Pathria, chapters 1 and 2.

Problems

(1.1) Stirling’s Approximation and Asymptotic Series.

One important approximation useful in statistical mechanics is Stirling’s approximation for \( n! \), valid for large \( n \). It’s not a traditional Taylor series: rather, it’s an asymptotic series. Later on in the course understanding the distinction may be important, so let’s study it here.

(a) Show, by converting the sum to an integral, that \( \log(n!) \sim (n+1/2) \log(n+1/2) - n \). Show that this is compatible with the more precise and traditional formula \( n! \approx (n/e)^n \sqrt{2\pi n} \); in particular, show that the difference of the logs goes to a constant as \( n \to \infty \). Show that the latter is compatible with the formula we’ll use below, \( n! \sim (2\pi/(n+1))^{1/2} e^{-(n+1)(n+1)^{n+1}} \), in that the difference of the logs goes to zero as \( n \to \infty \).

We want to expand this function for large \( n \). First, we interpolate between the integers to make factorial into an analytic function, evaluated (perversely) at \( z = n + 1 \): \( \Gamma(z) = (z - 1)! \).

Many formulas are equivalent: you need \( \Gamma(z+1) = z\Gamma(z) \), \( \Gamma(1) = 1 \), and \( \Gamma \) must be an analytic function.*

(b) Show, using the recursion relation, that \( \Gamma(z) \) is infinite (has a pole) at all the negative integers.

Stirling‡ found a nice expansion of \( \Gamma(z) \) in powers of \( 1/z = z^{-1} \):

\[
\begin{align*}
\Gamma[z] = & (z-1)! \sim (2\pi/z)^{1/2} e^{-z} z^z (1 + (1/12) z^{-1} + (1/288) z^{-2} - (139/51, 840) z^{-3} \\
& - (571/2, 488, 320) z^{-4} + (163, 879/209, 018, 880) z^{-5} \\
& + (5, 246, 819/75, 246, 796, 800) z^{-6} - (534, 703, 531/902, 961, 561, 601) z^{-7} \\
& - (4, 483, 131, 259/86, 684, 309, 913, 600) z^{-8} + \ldots)
\end{align*}
\]

* A typical definition is \( \Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt \): one can integrate by parts to show that \( \Gamma(z+1) = z\Gamma(z) \).

‡ Bender and Orszag, Advanced Mathematical Methods for Scientists and Engineers, p. 218.
This looks like a Taylor series in $1/z$, but is subtly different. For example, we might ask what the radius of convergence of this series is. The radius of convergence is the distance to the nearest singularity.

(c) Let $g(\zeta) = \Gamma(1/\zeta)$; then Stirling’s formula is some stuff times a Taylor series in $\zeta$. Plot the poles of $g(\zeta)$ in the complex $\zeta$ plane. Show, that the radius of convergence of Stirling’s formula applied to $g$ must be zero, and hence no matter how large $z$ is, Stirling’s formula eventually diverges.

Indeed, the coefficient of $z^{-j}$ eventually grows rapidly; Bender and Orszag show that the odd coefficients, for example, which start $A_1 = 1/12$, $A_3 = -139/51,840$ asymptotically grow as $A_{2j+1} \sim (-1)^j 2(2j)!/(2\pi)^{2(j+1)}$.

(d) Show explicitly, using the ratio test applied to the odd coefficients $A_{2j+1}$ above, that the radius of convergence of Stirling’s formula is indeed zero. (If you don’t remember about radius of convergence, check out the Web site mentioned at the top of the problem...)

This in no way implies that Stirling’s formula isn’t valuable! An asymptotic series of length $n$ approaches $f(z)$ as $z$ gets big, but for fixed $z$ it can diverge as $n$ gets larger and larger. In fact, asymptotic series are very common, and often are useful for much larger regions than are Taylor series.

(e) Compute 0! and 1! using Stirling’s formula, keeping the first few terms. Considering that this formula is expanding about infinity, it does pretty well!

Dyson argued that quantum electrodynamics is an asymptotic series. Check http://www.lassp.cornell.edu/sethna/Cracks/QED.html for a short discussion of how the most precise calculation in science takes the form of a series which cannot converge.
We can improve on the realism of the ideal gas by giving the atoms a small radius. If we make the potential energy infinite inside this radius ("hard spheres"), the potential energy is simple (zero unless the spheres overlap, which is forbidden). Let’s do this in two dimensions.

A two dimensional $L \times L$ box with hard walls contains an ideal gas of $N$ hard disks of radius $r \ll L$ (left figure). The disks are dilute: the summed area $N\pi r^2 \ll L^2$. Let $A$ be the effective volume allowed for the disks in the box: $A = (L - 2r)^2$.

(a) The area allowed for the second disk is $A - \pi(2r)^2$ (right figure), ignoring the small correction when the excluded region around the first disk overlaps the excluded region near the walls of the box. What is the allowed 2N-dimensional volume in configuration space, of allowed zero-energy configurations of hard disks, in this dilute limit? Ignore small corrections when the excluded region around one disk overlaps the excluded regions around other disks, or near the walls of the box. Leave your answer as a product of $N$ terms.

(b) What is the configurational entropy for the hard disks? Here, simplify your answer so that it does not involve a sum over $N$ terms, but valid to first order in the area of the disks $\pi r^2$. Show, for large $N$, that it is well approximated by $S_X \approx N k_B (1 + \log(A/N - b))$, with $b$ representing the effective excluded area due to the other disks. (You may want to derive the formula $\sum_{n=1}^{N} \log (A - (n - 1)\epsilon) = N \log (A - (N - 1)\epsilon/2) + O(\epsilon^2)$. What is the value of $b$, in terms of the area of the disk?

(c) Just as for the ideal gas, the internal energy is purely kinetic, and the kinetic energy and momentum-space entropy depend only on temperature and not on volume. So, if we isothermally expand this hard-disk gas from initial area $A_1$ to $A_2$, the heat flow $Q = T \Delta S$ is equal to the work done by the pressure. By differentiating both formulas for $Q$ with respect to $A_2$, find the pressure for the hard-sphere gas in the large $N$ approximation of part (b). Does it reduce to the ideal gas law for $b = 0$?
(1.3) **Jupiter!**

(See http://www.physics.cornell.edu/sethna/teaching/sss/jupiter/jupiter.htm.)

After Newton’s triumph in explaining Kepler’s laws, the next natural question was how the mutual gravitational forces between the planets affected their motion. It became clear that an exact solution to the two-body problem was possible because there were several conserved quantities, or integrals of the motion: energy, momentum, angular momentum, and one integral special to the inverse square law. After large efforts to identify similar conserved quantities in the three-body problem, a proof was constructed that there were not enough analytic integrals of the motion, and (more recently) with the demonstration that there are initial conditions where the motion is chaotic. The lack of an exact solution led to some insecurity. Simple calculations of the strength of Jupiter’s force on Earth suggested that, unless exceptional cancellation occurred, the Earth’s orbit should be significantly perturbed on historical time scales.

(a) Is the force of Jupiter on the Earth important on the time-scale of human civilization? Make a crude argument to justify your answer. For example, if the Earth were being pulled with constant gravitational field corresponding to the current force from Jupiter, how long would it take to build up enough potential energy to equal the binding energy to the Sun? For your convenience, the mass of Jupiter is $317.83 \ M_e$, the average radius of Jupiter’s orbit is $5.2 \ au$, and Jupiter’s year is $11.86$ earth years; the Sun is $332830 \ M_e$, and $G \approx 0.00012 \ au^3/M_e \ years^2$.

Let’s study a simpler problem, the **planar restricted three body problem**. We’ll assume that the Earth has negligible mass, that Jupiter goes in a circular orbit around the Sun, and that the Earth then moves by Newton’s laws in the plane of Jupiter’s orbit, experiencing the periodic potential of Jupiter and the Sun.

Download the program Jupiter from the appropriate link at the bottom of the page http://www.physics.cornell.edu/sethna/teaching/sss/jupiter/jupiter.htm. (Go to the directory with the binaries and select Jupiter.) Check that Jupiter doesn’t seem to send the Earth out of the Solar system. Try increasing Jupiter’s mass to $35000$. (If you type in a new value, you need to hit Enter to register it.)

If 100 Jupiters take 200 years to send Earth out of the solar system, why doesn’t one Jupiter eventually do so? Let’s see if we can understand why not.

(b) In the non-interacting planet approximation (where Earth and Jupiter are assumed to have zero mass), what topological surface is it in in the eighteen-dimensional phase space that contains the trajectory of the three bodies?

Try shifting “View” to “Earth’s trajectory”, and zoom in with the right mouse button to see the small effects of Jupiter on the Earth. (The left mouse button will launch new trajectories. Clicking with the right button will restore the original view.) Note that Earth’s orbit is broadened into a narrow torus. (The Earth’s position shifts depending on whether Jupiter is on the near or far side of the sun.) Try making Jupiter heavier.
(c) About how large can you make it before Earth’s orbit stops looking like a torus? (You can hit “Clear” and “Reset” to put the planets back to a standard starting point.) Admire the cool orbits when the mass becomes too heavy.

Thus, for “small” Jovian masses, the trajectory in phase space is warped and rotated a bit, so that its toroidal shape is visible looking at Earth’s position alone. (The circular orbit for zero Jovian mass is looking at the torus on edge.) The fact that the torus is preserved is what Kolmogorov, Arnol’d, and Moser (KAM) were able to prove, for small planetary masses and if Jupiter’s year is a sufficiently irrational multiple of Earth’s year.

The fact that the torus isn’t destroyed immediately is a serious problem for statistical mechanics! The orbit does not ergodically explore the entire allowed energy surface. This is a counterexample to Boltzmann’s ergodic “theorem”. That means that time averages are not equal to averages over the energy surface: our climate would be very unpleasant, on the average, if our orbit were ergodic.

Let’s use a Poincaré section to explore these tori, and the chaotic regions between them. If a dynamical system keeps looping back in phase space, one can take a cross-section of phase space and look at the mapping from that cross section back into itself (see figure).

The Poincaré section of a torus is a circle. The dynamics on the torus becomes a mapping of the circle onto itself.

(d) The original problem has an eighteen dimensional phase space. How many dimensions does the problem have in the center of mass frame? How many dimensions for the planar problem? How many for the restricted planar three body problem?

If we remove one more variable by going to a rotating coordinate system that rotates with Jupiter, the current state of our model can be described with four numbers: two positions and two momenta for the Earth. We can remove another variable by confining ourselves to a fixed “energy”. The true energy of the Earth isn’t conserved (because Earth feels
a periodic potential), but there is a conserved quantity which is like the energy in the rotating frame: more details described under “Help” or on the Web under “Description of the Three Body Problem”. This leaves us with a trajectory in three dimensions (so, for small Jovian masses, we have a torus embedded in a three-dimensional space). Finally, we take a Poincaré cross section: we plot a point of the trajectory every time Earth passes directly between Jupiter and the Sun. I plot the distance to Jupiter along the horizontal axis, and the velocity component towards Jupiter along the vertical axis; the perpendicular component of the velocity isn’t shown (and is determined by the “energy”).

Let’s be systematic about the breakdown of the torus as Jupiter’s mass increases. Set the View to Poincaré, and expand the window a bit. (I’ve set the dot size too small to see on my screen at the default setting, for some reason.) Set Jupiter’s mass to one of the stable values, and run for 1000 years. You should see a nice circular cross-section of a torus. Let’s be systematic. As you increase the mass (type in a mass, Enter, Reset and Run, repeat), watch the toroidal cross sections as they break down. Notice at $M_J = 22000 M_e$ the torus breaks into three circles.

(e) For trajectories inside the three circles in the Poincaré section, what is the average period of Earth’s year compared to Jupiter’s year, in the reference frame rotating with Jupiter? (This is called “mode locking”).

(f) Remember that for small Jovian mass the orbit appeared to fill out a torus in phase space. This torus will form a (perhaps warped) circle when we take the cross-section. Argue that it can fill out the circle only if the Jovian year is an irrational multiple of Earth’s (average) year. What will the cross-section look like if the ratio is rational, in the noninteracting planet approximation?

Chaos first arises in the neighborhood of periodic orbits. We’ll study the three-to-one mode locking at $M_J = 22000 M_e$. Select the preset for “Chaos” (or set $M_J$ to 22000 $M_e$, “View” to Poincaré, and Reset). Clicking on a point on the screen with the left mouse button will launch a trajectory with that initial position and velocity towards Jupiter; it sets the perpendicular component of the velocity to keep the current “energy”. (If you click on a point where energy cannot be conserved, the program will tell you so.) You can thus view the trajectories on a two-dimensional cross-section of the three-dimensional constant “energy” surface.

Notice that many initial conditions slowly fill out closed curves. These are topologically tori that have been squashed and twisted like rubber bands. Explore until you find some orbits that seem to fill out whole regions: these are chaotic bands. (You can “Continue” if the trajectory doesn’t run long enough to give you a complete feeling for the cross-section. You can zoom in with the right mouse button, and zoom out by expanding the window or by using the right button and selecting a box which extends outside the window.)

You’ve seen that near an orbit mode-locked to 3:1, there’s chaos. There are also chaotic bands near all the other rational ratios, if you zoom in enough. On the other hand, if the ratio is irrational and the motion smoothly covers the torus, then Jupiter’s effects can be proven to average out: in particular, the KAM theorem proved using fancy mathematical
methods that the tori for the non-interacting planet approximation were preserved for sufficiently small Jovian masses, if the ratio of Jovian year to Earth year was a good irrational. Near rational ratios (where the original orbit doesn’t fill out the torus) one almost immediately gets chaotic behavior.

What does this mean for statistical mechanics?

(1) It means that we’ll never prove the fundamental hypothesis that the time average behavior is given by an average over the energy surface — because it isn’t always true. Indeed, the KAM theorem shows that this isn’t a peculiarity of special equations or initial conditions: non-ergodicity happens in whole regions of Hamiltonian space.

(2) You might think that this is a peculiarity of having only a few particles. Surely if there are lots of particles, such funny behavior has to go away? On one of the early computers developed for the bomb project, Fermi, Pasta and Ulam tested this. They took a one-dimensional chain of atoms, coupled them with anharmonic potentials, and tried to look for thermalization. To quote them:

“Let us say here that the results of our computations were, from the beginning, surprising us. Instead of a continuous flow of energy from the first mode to the higher modes, all of the problems show an entirely different behavior. . . . Instead of a gradual increase of all the higher modes, the energy is exchanged, essentially, among only a certain few. It is, therefore, very hard to observe the rate of “thermalization” or mixing in our problem, and this was the initial purpose of the calculation.” E. Fermi, J. Pasta, S. Ulam, *Studies of Nonlinear Problems. I*, Los Alamos report LA-1940 (1955); reprinted in E. Fermi. Collected Papers, Vol II (Univ. of Chicago Press. Chicago, 1965), p. 978 (and in many other places).

It turns out that their system, in the continuum limit, gave a partial differential equation (the Kortweg-de Vries equation) that was even weirder than planetary motion: it had an infinite family of conserved quantities, and could be exactly solved using a kind of superpositions of fronts called “solitons”. This leads us far from our mission . . .

(iii) Ergodicity has been proven for the collisions of hard spheres in three dimensions. The kind of non-ergodicity found in planetary motion and in the Kortweg-de Vries equation has been seen in only a few other systems, mostly theoretical; anharmonic localized modes are a notable exception. (They were predicted and discovered here by Al Sievers: see, for example, “Experimental generation and observation of intrinsic localized spin wave modes in an antiferromagnet”, U. T. Schwarz, L. Q. English, and A. J. Sievers, *Phys. Rev. Lett.* 83 223 (1999) and “Statistical mechanics of a discrete nonlinear system”, K. O. Rasmussen, T. Cretegny, P. G. Kevrekidis, and N. Gronbech-Jensen, *Phys. Rev. Lett.* 84, 3740 (2000)).

(iv) Glasses fall out of equilibrium as they are cooled: they no longer ergodically explore around, but just oscillate about one of many metastable glassy states. There are many theoretical approaches to the glass transition that focus on this breaking of ergodicity. (One of many grew out of discussions with Daniel Fisher: see “Scaling Theory for the Glass Transition”, J. P. Sethna, J. D. Shore, and M. Huang, *Phys. Rev. B* 44, 4943 (1991) and (erratum) *Phys. Rev. B* 47, 14661 (1993).)
Thermodynamics was understood as an almost complete scientific discipline before statistical mechanics was invented. Stat mech can be thought of as the “microscopic” theory, which yields thermo as the “emergent” theory on long length and time scales where the fluctuations are unimportant.

The microcanonical stat mech distribution introduced in class studies the properties at fixed total energy \( E \), volume \( V \), and number of particles \( N \). We derived the microscopic formula
\[
S(N,V,E) = -k_B \log \Omega(N,V,E).
\]
The principle that entropy is maximal led us to the conclusion that two weakly-coupled systems in thermal equilibrium would exchange energy until their values of \( \frac{\partial S}{\partial E} \big|_{N,V} \) agreed, leading us to define the latter as the inverse of the temperature. By an analogous argument we find that systems that can exchange volume (by a thermally insulated movable partition) will shift until \( \frac{\partial S}{\partial V} \big|_{N,E} \) agrees, and that systems that can exchange particles (by semipermeable membranes) will shift until \( \frac{\partial S}{\partial N} \big|_{V,E} \) agrees.

How do we connect these statements with the definitions of pressure and chemical potential we get from thermodynamics? In thermo, one defines the pressure as the change in energy with volume \( \frac{\partial E}{\partial V} \big|_{N,S} \), and the chemical potential as the change in energy with number of particles \( \frac{\partial E}{\partial N} \big|_{V,S} \); the total internal energy satisfies
\[
dE = T \, dS - P \, dV + \mu \, dN.
\] (1.4.1)

(a) Show by solving equation (1.4.1) for \( dS \) that \( \frac{\partial S}{\partial V} \big|_{N,E} = P/T \) and \( \frac{\partial S}{\partial N} \big|_{V,E} = -\mu/T \) (simple algebra).

I’ve always been uncomfortable with manipulating \( dX \)'s. Let’s do this the hard way. Our “microcanonical” equation of state \( S(N,V,E) \) can be thought of as a surface embedded in four dimensions.

(b) Show that, if \( f \) is a function of \( x \) and \( y \), that \( \frac{\partial x}{\partial y} \big|_f \frac{\partial y}{\partial f} \big|_x \frac{\partial f}{\partial x} \big|_y = -1 \). (Draw a picture of a surface \( f(x,y) \), and draw a path that starts at \((x_0, y_0, f_0)\) and moves at constant \( f \) to \( y_0 + \Delta y \). The final point will be at \((x_0 + \frac{\partial x}{\partial y} f \Delta y, y_0 + \Delta y, f_0)\). Draw it at constant \( x \) back to \( y_0 \), and then at constant \( y \) back to \((x_0, y_0)\). What must \( f \) change to make this a single-valued function?) Applying this formula to \( S \) at fixed \( E \), derive the two equations in part (a) again.

(c) **Ideal Gas Thermodynamics.** Using the microscopic formula for the entropy of the ideal gas we derived in class,
\[
S(N,V,E) = \frac{5}{2} N k_B + N k_B \log \left[ \frac{V}{N h^3} \left( \frac{4 \pi m E}{3 N} \right)^{3/2} \right],
\] (1.4.2)
calculate \( T \), \( p \), and \( \mu \).

(d) **Maxwell Relations.** We can solve our microcanonical equation of state for the energy \( E(S,V,N) \): it’s the same surface in four dimensions, but looked at with a
different direction pointing "up". Now, the second derivatives of $E$ are symmetric: at fixed $N$, we get the same answer whichever order we take derivatives with respect to $S$ and $N$. Use this to show the Maxwell relation $\frac{\partial T}{\partial V}|_{S,N} = -\frac{\partial p}{\partial S}|_{V,N}$. Generate two other similar formulas by taking other second partial derivatives of $E$. There are a bewildering number of these relations.

(e) **Stat Mech check of the Maxwell relation.** Using equation (1.4.2) above, write formulas (non trivial!) for $T(S,V,N)$ and $P(S,V,N)$ for the ideal gas. Show explicitly that the Maxwell relation of part (d) is satisfied.
(1.5) Quantum Stat Mech: Density Matrices and Density of States.

(a) **Density matrices for photons.** Write the density matrix for a photon linearly traveling along \( z \) and linearly polarized along \( \hat{x} \), in the basis where \((1,0)\) and \((0,1)\) are polarized along \( \hat{x} \) and \( \hat{y} \). Write the density matrix for a right-handed polarized photon, \((1/\sqrt{2}, i/\sqrt{2})\), and the density matrix for unpolarized light. Calculate \( \text{Tr}(\hat{\rho}) \), \( \text{Tr}(\hat{\rho}^2) \), and \( S = -k_B \text{Tr}(\hat{\rho} \log \hat{\rho}) \). Interpret the values of the three traces physically: one is a check for pure states, one is a measure of information, and one is a normalization.

(b) **Density matrices for a spin.** (Adapted from Halperin’s course, 1976.) Let the Hamiltonian for a spin be
\[
H = -\frac{\hbar}{2} \mathbf{B} \cdot \hat{\sigma}
\]
where \( \hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \) are the three Pauli spin matrices, and \( \mathbf{B} \) may be interpreted as a magnetic field, in units where the gyromagnetic ratio is unity. Remember that \( \sigma_i \sigma_j - \sigma_j \sigma_i = 2i \epsilon_{ijk} \sigma_k \). Show that any \( 2 \times 2 \) density matrix may be written in the form
\[
\hat{\rho} = (1/2)(\mathbf{1} + \mathbf{p} \cdot \hat{\sigma}).
\]

Show that the equations of motion for the density matrix \( i\hbar \partial \hat{\rho} / \partial t = [H, \hat{\rho}] \) can be written as \( d\mathbf{p} / dt = -\mathbf{B} \times \mathbf{p} \).

In classical mechanics, the entropy goes to minus infinity as the temperature is lowered to zero; in quantum mechanics the entropy goes to zero, because states are quantized. This is Nernst’s theorem, the third law of thermodynamics. The classical phase-space volume has units of \( ((\text{momentum}) \times (\text{distance}))^3 \). It’s a little perverse to take the logarithm of a quantity with units, and the obvious candidate with these dimensions is Planck’s constant \( \hbar^3 \). Or should it be \( \bar{\hbar}^3 \)?

(c) **Arbitrary zero of the classical entropy.** Show that the choice of units changes the entropy per particle, and hence that Nernst’s theorem depends on getting this correct.

(d) **Fixing the zero of entropy: quantum Maxwell-Boltzmann ideal gas.** Consider \( N \) particles in a \( L \times L \times L \) box with periodic boundary conditions. Show that the single-particle energy eigenstates \( \exp(i\mathbf{k} \cdot \mathbf{x}) \) form a regular grid in \( k \) space: what is the spacing \( \Delta k \)? (Fixed boundary conditions would give a grid for only positive \( k \), with a different spacing.) Show that the many-particle energy eigenstates form a regular grid in \( 3N \)-dimensional \( \mathbf{k} \) space. Show that the constant-energy surfaces are spheres in this space. Assume that the particles are indistinguishable, but classical: only distinct fillings of single-particle eigenstates are different.* Calculate the entropy

* We’ll see soon that real quantum mechanics gives symmetry constraints on the many-body wave function, which changes the statistics from Maxwell-Boltzmann to either Fermi or Bose-Einstein. This calculation, however, remains valid at low densities and high pressures, where multiply occupied states are rare.
per particle in the limit $L \to \infty$, in analogy to the fixed boundary condition calculation in the text. Which version of Planck’s constant is the right one to normalize the units of phase space?