Pre-class Preparation


**Wednesday**  
Read: Chapter 3, Sec. 3.3 (Temperature) and 3.4 (Pressure & Chemical Potential; 3.4.1 is optional), Sec. 3.5 (Entropy & fussy stuff).

Pre-class question: 3.15: *What is the chemical potential?*. (Submit electronically by 9:30 Tuesday evening.)

**Friday**  
Read: Chapter 4, Sec. 4.1 (Liouville’s theorem), Sec. 4.2 (Ergodicity)  
Pre-class question: 4.6: *Perverse initial conditions*. (Submit electronically by 9:30 Thursday evening.)

**Monday**  
Read: Chapter 5, Sec. 5.1 (Engines & Heat Death)  
Pre-class question: 4.5: *No attractors in Hamiltonian systems*, and (if you have not yet studied heat engines) 5.5: *Pressure-volume diagram*. (Submit electronically by 9:30 Sunday evening.)

**Exercises**

Those in 4488 may choose two of the four exercises.

5.8: *The Arnol’d cat map.*


4.9: *2D turbulence and Jupiter’s great red spot*. (Hints are available in Python and Mathematica: http://pages.physics.cornell.edu/~sethna/StatMech/ComputerExercises.html.)

Class choose one

4.7: *Crooks: Exact results in non-equilibrium statistical mechanics.*

4.8: *Jarzynski: Exact results in non-equilibrium statistical mechanics.*
In-class exercises

Day 1

3.5 Hard sphere gas.

Fig. 1 Hard sphere gas.

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 us do this in two dimensions; three dimensions is no more complicated, but slightly harder to visualize.

A two-dimensional $L \times L$ box with hard walls contains a gas of $N$ hard disks of radius $r \ll L$ (Fig. 1). The disks are dilute; the summed area $N\pi r^2 \ll L^2$. Let $A$ be the effective area allowed for the disks in the box (Fig. 1): $A = (L - 2r)^2$.

Fig. 2 Excluded area around a hard disk.

(a) The area allowed for the second disk is $A - \pi (2r)^2$ (Fig. 2), 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$^1$ $\Omega^Q_{HD}$ of allowed zero-energy configurations of hard disks, in this dilute limit? Leave your answer as a product of $N$ terms.

Our formula in part (a) expresses $\Omega^Q_{HD}$ strangely, with each disk in the product only feeling the excluded area from the former disks. For large numbers of disks and small

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$^1$Again, ignore small corrections when the excluded region around one disk overlaps the excluded regions around other disks, or near the walls of the box. You may choose to include the $1/N!$ correction for identical particles if you wish, but be consistent with the ideal gas in part (c).
densities, we can rewrite $\Omega_{\text{HD}}^Q$ more symmetrically, with each disk feeling the same excluded area $A_{\text{excl}}$.

(b) Write $\log(\Omega_{\text{HD}}^Q)$ as a sum over the number of disks. Use $\log(1 - \epsilon) \approx -\epsilon$ and $\sum_{m=0}^{N-1} m = (N-1)(N-2)/2 \approx N^2/2$ to approximate $\log(\Omega_{\text{HD}}^Q) \approx N \log A - N \epsilon$, solving for $\epsilon$ and evaluating any sums over disks. Then use $-\epsilon \approx \log(1 - \epsilon)$ to write $\log(\Omega_{\text{HD}}^Q)$ in terms of $A - A_{\text{excl}}$.

(c) Find the pressure for the hard-disk gas in the large $N$ approximation of part (b). Does it reduce to the ideal gas law for $b = 0$? (Hint: Constant energy is the same as constant temperature for hard particles, since the potential energy is zero.)

Day 2

3.14 Entropy maximization and temperature. 🌐

Explain in words why, for two weakly coupled systems, that eqn 3.23

$$\rho(E_1) = \Omega_1(E_1)\Omega_2(E - E_1)/\Omega(E)$$

(1)

should be intuitively clear for a system where all states of energy $E$ have equal probability density. The discussion following eqn 3.23 introduces several ideas and quantities, but the main point is quick to derive. Using $S = k_B \log(\Omega)$, show in one step that maximizing the probability of $E_1$ makes the two temperatures $1/T = \partial S/\partial E$ the same, and hence that maximizing $\rho(E_1)$ maximizes the total entropy.

Day 2

3.1 Temperature and energy. 🌟

What units [joules, millijoules, microjoules, nanojoules, . . . , zeptojoules ($10^{-21}$ joules), yoctojoules ($10^{-24}$ joules)] would we use to measure temperature if we used energy units instead of introducing Boltzmann’s constant $k_B = 1.3807 \times 10^{-23}$ J/K?

Day 2

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2If this formula is not familiar, you can check the exact formula for the first few $N$, or convert the sum to an integral $\int_0^{N-1} mdm \approx \int_0^N mdm = N^2/2$. 
3.2 Large and very large numbers. ①

The numbers that arise in statistical mechanics can defeat your calculator. A googol is $10^{100}$ (one with a hundred zeros after it). A googolplex is $10^{10^{100}}$.3

Consider a monatomic ideal gas with one mole of particles ($N = \text{Avogadro’s number, } 6.02 \times 10^{23}$), room temperature $T = 300 \text{ K}$, and volume $V = 22.4 \text{ liters}$ (corresponding to atmospheric pressure).

(a) Which of the properties ($S$, $T$, $E$, and $\Omega(E)$) of our gas sample are larger than a googol? A googolplex? Does it matter what units you use, within reason?

If you double the size of a large equilibrium system (say, by taking two copies and weakly coupling them), some properties will be roughly unchanged; these are called intensive. Some, like the number $N$ of particles, will roughly double; they are called extensive. Some will grow much faster than the size of the system.

(b) Which category (intensive, extensive, faster) does each of the properties from part (a) belong to?

For a large system of $N$ particles, one can usually ignore terms which add a constant independent of $N$ to extensive quantities. (Adding $2\pi$ to $10^{23}$ does not change it enough to matter.) For properties which grow even faster, overall multiplicative factors often are physically unimportant.

Day 2

3.10 Triple product relation. (Thermodynamics, Mathematics)②

In traditional thermodynamics, there are many useful formulas like

$$dE = T\,dS - P\,dV,$$  \hspace{1cm} (2)

(see Section 6.4 and the inside front cover of this text). For example, if $V$ is held constant (and hence $dV = 0$ then $dE = T\,dS$ from eqn 2), giving $(\partial S/\partial E)|_V = 1/T$ (the definition of temperature, eqn 3.29).

(a) Use eqn 2 to rederive the traditional formula for the pressure $P$.

Let us consider a general formula of this type,

$$A\,dx + B\,dy + C\,df = 0.$$  \hspace{1cm} (3)

(b) What is $(\partial f/\partial x)|_y$? $(\partial f/\partial y)|_x$? $(\partial x/\partial y)|_f$? Use these to derive the triple product relation eqn 3.33, $(\partial x/\partial y)|_f(\partial y/\partial f)|_x(\partial f/\partial x)|_y = -1$.

I have always been uncomfortable with manipulating $dX$s.4 How can we derive these relations geometrically, with traditional partial derivatives? Our equation of state

3The firm Google is named after the number googol. They named their corporate headquarters the googleplex.

4They are really differential forms, which are mathematically subtle (see note 23 on p. 134).
$S(E,V,N)$ at fixed $N$ is a surface embedded in three dimensions. Figure 3.4 shows a triangle on this surface, which we can use to derive the general triple-product relation between partial derivatives.

(b) Derive the triple product relation \( \frac{\partial f}{\partial x} \bigg|_y \frac{\partial x}{\partial y} \bigg|_f \frac{\partial y}{\partial f} \bigg|_x = -1 \). (Hint: Consider the triangular path in Fig. 3.4, viewing \( f = S, \ x = E, \) and \( y = V, \) so the surface is \( S(E,V) \). The first side starts at the lower right at \( (E_0, V_0, S_0) \) and moves along the hypotenuse at constant \( S \) to \( V_0 + \Delta V \). The resulting vertex at the upper left will thus be at \( (E_0 + (\partial E/\partial V)S\Delta V, V_0 + \Delta V, S_0) \). The second side runs at constant \( E \) back to \( V = V_0 \), and the third side runs at constant \( V \) back to \( (E_0, V_0, S_0) \). The curve must close to make \( S \) a single-valued function; the resulting equation should imply the triple-product relation.)

Day 2

3.11 Maxwell relations. (Thermodynamics)

Consider the microcanonical formula for the equilibrium energy \( E(S,V,N) \) of some general system.\(^5\) One knows that the second derivatives of \( E \) are symmetric; at fixed \( N \), we get the same answer whichever order we take partial derivatives with respect to \( S \) and \( V \).

Use this to show the Maxwell relation

\[
\frac{\partial T}{\partial V} \bigg|_{S,N} = -\frac{\partial P}{\partial S} \bigg|_{V,N}.
\]

(This should take two lines of calculus or less.) Generate two other similar formulæ by taking other second partial derivatives of \( E \). There are many of these relations \(^2\).

Day 3

7.3 Phase-space units and the zero of entropy. (Quantum)

In classical mechanics, the entropy \( S = k_B \log \Omega \) goes to minus infinity as the temperature is lowered to zero. In quantum mechanics the entropy per particle goes to zero,\(^6\) because states are quantized and the ground state is the only one populated. This is Nernst’s theorem, the third law of thermodynamics.

The classical phase-space shell volume \( \Omega(E) \delta E \) (eqn 3.5) has units of \( ((\text{momentum}) \times \text{(distance)})^3 \). It is a little perverse to take the logarithm of a quantity with units. The natural candidate with these dimensions is Planck’s constant \( h^3 \); if we measure phase-space volume in units of \( h \) per dimension, \( \Omega(E) \delta E \) will be dimensionless. Of course, the correct dimension could be a constant times \( h \), like \( \hbar \ldots \)

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\(^5\)One can derive the formula by solving \( S = S(N,V,E) \) for \( E \). It is the same surface in four dimensions as \( S(N,V,E) \) (Fig. 3.4) with a different direction pointing ‘up’.

\(^6\)If the ground state is degenerate, the entropy does not go to zero, but it typically stays finite as the number of particles \( N \) gets big, so for large \( N \) the entropy per particle goes to zero.
(a) Arbitrary zero of the classical entropy. Show that the width of the energy shell $\delta E$ in the definition of $\Omega(E)$ does not change the microcanonical entropy per particle $S/N = k_B \log(\Omega(E))/N$ in a large system. Show that the choice of units in phase space does change the classical entropy per particle.

We want to choose the units of classical phase-space volume so that the entropy agrees with the quantum entropy at high temperatures. How many quantum eigenstates per unit volume of classical phase space should we expect at high energies? We will fix these units by matching the quantum result to the classical one for a particular system, and then check it using a second system. Let us start with a free particle.

(b) Phase-space density of states for a particle in a one-dimensional box. Show, or note, that the quantum momentum-space density of states for a free quantum particle in a one-dimensional box of length $L$ with periodic boundary conditions is $L/h$. Draw a picture of the classical phase space of this box $(p,x)$, and draw a rectangle of length $L$ for each quantum eigenstate. Is the phase-space area per eigenstate equal to $h$, as we assumed in Section 3.5?

This works also for $N$ particles in a three-dimensional box.

(c) Phase-space density of states for $N$ particles in a box. Show that the density of states for $N$ free particles in a cubical box of volume $V$ with periodic boundary conditions is $V^N/h^{3N}$, and hence that the phase-space volume per state is $h^{3N}$.

Let us see if this choice of units also works for the harmonic oscillator.

(d) Phase-space density of states for a harmonic oscillator. Consider a harmonic oscillator with Hamiltonian $\mathcal{H} = p^2/2m + \frac{1}{2}m\omega^2q^2$. Draw a picture of the energy surface with energy $E$, and find the volume (area) of phase space enclosed. (Hint: The area of an ellipse is $\pi r_1 r_2$ where $r_1$ and $r_2$ are the largest and smallest radii, corresponding to the major and minor axes.) What is the volume per energy state, the volume between $E_n$ and $E_{n+1}$, for the eigenenergies $E_n = (n + \frac{1}{2})\hbar\omega$?

Day 3

4.2 Liouville vs. the damped pendulum. (Mathematics, Dynamical systems)

The damped pendulum has a force $-\gamma p$ proportional to the momentum slowing down the pendulum. It satisfies the equations

$$\dot{x} = \frac{p}{M},$$
$$\dot{p} = -\gamma p - K \sin(x).$$  (5)

You show here that ideal gases should calculate entropy using phase-space units with $h = 1$. To argue this directly for interacting systems usually involves semiclassical quantization [3, chapter 48, p. 170] or path integrals [1]. But it must be true. We could imagine measuring the entropy difference between the interacting system and an ideal gas, by slowly and reversibly turning off the interactions between the particles, measuring the entropy flow into or out of the system. Thus, setting the zero of entropy for the ideal gas sets it for all systems.
At long times, the pendulum will tend to an equilibrium stationary state, zero velocity at \( x = 0 \) (or more generally at the equivalent positions \( x = 2m\pi \), for \( m \) an integer); \((p, x) = (0, 0)\) is an attractor for the damped pendulum. An ensemble of damped pendulums is started with initial conditions distributed with probability \( \rho(p_0, x_0) \). At late times, these initial conditions are gathered together near the equilibrium stationary state; Liouville’s theorem clearly is not satisfied.

**Fig. 3 Total derivatives.** The total derivative gives the local density as measured by a particle moving with the flow: \( d\rho/dt = d/dt (\rho(x(t), p(t), t)) \). Applying the chain rule gives the definition of the total derivative, \( d\rho/dt = \partial\rho/\partial t + \partial\rho/\partial x \dot{x} + \partial\rho/\partial p \dot{p} \).

(a) In the steps leading from eqn 4.5 to eqn 4.7, why does Liouville’s theorem not apply to the damped pendulum? More specifically, what are \( \partial \dot{p}/\partial p \) and \( \partial \dot{q}/\partial q \)?

(b) Find an expression for the total derivative \( d\rho/dt \) in terms of \( \rho \) for the damped pendulum. If we evolve a region of phase space of initial volume \( A = \Delta p \Delta x \) how will its volume depend upon time?

**References**

