^2 \Omega_B}{\partial E_B^2} \right)_{N_B, V_B} + \dots \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} (-E)^n \left( \frac{\partial^n \Omega_B}{\partial E_B^n} \right)_{N_B, V_B},\end{aligned}$$

where all partial derivatives are implicitly evaluated at  $E = 0$ .

Combining your results together with this expansion, show that the relationship

$$\Omega_B(E_T - E(\nu)) \propto e^{-\beta E(\nu)}$$

is exact in the limit  $N_B \rightarrow \infty$  of an infinitely large bath.

3. **The slide down.** Remarkably, the decomposition between system and bath (as well as our counting tools with partition functions) work equally well in a quantum setting as a classical setting. Consider a one-dimensional quantum harmonic oscillator, which has equally spaced discrete energy levels:  $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \dots$  (Warning: this  $\omega$  has nothing to do with what we were calling  $\omega$  in Problem 2, but the notation is reasonably standard in both cases. I'm sticking with it despite the possibility for confusion.) We assume the harmonic oscillator is in contact with a large thermal bath at temperature  $T$ .

(i) We have seen that the probability of occupying each state is given by the Boltzmann distribution:

$$P(\nu) = \frac{e^{-E(\nu)/k_B T}}{Q},$$

where  $E(\nu)$  is the energy of microstate  $\nu$  and  $Q$  is a normalization factor, also called the canonical partition function. For the quantum harmonic oscillator we have a relatively simple expression for  $E(\nu)$ . Use the equal spacing of energy levels to express the normalization factor  $Q$  as a function of  $T$ . [Hint: a geometric series can be summed exactly.]

(ii) By differentiating  $Q$  appropriately, determine the average energy  $\langle E \rangle$ , which should also be a function of  $T$ .

(iii) A common experiment is to measure how much energy must be put into a system to increase the temperature, the so-called heat capacity. In other words, the heat capacity measures the rate of energy increase with increasing temperature:

$$C = \frac{\partial \langle E \rangle}{\partial T}.$$

By writing  $\langle E \rangle$  in terms of a derivative of  $\ln Q$ , demonstrate that  $C$  is related to a second derivative of  $\ln Q$ . Use this observation to compute both the typical size of the energy fluctuations  $\langle \delta E^2 \rangle$  and the heat capacity  $C$ . Both of these quantities should be functions of the temperature.

(iv) Now imagine that the quantum harmonic oscillator is actually a three-dimensional harmonic oscillator but that the oscillations in the  $x$ ,  $y$ , and  $z$  dimensions are independent. Then

$$Q_{3D} = \sum_{x=0}^{\infty} \sum_{y=0}^{\infty} \sum_{z=0}^{\infty} e^{-(E_x + E_y + E_z)/k_B T}.$$

By separating out the three sums, relate  $Q_{3D}$  to  $Q_{1D}$  that you computed in part (a). What will be the new values of  $\langle E \rangle$ ,  $\langle \delta E^2 \rangle$ , and  $C$  for the three-dimensional oscillator?

(v) Repeat your logic from (iv) to determine  $\langle E \rangle$ ,  $\langle \delta E^2 \rangle$ , and  $C$  for  $N$  three-dimensional harmonic oscillators. Einstein considered this as a model for vibrations of the positions of  $N$  atoms around their equilibrium positions in a crystal. At that time, measurements of heat capacity in macroscopic materials could be handled in the lab even if the single-atom vibrations could not be directly measured. By detecting how  $C$  varied with temperature  $T$ , Einstein argued that one could infer microscopic information about the nature of the vibrations. Pretty cool!