

Instructor's Solutions Manual
to accompany

AN INTRODUCTION TO
Thermal Physics

Daniel V. Schroeder

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Preface

This *Instructor's Solutions Manual* contains solutions to all 486 problems in *An Introduction to Thermal Physics*. The solutions are not just hints or outlines—I have tried to include as many algebraic steps as a typical student would need to write out, plus enough prose to explain both the method of solution and the meaning of the results. Of course, one can always say more about almost any question or calculation; I'm sure that many students and instructors can add further insight to what is written here.

About 75 of the problems in the book require some sort of automatic computation, beyond what can be done with a simple pocket calculator. Although the problems themselves do not assume any particular computing environment, their solutions do. In this manual I have used three different microcomputer-based computing environments: the *Excel* spreadsheet program for making tables of numbers and some graphs; *Mathematica* for plotting formulas, for numerical integration and root finding, and for occasional symbolic computation; and *True BASIC* for the Monte Carlo simulations in Problems 8.26 through 8.32. I recognize that no computing environment is perfect in all respects, and that others will make different choices, for excellent reasons. My own choices were determined by trade-offs among such factors as personal familiarity, ease of use, readability of the printed record, portability between operating systems, apparent stability over time, and consistency within this manual. I would be interested to hear from instructors or students who have solved the more intricate problems using other computing environments.

If you haven't already, please browse the web site for the book, which (for the foreseeable future) is at the URL "<http://physics.weber.edu/thermal/>". There you will find some instructions on getting started with *Excel*, *Mathematica*, and *True BASIC*, plus a variety of other information about the book and about thermal physics. Perhaps most importantly, you will find a page listing corrections to the book, and a similar page for this manual. If you find errors in either that are not listed on the web pages, please let me know.

I am extremely grateful to the many instructors and students who have already used *An Introduction to Thermal Physics* and sent comments and suggestions. This manual has benefited from several corrections that were contributed by instructors using draft chapters. I am also indebted to Deb Badger for the use of her Macintosh G4 computer, which allowed me to run the *True BASIC* simulations in a reasonable amount of time.

DVS
Ogden, Utah
November 1, 2000

Note on this corrected edition: I have taken the opportunity to correct all of the known errors in the original edition of this manual. It is a pleasure to thank B. Blakie, L. Cominsky, M. Davis, A. Gavrin, J. Lockhart, and G. Wiegerinck for bringing many of these errors to my attention. I have also redrawn and improved a number of the illustrations, including all of the spreadsheet-generated graphs. Further corrections and suggestions are always welcome.

August 5, 2016

Energy in Thermal Physics

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Problem 1.1. (Fahrenheit temperature scale.)

- a) To take Celsius to Fahrenheit, we want a linear function that takes 0 to 32 and 100 to 212. Imagining a graph of this function, the vertical intercept must be 32 and the slope must be $(212 - 32)/(100 - 0) = 9/5$; therefore the function is

$$(T \text{ in } ^\circ\text{F}) = \frac{9}{5}(T \text{ in } ^\circ\text{C}) + 32.$$

Inverting this function is now just a matter of algebra:

$$(T \text{ in } ^\circ\text{C}) = \frac{5}{9}[(T \text{ in } ^\circ\text{F}) - 32].$$

- b) Plugging -273.15°C into the first formula gives the value -459.7 for absolute zero in degrees Fahrenheit.

Problem 1.2. To convert from Fahrenheit to Rankine, you would simply add 460, which raises the value of absolute zero (see the previous problem) to zero as desired. Rankine and kelvin temperatures are both measured from the same zero-point, so the conversion between them is just the factor of $9/5$ found in the previous problem, with no constant term added. A kelvin degree is *bigger* than a Rankine degree, so the conversion is

$$(T \text{ in } ^\circ\text{R}) = \frac{9}{5}(T \text{ in K}),$$

which is equivalent to

$$1^\circ\text{R} = \frac{5}{9}\text{ K}.$$

Room temperature, about 300 K , would therefore be $\frac{9}{5} \cdot 300 = 540$ on the Rankine scale.

Problem 1.3. (Kelvin temperature examples.)

- a) Human body temperature is “officially” 37°C , or 310 K . (In the U.S., this official temperature is traditionally converted to 98.6°F —a classic example of failing to round off insignificant digits.)
- b) Water is supposed to boil at 100°C , so that would be 373 K .
- c) I remember a night in Minnesota when the temperature was reported as -29°F . That converts to -34°C , which is 239 K .
- d) 196°C would be 77 K , so liquid nitrogen is about four times closer to absolute zero than room temperature is.
- e) 327°C would be 600 K , to three significant figures.

Problem 1.4. “Twice as hot” on the Celsius (or Fahrenheit) scale would make no sense, because the zero point is chosen arbitrarily. There’s no fundamental sense, for instance, in which 2°C is twice as hot as 1°C . But if we measure temperatures from absolute zero, then “twice as hot” makes perfect sense: the melting point of lead is twice room temperature; the sun’s surface is 20 times room temperature; and so on. This is another good reason to use kelvin temperatures.

Problem 1.5. I was taught to leave the thermometer in my mouth for at least three minutes. However, the bulb of the thermometer must come most of the way up to body temperature within 10 or 20 seconds; waiting three minutes is necessary only because we want a reading that is accurate to within a fraction of a degree. The numerical value of the “relaxation time” could therefore be anywhere from 10 or 20 seconds to three minutes, depending on exactly how we define it.

Problem 1.6. On a cold morning, when I step from the bathroom rug into the tub for my shower, the tub feels a lot colder to my feet than the rug. Yet they must be at essentially the same temperature, since they’ve been right next to each other all night long in a room that is pretty well insulated from the weather. In fact the rug is just as cold as the tub, but it sucks heat out of my feet much more slowly due to its relatively poor thermal contact and low heat capacity. For another example, see the quote on page 48.

Problem 1.7. (Thermal expansion of liquids.)

- a) The mercury thermometer from my medicine cabinet has a roughly cylindrical bulb that measures 4 mm in diameter by 5 mm long. Its volume is therefore about 60 mm^3 . Under a 1°C temperature increase, this much mercury should increase in volume by

$$\Delta V = \beta V \quad \Delta T = (1.81 \times 10^{-4} \text{ K}^{-1})(60 \text{ mm}^3)(1 \text{ K}) = 0.011 \text{ mm}^3.$$

The expansion, however, takes place inside a narrow tube with a length of 8.5 mm (the length of a 1°C increment on the scale) and unknown cross-sectional area. Assuming that the tube is cylindrical, its radius would have to be

$$r = \sqrt{\frac{\Delta V}{\pi \ell}} = \sqrt{\frac{0.011 \text{ mm}^3}{\pi(8.5 \text{ mm})}} = 0.02 \text{ mm},$$

so its diameter would be only 0.04 mm. No wonder it’s so hard to see the column of mercury, even with the optical magnification of the glass!

- b) As the water in a lake cools, the densest water will sink to the bottom and the less dense water will rise to the top. Below 4°C , this means that the *warmer* water will sink while the *colder* water rises. The first water to freeze will therefore be at the top; and since ice is even less dense, the ice floats on the surface. This ice then insulates the rest of the water from the cold weather, so even during a long, cold winter, only the smallest ponds freeze completely from top to bottom.

If the thermal expansion coefficient of water were always positive, then the coldest water in a lake would always be at the bottom, so ice would form first at the bottom.

If ice were also more dense than liquid water, the lake would freeze from the bottom up. Without the insulating layer of ice on top, many lakes would freeze completely, and any fish in these lakes would be frozen along with them. (If ice were still less dense than water, I suppose bits of ice would form at the bottom and then float to the surface.)

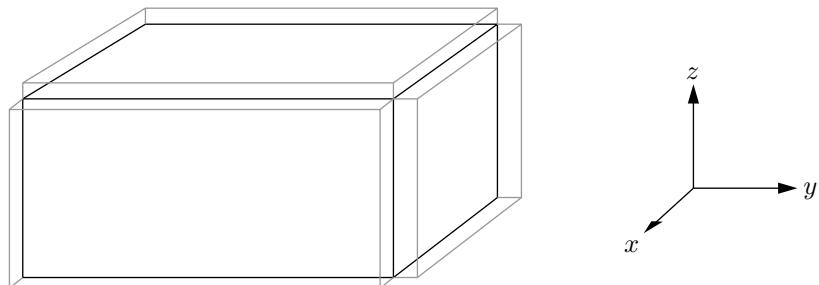
Problem 1.8. (Thermal expansion of solids.)

- a) Let's say the annual temperature extremes are -30 and $+40$ Celsius, for a total variation of 70 K. Under this variation, the change in length of a 1-km steel bridge would be

$$\Delta L = L \Delta T = (1.1 \times 10^{-5} \text{ K}^{-1})(1000 \text{ m})(70 \text{ K}) = 0.77 \text{ m} = 77 \text{ cm}.$$

To be safe, I'd design the bridge to accommodate at least a meter of thermal expansion.

- b) The two metals in the coil have different thermal expansion coefficients, so as the temperature increases, one expands more than the other, causing the coil to coil further and turn.
- c) Imagine a rectangular solid with dimensions L_x , L_y , and L_z . When the temperature increases, the solid expands in all three dimensions:



Assuming that the expansion is infinitesimal, we consider it to be equivalent to adding the three shaded slabs to the volume of the solid, neglecting the corner strips omitted from the diagram. Then the volume increase is

$$\Delta V = (\Delta L_x)L_yL_z + (\Delta L_y)L_xL_z + (\Delta L_z)L_xL_y.$$

Writing each ΔL in terms of the appropriate linear expansion coefficient, this becomes

$$\begin{aligned}\Delta V &= (\alpha_x L_x \Delta T)L_yL_z + (\alpha_y L_y \Delta T)L_xL_z + (\alpha_z L_z \Delta T)L_xL_y \\ &= (\alpha_x + \alpha_y + \alpha_z)V \Delta T.\end{aligned}$$

Comparing to the definition of the volume expansion coefficient β , we see that this result has the same form, with $\beta = \alpha_x + \alpha_y + \alpha_z$.

Alternatively, we can rewrite the definitions of α and β in terms of derivatives:

$$= \frac{1}{L} \frac{dL}{dT}; \quad \beta = \frac{1}{V} \frac{dV}{dT}.$$

(Technically, these should be partial derivatives, with pressure held fixed.) With the aid of the product rule, the derivation is now nothing but symbol-pushing:

$$\begin{aligned}\beta &= \frac{1}{V} \frac{dV}{dT} = \frac{1}{V} \frac{d}{dT} (L_x L_y L_z) = \frac{1}{V} \left[\frac{dL_x}{dT} L_y L_z + \frac{dL_y}{dT} L_x L_z + \frac{dL_z}{dT} L_x L_y \right] \\ &= \frac{1}{V} \left[(-_x L_x) L_y L_z + (-_y L_y) L_x L_z + (-_z L_z) L_x L_y \right] \\ &= \frac{1}{V} [-x + -y + -z] L_x L_y L_z = -x + -y + -z.\end{aligned}$$

Problem 1.9. For a mole of air at room temperature and atmospheric pressure,

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(8.31 \text{ J/mol K})(300 \text{ K})}{10^5 \text{ N/m}^2} = 0.025 \text{ m}^3 = 25 \text{ liters.}$$

Problem 1.10. Consider an “average” room measuring 4 meters square by 3 meters high. The number of air molecules (at room temperature and atmospheric pressure) is

$$N = \frac{PV}{kT} = \frac{(10^5 \text{ N/m}^2)(4 \text{ m})(4 \text{ m})(3 \text{ m})}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 1.2 \times 10^{27} \approx 10^{27}.$$

(That’s about 2000 moles.)

Problem 1.11. Since the rooms are connected by an open door, the pressure must be the same in each room; if it weren’t, air would rush from one room into the other. Also we’re told that the volume of each room is the same. Now look at the ideal gas law: $PV = NkT$. The left-hand-side is the same for both rooms, so Room B, which has a smaller T , must have a *larger* N , hence a larger mass of air.

Problem 1.12. The volume per molecule for an ideal gas at room temperature and atmospheric pressure is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{10^5 \text{ N/m}^2} = 4.1 \times 10^{-26} \text{ m}^3 = 41 \text{ nm}^3.$$

If we imagine each molecule being in a cube of this volume, then the width of the cube would be the cube root of this number, 3.5 nm. This is then a good estimate of the average distance between neighboring molecules. The diameter of a molecule like N_2 or H_2O , on the other hand, is only a few ångstroms, about ten times smaller than this average distance.

Problem 1.13. In each case we merely need to determine the total number of protons plus neutrons in one molecule (or for the solids, one atom). Since a mole of protons or neutrons has a mass of one gram, this same number is the mass of the sample in grams.

- a) Water is H_2O ; each hydrogen atom has just a single proton while the oxygen has 8 protons and 8 neutrons, so we have 18 nucleons total, and a mole of water therefore has a mass of 18 grams.

- b) Each nitrogen atom has 7 protons and 7 neutrons, so an N₂ molecule has 28 nucleons and a mole of them therefore has a mass of 28 grams.
- c) The atomic mass of lead is 207 (a weighted average over several common isotopes), so a mole of lead has a mass of 207 g.
- d) A quartz “molecule” has 28 nucleons in the silicon atom and 32 in the two oxygen atoms, for a total of 60, so a mole of quartz has a mass of 60 g.

Problem 1.14. For a mole of pure N₂, the mass would be 28 g; for O₂, the mass would be 32 g; and for Ar, the mass would be 40 g. For the mixture found in dry air, therefore, the mass would be the weighted average:

$$M = (0.78)(28 \text{ g}) + (0.21)(32 \text{ g}) + (0.01)(40 \text{ g}) = 28.96 \text{ g} \approx 29.0 \text{ g.}$$

Problem 1.15. The upward buoyant force on the balloon is equal to the weight of the air displaced. Assuming that this force is approximately in balance with gravity, we can write

$$\rho_0 V g = (M + \rho V)g \quad \text{or} \quad \rho_0 = \rho = M/V,$$

where ρ_0 is the density of the surrounding air, V is the volume of the balloon, M is the mass of the un lled balloon and payload, and ρ is the density of the air inside the balloon. According to the ideal gas law, the density of air is

$$\rho = \frac{mn}{V} = \frac{mP}{RT},$$

where m is the mass of one mole of air (29 g, as shown in the previous problem). This formula applies either inside or outside the balloon, with the same pressure in both places but different temperatures. Therefore the balance of forces implies

$$\frac{mP}{RT_0} = \frac{mP}{RT} = \frac{M}{V},$$

where T is the temperature inside the balloon and T_0 is the temperature outside. A bit of algebra then yields

$$\frac{1}{T} = \frac{1}{T_0} - \frac{M}{m} \frac{R}{PV}.$$

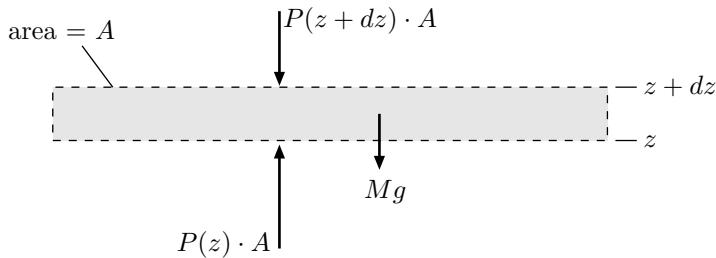
Let's assume an outside air temperature of 290 K, and atmospheric pressure. The volume of the balloon can be estimated from Figure 1.1: Comparing to the heights of the people standing underneath, I estimate the balloon in the foreground to have a diameter of about 50 feet or 15 meters, and therefore a volume of $\frac{4}{3}\pi r^3 = 1770 \text{ m}^3$. The mass of the un lled balloon and payload is assumed to be 500 kg, so the previous expression evaluates to

$$\frac{1}{T} = \frac{1}{290 \text{ K}} - \frac{500 \text{ kg}}{0.029 \text{ kg}} \frac{8.31 \text{ J/K}}{(10^5 \text{ N/m}^2)(1770 \text{ m}^3)} = \frac{1}{290 \text{ K}} - \frac{1}{1235 \text{ K}} = \frac{1}{379 \text{ K}}.$$

Thus the temperature inside the balloon must be about 379 K or just over 100°C. (Thanks to Chuck Niederriter for informing me that this is indeed a typical operating temperature.) Assuming this temperature, the mass of the air inside the balloon should be roughly

$$M_{\text{air}} = mn = \frac{mPV}{RT} = \frac{(0.029 \text{ kg})(10^5 \text{ N/m}^2)(1770 \text{ m}^3)}{(8.31 \text{ J/K})(379 \text{ K})} = 1600 \text{ kg},$$

more than three times the mass of the un lled balloon and payload!

Problem 1.16. (The exponential atmosphere.)

- a) Mechanical equilibrium requires that the vertical forces balance:

$$P(z + dz) \cdot A + Mg = P(z) \cdot A, \quad \text{or} \quad P(z + dz) - P(z) = \frac{Mg}{A},$$

where A is the area of the slab and M is its total mass. Plugging in $M = \rho A dz$, canceling the A 's, and dividing through by dz gives

$$\frac{P(z + dz) - P(z)}{dz} = \rho g \quad \text{or} \quad \frac{dP}{dz} = \rho g.$$

- b) The density of the gas is $\rho = M/V = Nm/V = Pm/kT$, where m is the average molecular mass and in the last step I've used the ideal gas law. Thus the differential equation becomes

$$\frac{dP}{dz} = \frac{mg}{kT} P.$$

- c) The function $P(z)$ is one whose derivative is some constant (namely mg/kT) times itself. The function Ae^{az} has this property, where $a = mg/kT$ and A is an arbitrary constant whose interpretation is the value of P when $z = 0$ (since $e^0 = 1$). Thus the solution is

$$P(z) = P(0) e^{-mgz/kT}.$$

The density $\rho(z)$ is just m/kT times $P(z)$, so it has the same exponential form with a different constant out in front. The constant, $P(0) m/kT$, must be $\rho(0)$ because the exponential again equals 1 at $z = 0$.

- d) I'll take $z = 0$ at sea level so that $P(0) = 1$ atm. I'll also take $T = 280$ K as an average temperature at the locations given. Air is 80% nitrogen (N_2), so the mass of a molecule in kilograms is about $.028/N_A$, hence the quantity kT/mg is roughly $RT/(.028 \text{ kg})(9.8 \text{ N/kg}) = 8500$ meters or about 28,000 feet. (This is the height at which the pressure has fallen to $1/e$ atmospheres.) Plugging in the elevations given, I find for Ogden (4700 feet), $P = e^{-.17}$ atm = .84 atm; Leadville (10500 feet), $P = .69$ atm; Mt. Whitney (14,500 feet), $P = .59$ atm; Mt. Everest (29,000 feet), $P = .35$ atm.

Problem 1.17. (The virial expansion.)

- a) Truncating the virial expansion after the second term, we have

$$PV = nRT \left(1 + \frac{B(T)}{(V/n)} \right).$$

For given values of P , T , and B , this is a quadratic equation for V/n . However, it is reasonable to assume that the second term on the right-hand side is small compared to the first, so we can find V/n accurately enough from the ideal gas law. At 100 K and 1 atm,

$$\frac{V}{n} = \frac{RT}{P} = \frac{(8.315 \text{ J/mol K})(100 \text{ K})}{1.013 \times 10^5 \text{ Pa}} = 0.00823 \text{ m}^3/\text{mol}.$$

Therefore the correction term under these conditions is

$$\frac{B(T)}{V/n} = \frac{160 \times 10^{-6} \text{ m}^3/\text{mol}}{0.00823 \text{ m}^3/\text{mol}} = 0.019.$$

In other words, the volume of the gas is about 2% less than the ideal gas law would predict (or at a given volume, the pressure is 2% less). Repeating the calculation for the other temperatures, I find:

T	$B/(V/n)$
100	0.019
200	0.0021
300	0.00017
400	+0.00027
500	+0.00041
600	+0.00043

Notice that at reasonably high temperatures, the correction to the ideal gas law is less than one part in a thousand (at atmospheric pressure).

- b) Attractive forces between molecules should reduce the pressure of a gas, yielding a negative second virial coefficient, while repulsive forces should increase the pressure, leading to a positive second virial coefficient. Apparently the forces between molecules can be either attractive or repulsive, with attractive forces dominating at low temperatures and repulsive forces dominating at high temperatures. Does this make sense? I think so. Molecules attract each other weakly when they're close but not "touching." At low temperatures, they'll be moving slowly enough for this attraction to have a significant effect on the pressure. But when molecules collide head-on, they repel each other strongly. At high temperatures, when the molecules are moving very fast, this should be the more significant effect.
- c) Solving the van der Waals equation for P , then factoring out nRT/V on the right-hand side, puts it into the form

$$PV = nRT \left(\frac{1}{1 - nb/V} - \frac{an}{RTV} \right).$$

The second term on the right-hand side is already in the form of a temperature-dependent coefficient over V/n , so it contributes to $B(T)$. To put the first term into the proper form, apply the binomial expansion (or recognize it as the sum of a geometric series):

$$[1 - (nb/V)]^{-1} \approx 1 + (-1)(-nb/V) + \frac{1}{2}(-1)(-2)(nb/V)^2 = 1 + nb/V + (nb/V)^2.$$

(This expansion should be valid at low density, when n/V is sufficiently small.) Thus the van der Waals equation takes the approximate form

$$PV \approx nRT \left(1 + \frac{b}{V/n} + \frac{b^2}{(V/n)^2} - \frac{a/RT}{V/n} \right).$$

From this expression we can read off the second and third virial coefficients,

$$B(T) = b \quad \frac{a}{RT}, \quad C(T) = b^2.$$

Since a and b are positive, $B(T)$ is positive in the high-temperature limit and negative in the low-temperature limit, as desired.

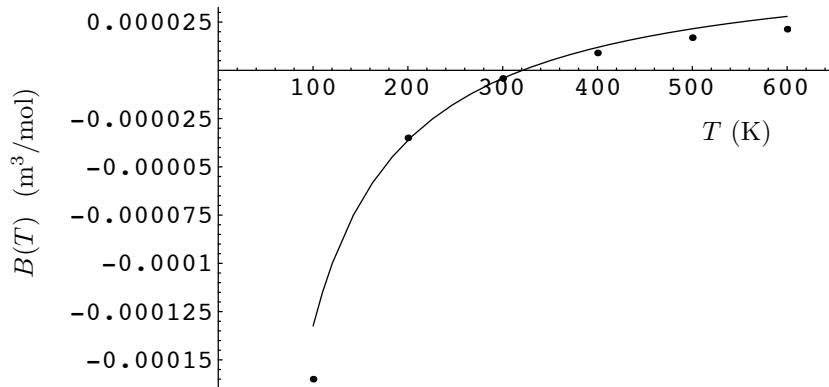
- d) First I'll estimate the values of a and b . In the high-temperature limit, $B(T) \rightarrow b$ so I want $b \approx 30 \times 10^{-6} \text{ m}^3/\text{mol}$ according to the data. On the other hand, I want $B(T) = 0$ at approximately 300 K, so at this temperature, $0 = b - (a/RT)$ or

$$a = bRT \approx (30 \times 10^{-6} \text{ m}^3/\text{mol})(8.3 \text{ J/mol K})(300 \text{ K}) \approx 0.10 \text{ J m}^3/\text{mol}^2.$$

(An interpretation of these numbers is given in the text on page 181.) To plot the formula and the data I gave the following instructions to Mathematica:

```
data = ListPlot[{{100, -.00016}, {200, -.000035}, {300, -.0000042},  
                 {400, .000009}, {500, .0000169}, {600, .0000213}}];  
vdl = Plot[.00003 - .1/(8.315*t), {t, 100, 600}];  
Show[data, vdl, PlotRange -> {{0, 650}, All}];
```

The plot showed that my estimated values of a and b were both too low, so I adjusted them by trial and error, eventually settling on the values $a = 0.16 \text{ J m}^3/\text{mol}^2$ and $b = 0.00006 \text{ m}^3/\text{mol}$, which gave the following graph:



This is about as good a fit to the data as I could get, adjusting only two parameters to fit six data points. So although the van der Waals equation does have the right qualitative features, and can be made to fit data in an approximate way, it is nowhere near exact.

Problem 1.18. In applying equation 1.21, it is often easier to multiply and divide the quantity k/m by Avogadro's number, so it becomes R/M , where M is the molar mass of the gas. Then, for N₂ at 300 K,

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.31 \text{ J/K})(300 \text{ K})}{0.028 \text{ kg}}} = 517 \text{ m/s.}$$

Problem 1.19. The mass of an oxygen molecule is 16 times that of a hydrogen molecule (32 nucleons vs. 2). The rms speed is inversely proportional to the square root of the mass, so we would expect the average speed of the hydrogen molecules to be greater, by a factor of $\sqrt{16} = 4$.

Problem 1.20. The atomic mass of fluorine is 19, so a UF₆ molecule containing uranium-238 has a molecular weight of 352. The rms speed at room temperature for such a molecule is

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.31 \text{ J/K})(300 \text{ K})}{0.352 \text{ kg}}} = 145.8 \text{ m/s.}$$

If instead the molecule contains uranium-235, the molecular weight is only 349. The rms speed is then larger by a factor of

$$\sqrt{\frac{352}{349}} = 1.0043,$$

a difference of 0.43%. Numerically, the rms speed of the lighter isotope is 146.4 m/s.

Problem 1.21. The hailstones strike the window at intervals of 1/30 second (on average). During this time, the average force exerted by the window on the hailstone must be

$$\bar{F}_x = m \frac{\Delta v_x}{\Delta t},$$

where Δv_x is the change in the component of the hailstone's velocity perpendicular to the window. Assuming elastic collisions and a velocity of 15 m/s at 45°, this change in velocity is $2v \cos 45^\circ = 21 \text{ m/s}$. The average pressure is just the average force divided by the surface area:

$$\bar{P} = \frac{\bar{F}}{A} = \frac{m \Delta v_x}{A \Delta t} = \frac{(0.002 \text{ kg})(21 \text{ m/s})}{(0.5 \text{ m}^2)(0.033 \text{ s})} = 2.5 \text{ N/m}^2.$$

This is less than atmospheric pressure by a factor of about 40,000. (However, the instantaneous pressure during a collision is much higher, and the force of each hailstone is localized, not distributed over the whole window.)

Problem 1.22. (Effusion.)

- a) As in equation 1.9, Newton's laws imply that each molecule colliding with the surface exerts an average pressure of

$$\overline{P} = \frac{m \Delta v_x}{A \Delta t}.$$

For an elastic collision, $\Delta v_x = 2v_x$, as in equation 1.11. If there are N molecules, the total pressure is the sum of N terms of this form, one for each molecule; the sum over v_x values can be written as N times the average, $N\overline{v_x}$. Therefore,

$$P = \frac{m \cdot 2N\overline{v_x}}{A \Delta t} \quad \text{or} \quad N = \frac{PA \Delta t}{2m\overline{v_x}}.$$

- b) This result follows directly from equation 1.15:

$$kT = m\overline{v_x^2} \quad \Rightarrow \quad (\overline{v_x^2})^{1/2} = \sqrt{\frac{kT}{m}}.$$

- c) What I called N in part (a) now becomes ΔN , the decrease in the number of molecules in the container. Substituting the result of part (b) for $\overline{v_x}$ then gives

$$\Delta N = \frac{PA \Delta t}{2m} \sqrt{\frac{m}{kT}}.$$

Now use the ideal gas law to eliminate P , divide through by Δt , and take the limit $\Delta t \rightarrow 0$ to obtain

$$\frac{dN}{dt} = \frac{A}{2V} \sqrt{\frac{kT}{m}} N = \frac{1}{\tau} N,$$

where the last equality defines the constant τ . This equation says that $N(t)$ is a function whose derivative is $1/\tau$ times itself; such a function is

$$N(t) = N(0)e^{-t/\tau}.$$

- d) To calculate τ , we first need the quantity $\sqrt{kT/m} = \sqrt{RT/M}$, where M is the molar mass of the gas. Assuming that the gas is air near room temperature, this quantity is

$$\sqrt{\frac{RT}{M}} = \sqrt{\frac{(8.3 \text{ J/mol K})(300 \text{ K})}{.029 \text{ kg/mol}}} = 293 \text{ m/s} \approx 300 \text{ m/s}.$$

The characteristic time for a 1-liter container punctured by a 1-mm² hole is then

$$\tau = \frac{2V}{A\sqrt{RT/M}} = \frac{2(.001 \text{ m}^3)}{(10^{-6} \text{ m}^2)(300 \text{ m/s})} = 6.7 \text{ seconds.}$$

- e) To estimate the volume of the tire, I'll take it to be a cylinder, 2 meters long and 2 cm in radius: $V = \pi(.02 \text{ m})^2(2 \text{ m}) = .0025 \text{ m}^3$. Then if τ is one hour, the area of the hole should be roughly

$$A = \frac{2V}{\tau\sqrt{RT/M}} = \frac{2(.0025 \text{ m}^3)}{(3600 \text{ s})(300 \text{ m/s})} = 5 \times 10^{-9} \text{ m}^2,$$

implying that the diameter of the hole is a little under a tenth of a millimeter.

- f) Suppose the volume of the space capsule is 50 m^3 , the area of the window is $.2 \text{ m}^2$, and the temperature inside is comfortable for humans. Then the characteristic time for the air to escape would be

$$\tau = \frac{2(50 \text{ m}^3)}{(.2 \text{ m}^2)(300 \text{ m/s})} = 1.7 \text{ s.}$$

This is the time for roughly $2/3$ of the air to escape. Even if they can open and close the window in half a second, the amount of air that escapes will be significant.

Problem 1.23. Helium has three degrees of freedom (translational only) per molecule, so $U = 3N \cdot \frac{1}{2}kT = \frac{3}{2}PV$ by the ideal gas law. (Note that P and V determine the product NT , so you don't need to know the temperature.) For $P = 10^5 \text{ N/m}^2$ and $V = 10^{-3} \text{ m}^3$, the product PV is 100 J so the total thermal energy is 150 J. For air (oxygen and nitrogen), however, there are five degrees of freedom (three translational, two rotational) at room temperature, so the total thermal energy is $\frac{5}{2}PV = 250 \text{ J}$.

Problem 1.24. Each lead atom has six degrees of freedom: three from kinetic energy and three from potential, corresponding to vibrations in the three orthogonal directions. The atomic mass of lead is about 207, so a gram of lead contains $1/207$ moles. Therefore the total thermal energy is approximately

$$U_{\text{thermal}} = \frac{f}{2}nRT = \frac{6}{2} \frac{1}{207} (8.31 \text{ J/K})(300 \text{ K}) = 36 \text{ J.}$$

Problem 1.25. Translation: Like any other gas molecule, a water vapor molecule has three translational degrees of freedom, for motion in the x , y , and z directions. Rotation: A water vapor molecule has no axis of symmetry, so it can rotate about all three perpendicular axes, giving three rotational degrees of freedom. Vibration: A water vapor molecule has *three* independent modes of vibration, which can be described in various ways. First consider stretching of the two O-H bonds. Each H atom can independently move in and out, toward and away from the O, so that's two modes of vibration; alternatively, we can take one mode to be the simultaneous motion of both H atoms in phase with each other, and the other to be simultaneous out-of-phase motion. But even with no stretching of the bonds, the angle between them can vary as the molecule flexes, with the two H atoms moving toward and away from each other. So in total there are three vibrational modes, each of which counts as two degrees of freedom (three kinetic, three potential). Add in the translational and rotational degrees of freedom and we have 12 degrees of freedom in total. (At ordinary temperatures, however, the two stretching modes are frozen out while the flexing mode is only partially active.)

Problem 1.26. The flow of energy from the battery to the resistor is work, not heat. Even though the resistor gets warm, there is no spontaneous flow of energy from the battery to the resistor that is caused by a difference in their temperatures. In fact, the battery could very well be cooler than the resistor, yet keep providing energy to it. The flow of energy from the resistor to the water, however, *is* a spontaneous one caused by the resistor being hotter than the water. This energy flow is therefore classified as heat, not work.

Problem 1.27. Temperature increase with no heat added: The resistor in the previous problem provides an example; it gets hot as the battery supplies energy in the form of work (not heat). Other examples would be “heating” a cup of tea in the microwave, or compressing air to pump up a bicycle tire, or simply rubbing your hands together. Heat input with no increase in temperature: I can think of two types of examples. The first is a phase change, like boiling a pot of water on the stove. Heat is constantly flowing in, but the temperature of the water remains at 100°C (or at whatever the boiling temperature is at your altitude). The second type of example is when the system does work on its surroundings to compensate for the energy put in as heat. For instance, you could have a gas in a cylinder with a flame under it, while letting the piston out fast enough that the gas actually cools.

Problem 1.28. Let’s say we have 200 g of water, initially at 20°C. Then the total energy required to bring it to 100° is (200)(80) calories or 67,000 J. The microwaves pump in 600 J per second, so the total time required should be $(67,000 \text{ J})/(600 \text{ J/s}) = 110 \text{ seconds}$, or about two minutes. (This coincides roughly with my experience.)

There is no heat involved in this process because heat is a spontaneous flow of energy from a hot object to a cold object. In this case there is no hotter object from which heat is flowing into the water. (If anything, heat is flowing *out* of the water into the cup and the surrounding air.) The transfer of energy from the magnetron into the water is classified as electromagnetic *work*.

Problem 1.29. The 5° temperature increase of the water requires the input of energy: specifically, 5 calories per gram, or 1000 calories total (4200 J). This energy *could* have entered as heat, but it also could have entered as work, for instance, by someone vigorously stirring or shaking the water. So the answer is that I can conclude *nothing* about how much heat was added to the water. (Probably the amount of heat added was no greater than 1000 cal, since there’s no easy way for the water to *lose* energy by doing work. But it’s not impossible, and it’s certainly permitted by the first law of thermodynamics.)

Problem 1.30. For this experiment I used about an ounce of water in an eight-ounce plastic bottle that was small enough to hold between my fingers and thumb for rapid shaking. I was able to shake it back and forth about four times per second, with the water traveling about a foot during each half-shake or about eight feet total per second. Using the water’s average speed to compute the kinetic energy that gets converted to thermal energy, I would then predict for each half-shake

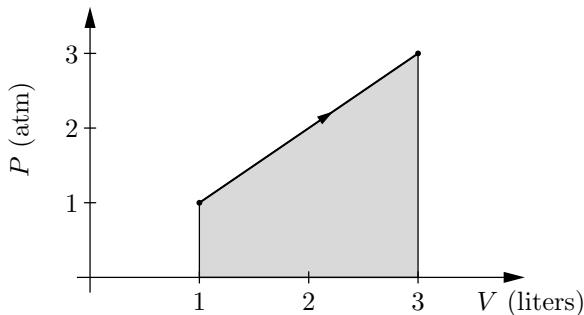
$$mc\Delta T = \frac{1}{2}mv^2 \quad \text{or} \quad \Delta T = \frac{v^2}{2c} = \frac{1}{2(4200 \text{ J/kg } ^\circ\text{C})} \left(\frac{0.3 \text{ m}}{0.125 \text{ s}} \right)^2 = 0.00069^\circ\text{C}.$$

With eight half-shakes per second, the temperature rise after one minute should therefore be about 0.3°C. What I actually found upon trying the experiment three times, shaking for three to five minutes each time, was a pretty consistent temperature rise of 1.0°C per minute. However, my theoretical calculation could be on the low side because I used only the average speed of the water, when perhaps I should have used the maximum speed. Also, as a control I tried simply holding the bottle in my hand for a few minutes, and this

produced a temperature increase of between 0.3 and 0.5°C per minute simply from the heat of my fingers. To do the experiment more accurately it would probably be best to use a bit more water, and to wear gloves or otherwise insulate the system from the heat of my fingers. But I've already demonstrated that kinetic energy can be converted to thermal energy, producing a temperature increase of the expected order of magnitude.

Problem 1.31. (A helium expansion example.)

a)



- b) The work done is minus the area under the graph (shaded). The easiest way to compute this area is to note that the average pressure during the process is 2 atm, so

$$W = \bar{P} \Delta V = (2 \text{ atm})(2 \text{ liters}) \approx (2 \times 10^5 \text{ Pa})(2 \times 10^{-3} \text{ m}^3) = 400 \text{ J.}$$

The minus sign indicates that 400 J of work is done *by* the gas on its surroundings.

- c) Each helium atom has three degrees of freedom, so at any point the thermal energy of the helium is $U = \frac{3}{2}NkT = \frac{3}{2}PV$. The change in energy during this process is

$$\begin{aligned} \Delta U &= \frac{3}{2}[P_f V_f - P_i V_i] = \frac{3}{2}[(3 \text{ atm})(3 \text{ liters}) - (1 \text{ atm})(1 \text{ liter})] \\ &= 12 \text{ liter atm} = 1200 \text{ J.} \end{aligned}$$

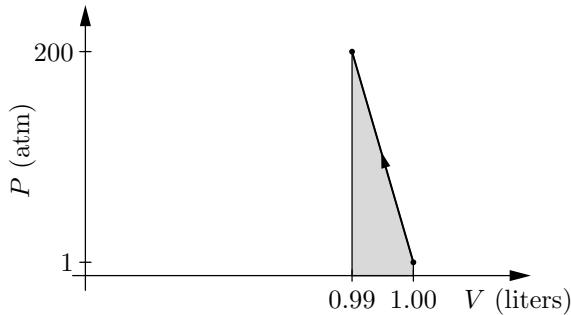
- d) By the first law,

$$Q = \Delta U - W = 1200 \text{ J} - (-400 \text{ J}) = 1600 \text{ J.}$$

This amount of heat *enters* the gas.

- e) To cause such an increase in pressure (and temperature) as the gas expands, you must provide heat, for instance, by holding a flame under the cylinder and letting the piston out slowly enough to allow the pressure to rise as desired.

Problem 1.32. (Compressing water.)



I've drawn the PV curve as a straight line only because this is the simplest plausible shape; probably it should be slightly concave-upward, to indicate that the more you compress the water, the harder it is to compress further. In any case, the average pressure during this process is *approximately* 100 atm, so the work done on the water is

$$W \approx \bar{P} \Delta V = (100 \text{ atm})(0.01 \text{ liter}) = 1 \text{ liter atm} = 100 \text{ J.}$$

This is as much work as you would do lifting a 10-kg object a meter off the ground (say a heavy bag of groceries from the floor to the table). Considering the enormous pressures involved, you may have expected the work to be much greater. However, work involves not just force but also displacement, and here the displacement (change in volume) is very small.

Problem 1.33. The work done on the gas is positive when its volume decreases (step *C*), negative when its volume increases (step *A*), and zero when its volume stays the same (step *B*). The net work done during the whole cycle is positive, since the average pressure is higher during step *C* than during step *A*. To determine the sign of the change in energy, note that for an ideal gas, $U = \frac{1}{2}NkT = \frac{1}{2}PV$, so any increase in P or V indicates an increase in U . Therefore the energy increases during steps *A* and *B*, but decreases during step *C*. For the whole cycle the energy must be unchanged, since both P and V are unchanged. To determine the sign of Q for each step, just use the first law: $Q = \Delta U - W$. Here are the results in tabular form:

	W	ΔU	Q
step <i>A</i> :		+	+
step <i>B</i> :	0	+	+
step <i>C</i> :	+		
whole cycle:	+	0	

Apparently, the net result of the cycle is to absorb energy as work and emit energy as heat. Furthermore, the heat emitted during step *C* could go to a different place than the source of heat during steps *A* and *B*, so this "machine" could move heat around. Similar cycles can act as refrigerators (see Chapter 4), but this particular cycle would not make a practical refrigerator because the absorption of heat does not always take place at a lower temperature than the emission of heat.

Problem 1.34. It's easiest to first compute the work done during each step, using $W = P \Delta V$. For steps *A* and *C* there is no work done because the volume doesn't change; for steps *B* and *D* the pressure is constant so we don't need to set up an integral. So, for instance, the work done on the gas during step *D* is $+P_1(V_2 - V_1)$.

Since each molecule has five degrees of freedom, the thermal energy of the gas at any point is $U = \frac{5}{2}NkT = \frac{5}{2}PV$. Therefore ΔU during any step is $\frac{5}{2}(P_f V_f - P_i V_i)$, where *f* stands for final and *i* stands for initial. For instance, during step *D*, $\Delta U = \frac{5}{2}P_1(V_2 - V_1)$.

The heat added to the gas during any step is just $Q = \Delta U - W$. So again for step *D* we have $Q = \frac{5}{2}P_1(V_2 - V_1) - P_1(V_2 - V_1) = \frac{3}{2}P_1(V_2 - V_1)$.

Here's a table of values for all four steps, computed in this way:

	W	ΔU	Q
step A:	0	$\frac{5}{2}V_1(P_2 - P_1)$	$\frac{5}{2}V_1(P_2 - P_1)$
step B:	$P_2(V_2 - V_1)$	$\frac{5}{2}P_2(V_2 - V_1)$	$\frac{7}{2}P_2(V_2 - V_1)$
step C:	0	$\frac{5}{2}V_2(P_2 - P_1)$	$\frac{5}{2}V_2(P_2 - P_1)$
step D:	$P_1(V_2 - V_1)$	$\frac{5}{2}P_1(V_2 - V_1)$	$\frac{7}{2}P_1(V_2 - V_1)$
whole cycle:	$(P_2 - P_1)(V_2 - V_1)$	0	$(P_2 - P_1)(V_2 - V_1)$

I found the entries in the last row by adding up each of the columns and simplifying the result as much as possible.

What's actually happening must be something like the following: During step A we hold the piston fixed but put heat in (say from a flame); during step B we let the piston out and continue putting heat in at such a rate as to maintain constant pressure; during step C we hold the piston fixed but suck heat out, perhaps by immersing the whole thing in an ice bath; and during step D we push in the piston while still sucking heat out so the pressure again remains steady.

The net work done on the gas during the whole cycle is negative; in other words, the net work done *by* the gas is positive. This is as expected, because the pressure is higher when the gas is expanding than when it is being compressed. Notice that the net work is just minus the area enclosed by the rectangular cycle on the diagram. The net change in the energy of the gas is zero, as it must be: the state of the gas (as determined by its pressure and volume) is the same at the end of a cycle as at the beginning. Therefore the net heat put into the gas must be minus the net work done, as indeed it is. In summary, this procedure results in a net conversion of heat input into work output.

Problem 1.35. Using the ideal gas law to eliminate T from equation 1.39 gives

$$V \left(\frac{PV}{Nk} \right)^{f/2} = \text{constant.}$$

Raising both sides of this equation to the power $2/f$ then gives

$$P \cdot V^{(1+\frac{f}{2})\frac{2}{f}} = Nk \cdot (\text{constant})^{2/f}.$$

The right-hand side of this equation is just some new constant, while the exponent on V is $\frac{2}{f} + 1 = (2+f)/f = \gamma$, the adiabatic exponent. Therefore, during adiabatic compression or expansion of an ideal gas,

$$P \cdot V^\gamma = \text{constant.}$$

Problem 1.36. (Pumping up a bicycle tire.)

- a) From equation 1.40 (derived in the previous problem), we have

$$P_f V_f^\gamma = P_i V_i^\gamma, \quad \text{or} \quad V_f = V_i \left(\frac{P_i}{P_f} \right)^{1/\gamma} = (1 \text{ liter}) \left(\frac{1 \text{ atm}}{7 \text{ atm}} \right)^{5/7} = 0.25 \text{ liters},$$

where i and f refer to initial and final, and I've set $\gamma = 7/5$ for air, which has five degrees of freedom per molecule at ordinary temperatures.

- b) The pressure as a function of volume is $P = \text{constant}/V^\gamma$, where the constant can be evaluated from the initial conditions as $P_i V_i^\gamma$. The work done is then

$$\begin{aligned} W &= \int P dV = P_i V_i^\gamma \int_{V_i}^{V_f} V^{-\gamma} dV = P_i V_i^\gamma \left(\frac{V^{-\gamma+1}}{\gamma-1} \right) \Big|_{V_i}^{V_f} \\ &= \frac{P_i V_i^\gamma}{\gamma-1} \left(\frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}} \right) = \frac{P_i V_i}{\gamma-1} \left[\left(\frac{V_i}{V_f} \right)^{\gamma-1} - 1 \right] \\ &= \frac{1 \text{ liter atm}}{2/5} [(4.0)^{2/5} - 1] = 1.86 \text{ liter atm} = 188 \text{ J}. \end{aligned}$$

- c) From equation 1.39 we can write $V_f T_f^{f/2} = V_i T_i^{f/2}$, or

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{2/f} = (300 \text{ K}) \left(\frac{1 \text{ liter}}{0.25 \text{ liters}} \right)^{2/5} = (300 \text{ K})(1.74) \approx 520 \text{ K}.$$

Problem 1.37. From equation 1.39 we can write $V_f T_f^{f/2} = V_i T_i^{f/2}$, where i represents the initial state and f represents the final state. I'll assume an initial temperature of 300 K and $f = 5$ for air. Solving for T_f then gives

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{2/f} = (300 \text{ K})(20)^{2/5} = (300 \text{ K})(3.31) \approx 1000 \text{ K}.$$

This is presumably hot enough to ignite the fuel as soon as it is injected, without the aid of a spark plug.

Problem 1.38. Since the bubbles each contain the same number of molecules and each end up at the same pressure, the ideal gas law tells us that whichever one has the higher temperature at the surface also has the larger volume: $V = NkT/P$. And the one with the higher temperature is the one with the larger energy content, by the equipartition theorem: $U = NfkT/2$. So the question is, which bubble has more energy at the surface? Since both bubbles expand, they both lose energy as they do work on the surrounding water. Apparently, bubble B absorbs heat to replace this lost energy and thus remains at the initial temperature. Since bubble A does not absorb any heat, its energy drops. So bubble B, the one that does absorb heat, ends up at the higher temperature and thus has the larger volume.

Problem 1.39. (Bulk modulus and speed of sound.)

- a) During an isothermal compression, according to the ideal gas law,

$$\frac{dP}{dV} = \frac{d}{dV} \frac{NkT}{V} = \frac{NkT}{V^2},$$

and therefore the bulk modulus is

$$B_{\text{isothermal}} = V \frac{dP}{dV} = \frac{NkT}{V} = P.$$

During an adiabatic compression, on the other hand, the pressure of an ideal gas obeys $PV^\gamma = C$ for some constant C . This implies

$$\frac{dP}{dV} = \frac{d}{dV} \frac{C}{V^\gamma} = -\gamma \frac{C}{V^{\gamma+1}},$$

and therefore

$$B_{\text{adiabatic}} = V \frac{dP}{dV} = \gamma \frac{C}{V^\gamma} = \gamma P.$$

Since γ is always greater than 1, the adiabatic bulk modulus is always larger than the isothermal bulk modulus. This makes sense, because it's harder to compress a gas adiabatically (as its temperature rises) than isothermally.

- b) Sound typically travels *much* faster than heat, so there's no way that heat could flow back and forth between the compressed and rarefied portions of sound wave fast enough to accomplish any temperature equilibration. Therefore we can treat these compressions as approximately adiabatic, with no significant heat flow at all.
- c) Let m be the average mass of a gas molecule. Then the density, ρ , is $Nm/V = mP/kT$ by the ideal gas law. The speed of sound is therefore

$$c_s = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{\gamma P}{mP/kT}} = \sqrt{\frac{\gamma kT}{m}} = \sqrt{\frac{\gamma RT}{M}},$$

where M is the mass of a mole of the gas. This result is the same as equation 1.21 for the rms speed of the gas molecules, except that the 3 is here replaced by γ . In other words, the speed of sound is slower than the rms molecular speed, by a factor of $\sqrt{3/\gamma}$. (Note that γ is always between 1 and 5/3, being largest for a monatomic gas.) This result makes sense: The sound wave is carried by the molecules, so its speed should be comparable to the average molecular speed, and definitely no faster. Numerically, for air at room temperature,

$$c_s = \sqrt{\frac{1.4(8.31 \text{ J/K})(300 \text{ K})}{0.029 \text{ kg}}} = 347 \text{ m/s.}$$

- d) At high altitude, the pressure of the atmosphere is less than at sea level. But the result of part (c) shows that for an ideal gas, the speed of sound is independent of pressure—it depends only on temperature. (Both B and ρ are proportional to pressure, but this dependence cancels in the ratio B/ρ .) If the environment throws your bagpipes out of tune, it must be the temperature, not the lower pressure, that causes this effect. In fact, the concert referred to was in a heated auditorium so there should have been no significant effect due to temperature either. In any case, the musician managed to tune his pipes just fine and the performance was superb.

Problem 1.40. (Dry adiabatic lapse rate.)

- a) Starting from the first law and setting $Q = 0$,

$$dU = Q + W = W = -P dV.$$

For an ideal gas, $U = \frac{f}{2}NkT$, so

$$\frac{f}{2}Nk dT = -P dV. \quad (1.35)$$

In this equation there are three variables— T , V , and P . In this problem we want to eliminate V in favor of T and P . One way to do this is to start with the ideal gas law and consider a small change in each side of the equation:

$$d(PV) = Nk dT.$$

The left-hand side is $P dV + V dP$, by the product rule for derivatives, so

$$P dV = Nk dT \quad V dP = Nk dT - \frac{NkT}{P} dP,$$

where I've used the ideal gas law again in the last step. Therefore equation 1.35 becomes

$$\frac{f}{2}Nk dT = Nk dT + \frac{NkT}{P} dP.$$

Cancelling the Nk and collecting terms gives

$$\frac{f+2}{2}dT = \frac{T}{P}dP, \quad \text{or} \quad \frac{dT}{dP} = \frac{2}{f+2} \frac{T}{P}.$$

(You can also derive this differential equation from the solutions for T and P in terms of V , equations 1.39 and 1.40.)

- b) The result of part (a) can be written

$$dT = \frac{2}{f+2} \frac{T}{P} dP;$$

this is the change in temperature under an infinitesimal adiabatic change in pressure dP . If this change occurs because the air mass is rising a distance dz , and if the vertical forces on it are balanced throughout this process, then the result of Problem 1.16(b) tells us that

$$dP = \frac{mg}{kT} P dz,$$

where m is the average mass of an air molecule. Therefore the change in temperature is

$$dT = \frac{2}{f+2} \frac{T}{P} \frac{mg}{kT} P dz = \frac{2}{f+2} \frac{mg}{k} dz,$$

and the temperature gradient is

$$\frac{dT}{dz} = \frac{2}{f+2} \frac{mg}{k} = \frac{2}{f+2} \frac{Mg}{R},$$

where M is the molar mass of air, 29 g/mol. Plugging in $f = 5$ and $g = 9.8 \text{ N/kg}$, the numerical value comes out to

$$\frac{dT}{dz} = \frac{2 (.029 \text{ kg})(9.8 \text{ N/kg})}{7 \cdot 8.315 \text{ J/mol K}} = .0098 \text{ K/m} = 9.8 \text{ K/km}.$$

Problem 1.41. (Measuring a heat capacity.)

- a) The heat gained by the water is

$$m_w c_w (\Delta T)_w = (250 \text{ g})(4.186 \text{ J/g } ^\circ\text{C})(4^\circ\text{C}) = 4186 \text{ J.}$$

- b) The heat lost by the metal must be the same as the heat lost by the water, 4186 J, since there are no other energy transfers going on and energy must be conserved.
c) The heat capacity of the chunk of metal must therefore be

$$C_m = \frac{Q}{\Delta T_m} = \frac{4186 \text{ J}}{76^\circ\text{C}} = 55 \text{ J}/^\circ\text{C.}$$

- d) The specific heat capacity is the heat capacity per unit mass,

$$c_m = \frac{C_m}{m_m} = \frac{55 \text{ J}/^\circ\text{C}}{100 \text{ g}} = 0.55 \text{ J/g } ^\circ\text{C.}$$

Problem 1.42. The heat lost by the water should be approximately equal to the heat gained by the pasta. Therefore,

$$m_w c_w (T_w - T_f) = m_p c_p (T_f - T_p),$$

where w stands for water, p for pasta, and f for the common final temperature. Solving for T_f gives

$$\begin{aligned} T_f &= \frac{m_w c_w T_w + m_p c_p T_p}{m_w c_w + m_p c_p} \\ &= \frac{(1500 \text{ g})(4.186 \text{ J/g } ^\circ\text{C})(100^\circ\text{C}) + (340 \text{ g})(1.8 \text{ J/g } ^\circ\text{C})(25^\circ\text{C})}{(1500 \text{ g})(4.186 \text{ J/g } ^\circ\text{C}) + (340 \text{ g})(1.8 \text{ J/g } ^\circ\text{C})} = 93.3^\circ\text{C}. \end{aligned}$$

So we would expect the water temperature to drop by nearly 7°C , assuming that equilibration happens faster than the stove can provide any significant additional heat. To prevent the water temperature from dropping so much, it might be wise to use a bigger pot of water.

Problem 1.43. Suppose we have 18 g of water, which makes exactly one mole. The total heat capacity is $18 \cdot 4.186 \text{ J/K}$, so the heat capacity per molecule is

$$\frac{C}{N} = \frac{18 \cdot 4.186 \text{ J/K}}{6.02 \times 10^{23}} = 1.25 \times 10^{-22} \text{ J/K} = 9.07 k.$$

If all the thermal energy were stored in quadratic degrees of freedom, then each would get a heat capacity of $k/2$, so there would have to be 18 degrees of freedom per molecule—an unrealistically large number. In fact, much of the thermal energy is stored in the energy of intermolecular interactions, and these energies are not quadratic functions of position.

Problem 1.44. The heat capacity (at constant *pressure*) of a mole of monatomic gas should be $\frac{5}{2}R = 20.8 \text{ J/K}$; looking through the table I see that this prediction is pretty much exact for all monatomic gases listed: Ar, H, He, and Ne. For a diatomic gas with two rotational degrees of freedom but no vibration, C_P should be $\frac{7}{2}R = 29.1 \text{ J/K}$; this prediction is extremely close for CO and N₂, but just a little high for H₂, just a little low for O₂, and significantly too low for Cl₂. The linear polyatomic molecule CO₂ should also have two rotational degrees of freedom, but its C_P value of 37.1 J/K indicates that some vibration is also active, probably a “flopping” that doesn’t actually stretch the bonds. The other polyatomic gases should have C_P values of at least $\frac{8}{2}R = 33.3 \text{ J/K}$, plus any further contributions from vibrational modes. Water comes closest among those listed to the prediction of pure rotation, followed by ammonia (NH₃) and then methane (CH₄). The larger hydrocarbons, ethane and propane, obviously have quite a bit of vibrational energy even at room temperature.

For one mole of an elemental solid, assuming all vibrational degrees of freedom are active, the equipartition prediction is $C_P = 3R = 24.9 \text{ J/K}$, plus any correction due to the small difference between C_P and C_V . Aluminum, copper, iron, and lead all come reasonably close to this prediction, with small discrepancies that are easily understood in terms of Figure 1.14. Diamond and graphite are significant anomalies, with heat capacities much lower, indicating that many of their vibrational degrees of freedom are still frozen out at room temperature. Solid compounds have more atoms per mole and therefore larger molar heat capacities. Both NaCl and CaCl₂ seem to have essentially all degrees of freedom active, but C_P values of the more complicated compounds are all somewhat on the low side, indicating that at least some of the bonds are too stiff to vibrate easily at room temperature. The most extreme example is glucose, which would have a heat capacity of about 500 J/K if all vibrational modes were active.

For liquids we can make no precise predictions, but notice that the heat capacity of mercury is not much larger than we would predict for a solid, while the molar heat capacities of water and ethyl alcohol are significantly larger as expected.

Problem 1.45. (Partial derivative practice.)

- a) Starting with $w = xy$ and $x = yz$, I find $w = y^2z$ and also $w = x^2/z$.
- b) To compute $(\partial w / \partial x)_y$ one should start with a formula for w purely in terms of x and y —in this case, $w = xy$. Treating y as a constant, I find $(\partial w / \partial x)_y = y$. On the other hand, to compute $(\partial w / \partial x)_z$ one should start with the formula $w = x^2/z$; then it’s easy to see that $(\partial w / \partial x)_z = 2x/z$. Since $y \neq 2x/z$, these partial derivatives are not equal. (Instead, $y = x/z$.)
- c) From $w = xy$ one can also see that $(\partial w / \partial y)_x = x$. On the other hand, from $w = y^2z$ one can see that $(\partial w / \partial y)_z = 2yz = 2x$. So these partial derivatives aren’t equal either. Finally, from $w = x^2/z$ one can see that $(\partial w / \partial z)_x = -x^2/z^2$, while from $w = y^2z$ one can see that $(\partial w / \partial z)_y = y^2 = +x^2/z^2$, unequal yet again.

Problem 1.46. (Compressibility and general *P-V-T* relations.)

- a) For a thermal expansion process at fixed pressure,

$$dV_1 = \left(\frac{\partial V}{\partial T} \right)_P dT = \beta V dT,$$

where β is the thermal expansion coefficient, $\beta = (1/V)(\partial V/\partial T)_P$.

- b) For a compression process at fixed temperature,

$$dV_2 = \left(\frac{\partial V}{\partial P} \right)_T dP = -\kappa_T V dP,$$

where κ_T is the isothermal compressibility.

- c) If these two processes are to result in no net change in volume, then $dV_2 = -dV_1$, and therefore,

$$\kappa_T V dP = -\beta V dT, \quad \text{or} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa_T} = \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T},$$

where in the last step I've used the definitions of β and κ_T .

- d) For an ideal gas,

$$\begin{aligned} \beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{\partial}{\partial T} \left(\frac{NkT}{P} \right) = \frac{1}{V} \frac{Nk}{P} = \frac{1}{T}; \\ \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \frac{\partial}{\partial P} \left(\frac{NkT}{P} \right) = -\frac{1}{V} \left(-\frac{NkT}{P^2} \right) = \frac{1}{P}; \\ \left(\frac{\partial P}{\partial T} \right)_V &= \frac{\partial}{\partial T} \left(\frac{NkT}{V} \right) = \frac{Nk}{V} = \frac{P}{T}. \end{aligned}$$

So indeed, $(\partial P/\partial T)_V = \beta/\kappa_T$.

- e) Treating the temperature change as approximately infinitesimal, the required pressure change for water would be

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT = \frac{\beta}{\kappa_T} dT = \frac{2.57 \times 10^{-4} \text{ K}^{-1}}{4.52 \times 10^{-10} \text{ Pa}^{-1}} (10 \text{ K}) = 5.69 \times 10^6 \text{ Pa} = 56 \text{ atm}.$$

Similarly, for mercury,

$$dP = \frac{\beta}{\kappa_T} dT = \frac{1.81 \times 10^{-4} \text{ K}^{-1}}{4.04 \times 10^{-11} \text{ Pa}^{-1}} (10 \text{ K}) = 4.48 \times 10^7 \text{ Pa} = 440 \text{ atm}.$$

To measure C_V we would need to keep the volume fixed while increasing the temperature by at least a few degrees. As just shown, this requires fairly large pressures, for which we would need heavy-duty equipment (expensive and, for an amateur like me, dangerous). So I'd much prefer to stay at atmospheric pressure and simply measure C_P .

Problem 1.47. The amount of heat that I want to remove from the tea is

$$Q = (200 \text{ g})(1 \text{ cal/g } ^\circ\text{C})(35^\circ\text{C}) = 7000 \text{ cal}.$$

This heat enters the ice, brings it up to 0°C , melts it, and then brings the melted water up to 65°C . If the mass of the ice is m , then

$$Q = m(0.5 \text{ cal/g } ^\circ\text{C})(15^\circ\text{C}) + m(80 \text{ cal/g}) + m(1 \text{ cal/g } ^\circ\text{C})(65^\circ\text{C}).$$

Solving for m gives $m = 46 \text{ g}$.

Problem 1.48. Consider a 1-m² patch of snow-covered ground, which is covered by 1 m³ of ice (and an equal amount of air mixed with it, which we can neglect). That's nearly 1000 kg, so if it's already at 0°C, the energy needed to melt it is 80 million calories or 335 MJ. Now direct sunlight provides to this patch of ground 1000 J/s, but only 10%, or 100 J/s, is absorbed. A full day of sunshine in late spring might be equivalent to 8 hours, or about 30,000 seconds, of direct sunlight. So in one day the snow absorbs about 3 MJ of solar energy. That means it should take more than 100 days, or 14 weeks, for the snow to melt! Probably, though, the snow absorbs more energy from other sources such as the air and any nearby rocks or trees.

Problem 1.49. Neglecting the final volume of the water, the work done by the collapsing atmosphere is simply PV , where V is the volume of the initial 1.5 moles of gas. But by the ideal gas law,

$$W = PV = nRT = (1.5 \text{ mol})(8.31 \text{ J/mol K})(298 \text{ K}) = 3717 \text{ J} \approx 4 \text{ kJ.}$$

So of the total 286 kJ of heat produced, only about 4 kJ comes from work done by the atmosphere. The other 282 kJ must come from the internal energy of the system, mainly chemical energy in the molecular bonds.

Problem 1.50. (Combustion of methane.)

- a) From the table on page 404, line 8, the change in enthalpy upon forming one mole of methane from elemental carbon and hydrogen is -74.81 kJ; the change in enthalpy for the reverse reaction is therefore +74.81 kJ.
- b) From the same table, ΔH to form one mole of CO₂ is 393.51 kJ (line 14), while ΔH to form two moles of H₂O vapor is $2 \times (-241.82 \text{ kJ}) = -483.64 \text{ kJ}$ (page 405, line 5).
- c) Imagine first converting the mole of methane into elemental carbon and hydrogen, then taking these elements and some oxygen and converting them into CO₂ and H₂O. The total change in enthalpy for all these steps is

$$\Delta H = +74.81 \text{ kJ} + (-393.51 \text{ kJ}) + (-483.64 \text{ kJ}) = -802.34 \text{ kJ.}$$

Now the actual reaction doesn't occur by this sequence of steps, but the end result is the same, so the net change in enthalpy must be the same: a decrease of 802 kJ.

- d) In a constant-pressure process with no other work done, the heat given off is precisely equal to the decrease in enthalpy, in this case, 802 kJ.
- e) In a constant-pressure process, $\Delta U = \Delta H - P\Delta V$. This reaction starts with three moles of gas and ends with three moles of gas, so ΔV is almost exactly zero (by the ideal gas law). Therefore ΔU is the same as ΔH , -802 kJ. However, if the H₂O ends up as a liquid, things are a bit more interesting. Then ΔH to form the H₂O from its elemental constituents is instead $2 \times (-285.83 \text{ kJ}) = -571.66 \text{ kJ}$ (page 405, line 4), and the computation in part (c) yields a net ΔH of -890.36 kJ. But the volume of the system decreases substantially, because it starts with three moles of gas and ends up with only one (while the volume of the liquid is negligible):

$$\Delta V = \frac{RT}{P}\Delta n = -\frac{2RT}{P}.$$

The change in the system's energy is therefore

$$\begin{aligned}\Delta U &= \Delta H - P\Delta V = \Delta H + 2RT = (-890.36 \text{ kJ}) + 2(8.315 \text{ J/K})(298 \text{ K}) \\ &= -890.36 \text{ kJ} + 4.96 \text{ kJ} = -885.40 \text{ kJ.}\end{aligned}$$

The heat given off is a bit *more* than the amount of energy lost by the system; the difference comes from work done by the atmosphere as it compresses the system to a smaller volume.

- f) A mole of methane has a mass of only 16 g, but two moles of O₂ have a total mass of 64 g, giving a total of 80 g = 0.080 kg for the mass of fuel to produce the reaction given here. If the sun were composed entirely of such fuel in the correct proportions, it would contain

$$\frac{2 \times 10^{30}}{0.080} = 2.5 \times 10^{31}$$

moles of methane, which could give off a total of roughly

$$2.5 \times 10^{31} \times 800,000 \text{ J} = 2 \times 10^{37} \text{ J}$$

of heat, by the reaction considered here. But at a rate of about 4×10^{26} watts, this fuel would last only

$$\frac{2 \times 10^{37} \text{ J}}{4 \times 10^{26} \text{ J/s}} = 5 \times 10^{10} \text{ seconds,}$$

or about 1600 years. Other chemical fuels might give somewhat longer lifetimes, but no chemical fuel could power the sun for more than a few thousand years.

Problem 1.51. Imagine the combustion of the glucose occurring in two steps: First we convert the glucose into elemental substances in their most stable states (graphite, H₂, and O₂); then we combine these elements with the additional oxygen to form carbon dioxide and water. The change in enthalpy for the first step is just minus the enthalpy of formation of a mole of glucose, so it can be read directly off the table on page 404: $\Delta H_1 = +1273 \text{ kJ}$. For the second step we add the enthalpy of formation of six moles of CO₂ to the enthalpy of formation of six moles of H₂O:

$$\Delta H_2 = 6(-393.5 \text{ kJ}) + 6(-285.8 \text{ kJ}) = -4076 \text{ kJ.}$$

The net change in enthalpy for the actual reaction is just the sum of the changes during the two hypothetical steps, -2803 kJ. The absolute value of this number, +2803 kJ, is called the "enthalpy of combustion" of glucose. (Problems 5.6 and 5.7 address the question of how much of this energy can be extracted as work rather than heat.)

Problem 1.52. As of this writing, the price of "regular" (85-octane) gasoline in Utah is about \$1.50 per gallon. So the price per kcal is

$$\frac{150 \text{ cents}}{31,000 \text{ kcal}} = 0.0048 \text{ cents/kcal.}$$

In other words, you get a little over 200 kilocalories per penny. The price of the cheapest corn flakes at the local Albertson's is 10 cents per ounce (35-ounce bag of Good Day brand, \$3.49), so the price per kcal is

$$\frac{10 \text{ cents}}{100 \text{ kcal}} = 0.10 \text{ cents/kcal.}$$

That is, you get only 10 kilocalories for a penny. Thus, the price of corn flakes, per calorie, is about 20 times higher than the price of gasoline. (And if you buy the smallest box of Kellogg's brand, the price is another two and a half times higher, 50 times as much as gasoline.) Still, I don't recommend gasoline as a way of cutting down on grocery bills.

Problem 1.53. On page 405 we see that the enthalpy of formation of a mole of atomic hydrogen is 217.97 kJ. To convert this enthalpy change to an *energy* change, we need to subtract off the $P\Delta V$ term:

$$\begin{aligned}\Delta U &= \Delta H - P\Delta V = \Delta H - (\Delta n)RT \\ &= 217.97 \text{ kJ} - \frac{1}{2}(8.31 \text{ J/K})(298 \text{ K}) = 217.97 \text{ kJ} - 1.24 \text{ kJ} = 216.73 \text{ kJ.}\end{aligned}$$

(The 1.24-kJ difference between ΔU and ΔH is the work that you must do to make room for the additional half-mole of gas created during dissociation.) Now, to get the energy required to dissociate a single molecule, we divide by the number of molecules:

$$\epsilon_{\text{diss.}} = \frac{\Delta U}{N_{\text{H}_2}} = \frac{216.7 \text{ kJ}}{\frac{1}{2} \cdot 6.02 \times 10^{23}} = 7.20 \times 10^{-19} \text{ J} = 4.49 \text{ eV.}$$

Problem 1.54. (Climbing Mt. Ogden.)

- a) To lift her weight to the summit, the hiker must perform mechanical work equal to her increase in gravitational potential energy:

$$W = mgh = (60 \text{ kg})(9.8 \text{ N/kg})(1500 \text{ m}) = 880 \text{ kJ} = 210 \text{ kcal.}$$

But if she's only 25% efficient, she must "burn" four times this much fuel, or 840 kcal. That's about 8.5 bowls of corn flakes (without milk). (Note that I'm neglecting the small differences between energy and enthalpy in this problem, since all we want are rough estimates.)

- b) Of the total of 840 kcal, 75%, or 630 kcal, is converted to thermal energy. If this energy is uniformly distributed over the hiker's 60-kg body, each kilogram gets 10.5 kcal. Assuming that her body is mostly water (for purposes of computing its heat capacity), this energy would be enough to raise her body temperature by 10.5°C. If this were really the result, it would be fatal!
- c) Evaporating a kilogram of water takes 580 kcal (at 25°C), and we have 630 kcal of energy to dispose of, so we can evaporate

$$\frac{630 \text{ kcal}}{580 \text{ kcal/kg}} = 1.1 \text{ kg.}$$

That's 1.1 liters of water that the hiker should replace. (However, the metabolism of 8.5 ounces of carbohydrates produces about 140 grams of water as a byproduct. This leaves slightly less than a liter that she needs to drink. But I would recommend playing it safe and carrying at least two liters of water on such a hike.)

Problem 1.55. (Gravitationally bound systems.)

- a) The kinetic and potential energies of the system are

$$U_k = 2 \cdot \frac{1}{2}mv^2 = mv^2; \quad U_p = -\frac{Gm^2}{2r}.$$

To show how these are related, apply Newton's second law to the motion of one of the particles:

$$F = ma \quad \Rightarrow \quad \frac{Gm^2}{(2r)^2} = m \frac{v^2}{r}.$$

Multiply each side of this equation by $2r$, and the left-hand side is the magnitude of the potential energy. Therefore,

$$U_p = -2mv^2 = -2U_k.$$

- b) The total energy of such a system is

$$U_{\text{total}} = U_k + U_p = U_k - 2U_k = -U_k.$$

Therefore, increasing the total energy *decreases* the kinetic energy. In other words, if I add one unit of total energy, the potential energy increases (becomes less negative) by two units, while the kinetic energy decreases by one unit.

- c) The total kinetic energy of the star would be $N \frac{3}{2}kT$, so the total (kinetic + potential) energy would be

$$U_{\text{total}} = -U_k = -\frac{3}{2}NkT,$$

and the heat capacity would be

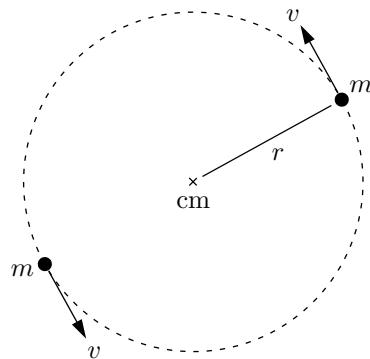
$$C = \frac{dU}{dT} = -\frac{3}{2}Nk.$$

The heat capacity is negative, of course. (Since the star exists in empty space and doesn't really have a well-defined volume, this quantity shouldn't be called C_V or C_P .)

- d) The total potential energy of the star should be a function of G , M , and R . The SI units of these quantities are

$$[G] = \frac{\text{N} \cdot \text{m}^2}{\text{kg}^2}; \quad [M] = \text{kg}; \quad [R] = \text{m}.$$

Note that N, m, and kg are independent units: None of them can be written in terms of the others. Taking these as our three basic units, we need a combination of G , M , and R that has units of $\text{J} = \text{N} \cdot \text{m}$. To get this combination we need exactly one factor of G (the only place we can get N). Then we need two factors of M (to cancel the kg^2 in G), and we must divide by one factor of R (to cancel a factor of m). Up to a



dimensionless constant, then, the potential energy must be GM^2/R . It must also be negative, since gravity is attractive.

- e) Using $\frac{3}{2}NkT$ for the kinetic energy and the result of part (d) for the potential energy, the relation $U_k = \frac{1}{2}U_p$ becomes

$$\frac{3}{2}NkT \approx \frac{1}{2}\left(-\frac{GM^2}{r}\right) = \frac{GM^2}{2R}.$$

Solving for T gives

$$T \approx \frac{GM^2}{3NkR} = \frac{GM}{3kR} \frac{M}{N}.$$

The factor M/N is the mass per particle, which is approximately half the mass of a proton (since the electrons are much lighter than the protons). Numerically, then,

$$T \approx \frac{(6.7 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(2 \times 10^{30} \text{ kg}) \frac{1}{2}(1.67 \times 10^{-27} \text{ kg})}{3(1.38 \times 10^{-23} \text{ J/K})(7 \times 10^8 \text{ m})} \approx 4 \times 10^6 \text{ K.}$$

This is *much* higher than the sun's "surface" temperature of only 6000 K (see Section 7.4). But careful calculations show that the sun's central temperature is 15 million kelvin, so this estimated average is probably a little on the low side.

Problem 1.56. The thermal conductivity of air is 0.026 W/m K, so the rate of heat conduction through this layer of air should be

$$\frac{Q}{\Delta t} = \frac{(0.026 \text{ W/m K})(1 \text{ m}^2)(20 \text{ K})}{0.001 \text{ m}} = 520 \text{ W},$$

about ten times less than the rate of heat loss through a 3.2-mm pane of glass under the same conditions (as calculated in the text).

Problem 1.57. (R values and heat loss through a window.)

- a) For plate glass,

$$R = \frac{\Delta x}{k_t} = \frac{3.2 \times 10^{-3} \text{ m}}{0.8 \text{ W/m K}} = 0.0040 \frac{\text{K m}^2}{\text{W}}.$$

For a 1-mm layer of air,

$$R = \frac{10^{-3} \text{ m}}{0.026 \text{ W/m K}} = 0.038 \frac{\text{K m}^2}{\text{W}},$$

nearly ten times as much.

- b) Because we're dealing only with temperature *differences*, the conversion for temperature units is $1^\circ\text{F} = \frac{5}{9} \text{ K}$. To figure out what a Btu is, I need to compute the energy needed to raise the temperature of a pound (453.6 g) of water by 1°F :

$$1\text{Btu} = (453.6 \text{ g})(4.186 \text{ J/g K})(\frac{5}{9} \text{ K}) = 1055 \text{ J.}$$

(A standard reference gives the value 1054 J, indicating that my value of 4.186 J/g K for the heat capacity of water is probably at a different temperature than that used in the definition of the Btu.) One SI unit of R is therefore

$$\left(1 \frac{\text{°C m}^2}{\text{W}}\right) \left(\frac{1 \text{ °F}}{\frac{5}{9} \text{ K}}\right) \left(\frac{3.281 \text{ ft}}{1 \text{ m}}\right)^2 \left(\frac{1054 \text{ J}}{1 \text{ Btu}}\right) \left(\frac{1 \text{ hr}}{3600 \text{ s}}\right) = 5.67 \frac{\text{°F ft}^2 \text{ hr}}{\text{Btu}}.$$

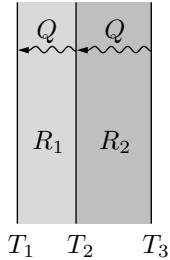
Multiplying the values in part (a) by this conversion factor gives in English units $R = 0.023$ for plate glass and $R = 0.22$ for a 1-mm air layer.

- c) Written in terms of R , the Fourier heat conduction law is

$$\frac{Q}{\Delta t} = A \frac{\Delta T}{R}.$$

For the double-layer situation shown at right, the intermediate temperature T_2 will settle down to a constant value that causes the rate of heat flow to be the same through both layers. Since the areas of the layers are the same,

$$\frac{T_2 - T_1}{R_1} = \frac{T_3 - T_2}{R_2}.$$



Solving for T_2 gives $T_2 = (T_3 R_1 + T_1 R_2) / (R_1 + R_2)$. The “total” R , meanwhile, should be defined by

$$\frac{Q}{\Delta t} = A \frac{T_3 - T_1}{R_{\text{total}}}.$$

But $Q/\Delta t$ and A are the same here as for either layer individually, so

$$\frac{T_3 - T_1}{R_{\text{total}}} = \frac{T_3 - T_2}{R_2}.$$

Plugging in the previous expression for T_2 and doing a bit of algebra yields for the right-hand side $(T_3 - T_1)/(R_1 + R_2)$, so R_{total} is simply $R_1 + R_2$.

- d) Adding the R values of a piece of plate glass and two 1-mm air layers, I obtain a total R of 0.081 in SI units or 0.46 in English units. The rate of heat loss through a 1-m² window, with an indoor-outdoor temperature difference of 20 K, is therefore approximately

$$\frac{Q}{\Delta t} = \frac{(1 \text{ m}^2)(20 \text{ K})}{0.081 \text{ K m}^2/\text{W}} = 250 \text{ W},$$

or 20 times less than the naive estimate given in the text, which neglected the air layers.

Problem 1.58. In SI units, the R value of a 3.5-inch (8.9-cm) thickness of still air is

$$R = \frac{0.089 \text{ m}}{0.026 \text{ W/m K}} = 3.42 \text{ K m}^2/\text{W}.$$

To get the value in English units we multiply by the conversion factor 5.67, derived in the previous problem:

$$R = 19.4 \text{ }^{\circ}\text{F ft}^2 \text{ hr/Btu.}$$

As expected, this is even more than the R value of berglass batting (10.9); the batting inhibits convection a great deal, but not completely. The R value of a vertical air space without the batting is of course much less still (1.0), because there will be quite a bit of convection. But even then, a thin layer of air on each side of the space will be essentially still, “stuck” to the adjacent solid wall. If those layers are each 1 mm thick, they provide a total R value of 0.44 (as computed in the previous problem), so we would expect the R value of the entire air space to be somewhat larger than that, as it is.

Problem 1.59. The rate of heat loss through any window, wall, or ceiling can be written in terms of the R value as

$$\frac{Q}{\Delta t} = \frac{A}{R} \Delta T.$$

Thus, for each separate part of the house’s outer surface I need to compute the ratio A/R ; the total rate of heat loss will then be the sum of the rates through each part.

Based on the R value for berglass batting given in the previous problem, I would guess that the exterior walls of my house have a total R value of around 15, when you include the plaster, brick, and so on. My ceiling has about 6 inches of blown insulation, so its R value is also probably around 15. The total area of my exterior walls and ceiling is about 2200 ft^2 (not counting windows or the underground part of the basement), so for the walls and ceiling I estimate roughly

$$\frac{A}{R} = \frac{2200 \text{ ft}^2}{15 \text{ }^{\circ}\text{F ft}^2 \text{ hr/Btu}} \approx 150 \frac{\text{Btu/hr}}{^{\circ}\text{F}}.$$

My windows, on the other hand, are almost all single-pane (it’s an old house), with an R value of about 0.5, as computed in Problem 1.57. Their total area is about 120 ft^2 , so they contribute another

$$\frac{A}{R} = \frac{120 \text{ ft}^2}{0.5 \text{ }^{\circ}\text{F ft}^2 \text{ hr/Btu}} \approx 240 \frac{\text{Btu/hr}}{^{\circ}\text{F}}.$$

(This is more than all the walls and ceiling combined! So to save on my heating bill, I should invest first in storm windows, not more ceiling insulation.)

I keep my thermostat at about 65°F , and my utility bill conveniently reports that the average temperature last January was 33°F , so the total rate of heat conduction from my house should be roughly

$$\frac{Q}{\Delta t} = \left(150 \frac{\text{Btu/hr}}{^{\circ}\text{F}} + 240 \frac{\text{Btu/hr}}{^{\circ}\text{F}} \right) (32^{\circ}\text{F}) = 12,500 \text{ Btu/hr} (= 3.7 \text{ kW}).$$

Multiplying by 24×30 , I find that the total conductive heat loss from my house during the month should have been roughly 9 million Btu, or 90 therms. At \$0.54 per therm for gas heat, that would cost \$49 to replace. In fact, my gas bill reports that I used 102 therms, at a total cost of \$54.67 (plus various surcharges). (Frankly, I'm amazed that my estimate came this close to the actual gas usage. I've never actually looked inside my walls, much less carefully computed their R values. The effective R values of the windows are also quite uncertain, due to the variable-thickness air layers as well as shades and blinds. And I've totally neglected such factors as air leakage, direct solar heating, the hot exhaust gases that go up the chimney, and gas used by my hot water heater.)

Problem 1.60. To make a rough estimate, imagine that the handle is divided into two halves: a half nearer the burner at 200°C , and the half that I wish to grab, initially at 25°C . This half will definitely be too hot to grab when its temperature reaches 75°C , an increase of about 50° above room temperature. The heat required to accomplish this increase is

$$Q = mc\Delta T = \rho V c \Delta T = \rho A \ell c \Delta T,$$

where ρ is the density of iron, c is the specific heat, A is the handle's cross-sectional area, and ℓ is the length of the half-handle. On the other hand, by the Fourier heat conduction law, the heat that flows past the handle's mid-point is

$$Q = k_t A \frac{dT}{dx} \Delta t,$$

where dT and dx can be approximated by taking differences between the mid-points of the two half-handles: $dT \approx 150^\circ\text{C}$ on average, and $dx = \ell$. Equating the two expressions for Q and solving for Δt then gives

$$\Delta t = \frac{\rho c A \ell \Delta T}{k_t A (dT/dx)} \approx \frac{\rho c \ell^2 \Delta T}{k_t dT} = \frac{(7900 \text{ kg/m}^3)(450 \text{ J/kg }^\circ\text{C})(0.1 \text{ m})^2(50^\circ\text{C})}{(80 \text{ W/m }^\circ\text{C})(150^\circ\text{C})} = 150 \text{ s},$$

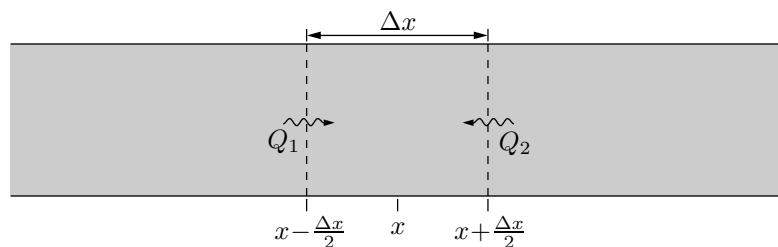
or about two and a half minutes. Seems about right, in my experience.

Problem 1.61. For the numbers given, the rate of heat conduction should be

$$\frac{Q}{\Delta t} = k_t A \frac{dT}{dx} = (2.5 \text{ W/m }^\circ\text{C})(1 \text{ m}^2) \frac{20^\circ\text{C}}{1000 \text{ m}} = 0.05 \text{ W}.$$

A twentieth of a watt doesn't sound like much, but that's just for one square meter. The surface area of the whole earth is $4\pi r^2 = 4\pi(6.4 \times 10^6 \text{ m})^2 = 5.1 \times 10^{14} \text{ m}^2$, so the total rate of heat conduction through earth's crust should be 2.6×10^{13} watts, assuming that this particular location is representative of the average.

Problem 1.62. (The heat equation.)



Consider the segment of the rod between the two dashed lines, centered on point x with width Δx . The rate of heat flow into this segment from the left is

$$\frac{Q_1}{\Delta t} = -k_t A \frac{dT}{dx} \Big|_{x=\frac{x}{2}}$$

(according to the Fourier heat conduction law), where A is the cross-sectional area of the rod. Similarly, the rate of heat flow into the segment from the right is

$$\frac{Q_2}{\Delta t} = +k_t A \frac{dT}{dx} \Big|_{x+\frac{\Delta x}{2}},$$

with a plus sign because I'm defining Q_2 to be positive when heat flows *into* the segment. Thus the total rate of heat flow into the segment is

$$\frac{Q}{\Delta t} = k_t A \left(\frac{dT}{dx} \Big|_{x+\frac{\Delta x}{2}} - \frac{dT}{dx} \Big|_{x=\frac{x}{2}} \right) = k_t A \Delta x \frac{d^2 T}{dx^2}.$$

On the other hand, the heat input Q can be written as $C \Delta T$, where C is the heat capacity of the segment. The heat capacity, in turn, can be written as mc , where m is the mass of the segment and c is the specific heat. Therefore the previous equation becomes

$$\frac{mc \Delta T}{\Delta t} = k_t A \Delta x \frac{d^2 T}{dx^2}.$$

But $m/(A \Delta x)$ is just the density of the rod, ρ , while $\Delta T/\Delta t$ is the derivative of the segment's temperature with respect to time. Finally, therefore, we can write

$$\frac{\partial T}{\partial t} = \frac{k_t}{\rho c} \frac{\partial^2 T}{\partial x^2} = K \frac{\partial^2 T}{\partial x^2},$$

with partial derivatives to denote the idea that T is now considered a function of both x and t .

To check the trial solution

$$T(x, t) = T_0 + \frac{A}{\sqrt{t}} e^{-x^2/4Kt}$$

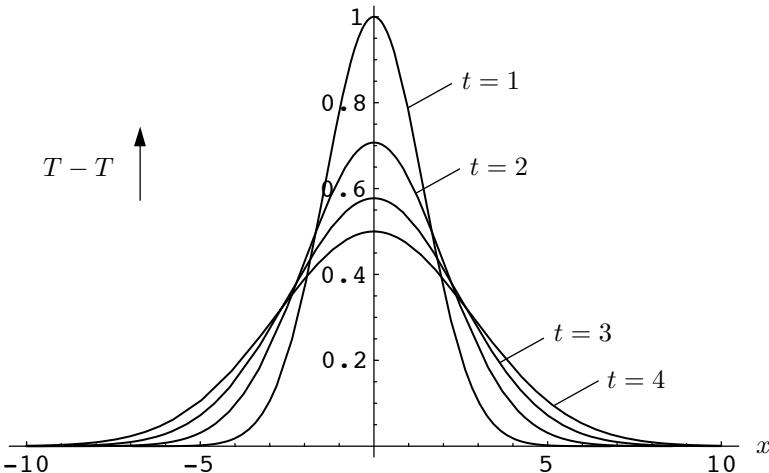
(where A now represents an arbitrary constant), we just evaluate its derivatives:

$$\begin{aligned} \frac{\partial T}{\partial t} &= \frac{1}{2} A t^{-3/2} e^{-x^2/4Kt} + \frac{A}{\sqrt{t}} \left(\frac{x^2}{4Kt^2} \right) e^{-x^2/4Kt} = \frac{A}{\sqrt{t}} \left(\frac{x^2}{4Kt^2} - \frac{1}{2t} \right) e^{-x^2/4Kt}; \\ \frac{\partial T}{\partial x} &= \frac{A}{\sqrt{t}} \left(-\frac{x}{2Kt} \right) e^{-x^2/4Kt}; \\ \frac{\partial^2 T}{\partial x^2} &= \frac{A}{\sqrt{t}} \left[-\frac{1}{2Kt} e^{-x^2/4Kt} + \left(-\frac{x}{2Kt} \right)^2 e^{-x^2/4Kt} \right]. \end{aligned}$$

Multiplying the last line through by K and comparing to the first line, we see that they agree and so this trial solution does indeed work. What does it look like? Plotted as a function of x , it is a Gaussian “bell curve” that gets shorter and broader as t increases. To plot it for four different t values I used the Mathematica instruction

```
Plot[Evaluate[Table[Exp[-x^2/(4t)]/Sqrt[t],{t,1,4}]],{x,-10,10}];
```

This produced the following graph:



(I'm using units of x , t , and T such that A and K are both numerically equal to 1.) Physically, this solution corresponds to a “pulse” of excess energy that is placed at $x = 0$ at time $t = 0$. At $t = 0$ the excess energy is all at the same place, so the pulse is initially high and narrow. It then spreads out according Fourier's law, quickly at first (when the temperature gradients are large) and slowly later on (when the temperature gradients are small). As $t \rightarrow \infty$ the pulse becomes infinitely wide, as the rod's temperature becomes uniform.

Problem 1.63. Substituting kT/P for V/N in equation 1.62 for the mean free path ℓ , we have

$$\ell = \frac{1}{4\pi r^2} \frac{kT}{P}, \quad \text{or} \quad P = \frac{1}{2\pi r^2} \frac{kT}{\ell}.$$

Setting $T = 300$ K, $r = 1.5$ Å, and $\ell = 10$ cm, I find

$$P = \frac{1}{4\pi(1.5 \times 10^{-10} \text{ m})^2} \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{0.1 \text{ m}} = 0.15 \text{ Pa} = 1.5 \times 10^{-6} \text{ atm.}$$

That's well within the range of a good mechanical pump, and nowhere near the state of the art in laboratory vacuum systems. Therefore, in a good laboratory vacuum system, molecules will collide with the walls of the apparatus much more often than they collide with each other.

Problem 1.64. A helium molecule (atom) is quite small. If we take $r = 0.5 \text{ \AA}$, or 3 times smaller than the value I used for air on page 42, then at the same temperature and pressure, helium should have a mean free path equal to 9 times that of air: $\ell = 1.4 \text{ m}$. Also, since the mass of a helium molecule is only about 1/7 that of an air molecule, its rms speed at a given temperature should be greater by a factor of $\sqrt{7} \approx 2.6$; this gives $\bar{v} \approx 1300 \text{ m/s}$ at room temperature. The final difference between helium and air is that a helium molecule has only three degrees of freedom, so C_V/V for helium should be 3/5 the value for air, according to equation 1.66. Combining these effects, I would predict the k_t for helium is larger than for air by a factor of

$$9 \times \sqrt{7} \times (3/5) \approx 14,$$

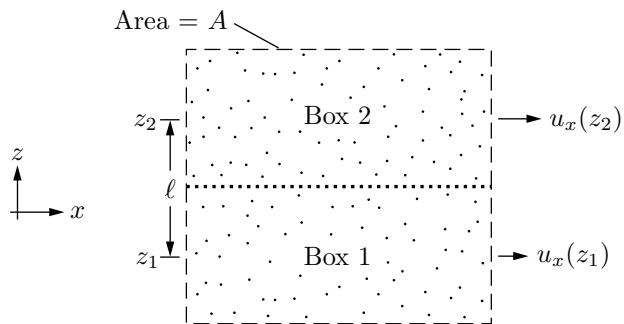
in other words, $k_t \approx 0.4 \text{ W/m K}$ at room temperature. From Figure 1.19, however, I see that the ratio of k_t for helium to k_t for air is only about 8. Probably, then, I under-estimated the effective radius of a helium atom.

Problem 1.65. Even if we don't know the size or mass of a gas molecule, the analysis of Section 1.2 still predicts that the rms speed is $v_{\text{rms}} = \sqrt{2RT/M}$, where M is the molar mass. Assuming that we know from chemistry how much of our gas it takes to make a mole, we can easily measure both R and M so we can calculate $v_{\text{rms}} \approx \bar{v}$. We can also easily measure the heat capacity of the gas, so if we measure its thermal conductivity k_t , then equation 1.65 allows us to calculate the mean free path ℓ . Now look at equation 1.62 for the mean free path:

$$\ell \approx \frac{1}{4\pi r^2} \frac{V}{N} = \frac{r/3}{\frac{4}{3}\pi r^3} \frac{V}{N}.$$

The quantity $\frac{4}{3}\pi r^3$ is roughly the volume of a molecule itself, or equivalently, the volume per molecule in a condensed phase (liquid or solid) of the same substance. Not all gases are easily liquefied using 19th-century technology, so let's pick one that is, say water vapor, whose volume in the gas phase (at atmospheric pressure) is easily measured to be about 1000 times greater than in the liquid phase. Therefore r , the radius of a molecule, is smaller than ℓ by a factor of a few hundred and can be estimated from our value of ℓ . And of course, once we know r , we can estimate how many molecules are in a mole (18 cm^3) of water and hence determine Avogadro's number.

Problem 1.66. (Viscosity of an ideal gas.)



Consider two “boxes” within the gas, as illustrated above. Each box has height ℓ , cross-sectional area A , and contains N gas molecules, each of mass m . During a time interval Δt equal to the average time between molecular collisions, roughly half the molecules in Box 1 will move upward into Box 2, while roughly half the molecules in Box 2 will move downward into Box 1. If the average x velocities (u_x) of the molecules within the two boxes differ, then there will be a net transfer of momentum from Box 1 to Box 2, given by

$$\Delta p_x \approx \frac{1}{2} N m u_x(z_1) - \frac{1}{2} N m u_x(z_2) = \frac{1}{2} N m \Delta u_x.$$

The backward force exerted on Box 2 by Box 1 is the rate of momentum transfer per unit time, so the force per unit area is

$$\frac{|F_x|}{A} \approx \frac{1}{A} \frac{|\Delta p_x|}{\Delta t} = \frac{N m \Delta u_x}{2 A \Delta t} = \frac{N m \bar{v} \Delta u_x}{2 A \ell},$$

where in the last step I’ve substituted ℓ/\bar{v} for the average collision time. The combination $Nm/A\ell$ is the density of the gas (ρ), while the difference Δu_x can be written as $\ell \ du_x/dz$, leaving us with

$$\frac{|F_x|}{A} \approx \left(\frac{1}{2} \rho \bar{v} \ell \right) \frac{du_x}{dz}.$$

This result has the same form as equation 1.69, with the expression in parentheses playing the role of the viscosity coefficient η .

How does this expression depend on temperature? Since $\rho = Nm/V$ while $\ell \propto V/N$, the product $\rho \ell$ depends only on the size and mass of the gas molecules, not on the current conditions (density, pressure, or temperature). Therefore the only temperature dependence in η comes from $\bar{v} \approx v_{rms}$, which is directly proportional to \sqrt{T} as shown in Section 1.2.

For air at room temperature, we can evaluate ρ by considering a quantity of one mole, with a mass of 29 g and a volume of 25 liters. The viscosity should therefore be roughly

$$\eta \approx \frac{1}{2} \left(\frac{0.029 \text{ kg}}{0.025 \text{ m}^3} \right) (1.5 \times 10^{-7} \text{ m})(500 \text{ m/s}) = 4.3 \times 10^{-5} \text{ Pa s.}$$

This is slightly more than twice the experimental value quoted in the text, but at least it’s of the right order of magnitude.

Problem 1.67. As in the example in the text, let’s assume that the food coloring is already spread evenly through one half of some region of space whose width is Δx and whose cross-sectional area is A . Then we can write roughly

$$\frac{N}{A \Delta t} \approx D \frac{N/V}{\Delta x} \approx D \frac{N}{A(\Delta x)^2},$$

with the same N on each side to indicate that we want a substantial fraction of the molecules to cross from one side of the region to the other. Canceling the N ’s and A ’s and solving for Δx gives

$$\Delta x \approx \sqrt{D \Delta t} = \sqrt{(10^{-9} \text{ m}^2/\text{s})(60 \text{ s})} = 2.5 \times 10^{-4} \text{ m},$$

or about a quarter of a millimeter, assuming the same diffusion coefficient as in the text.

Problem 1.68. Suppose that the perfume has already spread over half of the room, densely enough to barely be smelled. How long will it take to then spread over the entire room? If the length of the room is Δx and its cross-sectional area is A , then we can write, as in equation 1.71,

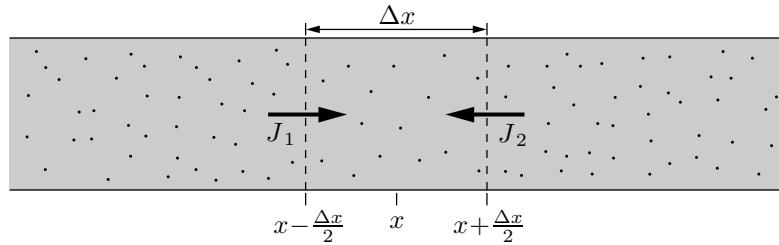
$$\frac{N}{A \Delta t} \approx D \frac{N/V}{\Delta x} \approx D \frac{N}{A(\Delta x)^2},$$

with the same N on each side to indicate that we want a substantial fraction of the molecules to cross from one side of the room to the other. Canceling the N 's and A 's and solving for Δt then gives

$$\Delta t \approx \frac{(\Delta x)^2}{D} \approx \frac{(4 \text{ m})^2}{10^{-5} \text{ m}^2/\text{s}} \approx 10^6 \text{ s} \approx 2 \text{ weeks},$$

where I've assumed that the room is a few meters across and used a typical D value for diffusion through air. Obviously this is much longer than you would actually have to wait to smell the perfume, so convection must be the dominant transport mechanism in this situation.

Problem 1.69. Consider the segment of the pipe shown below, with fluxes J_1 and J_2 coming in from the left and right:



Since flux is the number of particles crossing a surface per units area per unit time, the rate of change of the number of particles within the segment is equal to the total flux times the cross-sectional area:

$$\frac{dN}{dt} = (J_1 + J_2) A.$$

Dividing by the volume of the segment gives the rate of change of the number density:

$$\frac{dn}{dt} = \frac{dN/dt}{A \Delta x} = \frac{1}{\Delta x} (J_1 + J_2).$$

Now express each flux in terms of dn/dx using Fick's (rst) law, being careful with the signs:

$$\frac{dn}{dt} = \frac{1}{\Delta x} \left(-D \frac{dn}{dx} \Big|_{x-\frac{\Delta x}{2}} + D \frac{dn}{dx} \Big|_{x+\frac{\Delta x}{2}} \right).$$

The right-hand side is just D times the second derivative of n with respect to x , so we finally arrive at the partial differential equation

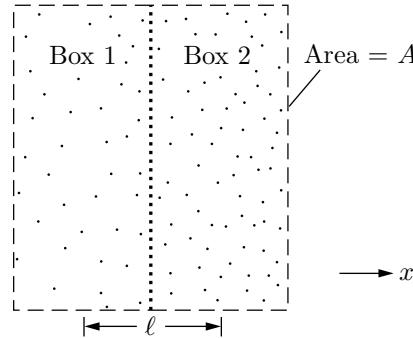
$$\frac{dn}{dt} = D \frac{d^2n}{dx^2}.$$

This equation has exactly the same form as the heat equation derived in Problem 1.62, with temperature here replaced by n and the constant K here replaced by D . Therefore particle diffusion behaves in the same way (mathematically) as heat conduction, and any solution of the heat equation can be carried over immediately to the case of diffusion. In particular, the spreading Gaussian solution discussed in Problem 1.62 becomes

$$n(x, t) = n_0 + \frac{a}{\sqrt{t}} e^{-x^2/4Dt},$$

representing an initially localized concentration of particles (above the background concentration n_0) that spreads out quickly at first and more slowly later on.

Problem 1.70. Consider two “boxes” within the gas, each of width ℓ (the mean free path) and cross-sectional area A :



During a time interval Δt equal to the average time between collisions (ℓ/\bar{v}), about half the molecules in Box 1 will move to Box 2, while about half the molecules in Box 2 move to Box 1. Denoting the concentrations of molecules within the boxes as n_1 and n_2 , the net migration of molecules from left to right is then roughly

$$\frac{1}{2}n_1A\ell - \frac{1}{2}n_2A\ell = \frac{1}{2}A\ell(n_1 - n_2),$$

and the flux is this quantity divided by A and by Δt :

$$J_x \approx \frac{A\ell(n_1 - n_2)}{2A\Delta t} = \frac{\ell(n_1 - n_2)}{2\ell/\bar{v}} = \frac{1}{2}\ell\bar{v}\frac{dn}{dx}.$$

Comparing to Fick’s law (equation 1.70), we can read off the diffusion coefficient as approximately $\frac{1}{2}\ell\bar{v}$. For air at room temperature, this evaluates to

$$D \approx \frac{1}{2}\ell\bar{v} = \frac{1}{2}(1.5 \times 10^{-7} \text{ m})(500 \text{ m/s}) = 4 \times 10^{-5} \text{ m}^2/\text{s},$$

about twice the experimental value quoted in the text. Since ℓ is proportional to $V/N = kT/P$ while \bar{v} is proportional to \sqrt{T} , the diffusion coefficient should be proportional to $T^{3/2}/P$. Therefore, at fixed pressure, doubling the temperature should increase the diffusion coefficient by a factor of about 2.8.

2 The Second Law

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Problem 2.1. (Flipping four coins.)

- a) Here are all the possible outcomes, 16 in total:

TTTT	TTHH	THHH
	THTH	HTHH
TTTH	THHT	HHTH
TTHT	HTTH	HHHT
THTT	HTHT	
HTTT	HHTT	HHHH

- b) The macrostates are:

0 heads, $\Omega = 1$, probability = $1/16$
1 head, $\Omega = 4$, probability = $4/16$
2 heads, $\Omega = 6$, probability = $6/16$
3 heads, $\Omega = 4$, probability = $4/16$
4 heads, $\Omega = 1$, probability = $1/16$

- c) For $N = 4$ and $n = 0$, equation 2.6 gives $\Omega = 4!/(0! \cdot 4!) = 1$, since $0! = 1$. For $n = 1$, we have $\Omega = 4!/(1! \cdot 3!) = 24/6 = 4$. For $n = 2$, $\Omega = 4!/(2! \cdot 2!) = 24/4 = 6$. For $n = 3$ the formula predicts the same result as for $n = 1$, namely 4. And for $n = 4$ it's again 1, the same as for $n = 0$.

Problem 2.2. (Flipping 20 coins.)

- a) Each coin has two possible states, and the coins are independent, so the total number of microstates is $2^{20} = 1048576$, or a little over a million.
b) The sequence given corresponds to just one particular microstate. If the coins are fair every microstate is equally probable, so the probability of any one of them, including this, is $1/2^{20}$ or a little less than one in a million. (And yet, amazingly, I got exactly that sequence, on the first try, when I was writing the problem!)
c) The number of ways of getting exactly 8 heads is

$$\binom{20}{8} = \frac{20 \cdot 19 \cdot 18 \cdot 17 \cdot 16 \cdot 15 \cdot 14 \cdot 13}{8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1} = 125970.$$

So the probability of getting exactly 8 heads is $125970/1048576 = 12.0\%$.

Problem 2.3. (Flipping 50 coins.)

- a) There are two possible states for the first coin, and for each of these, two for the second, and for each of these, two for the third, and so on. So the total number of microstates is $2^{50} = 1.13 \times 10^{15}$.
- b) The number of ways of getting exactly 25 heads is

$$\Omega(25) = \binom{50}{25} = \frac{50!}{(25!)^2} = 1.26 \times 10^{14}.$$

- c) The *probability* of getting exactly 25 heads is equal to the fraction of all states that have 25 heads:

$$\mathcal{P}(25) = \frac{\Omega(25)}{2^{50}} = 0.112.$$

- d) The probability of getting 30 heads would be

$$\mathcal{P}(30) = \frac{\Omega(30)}{2^{50}} = \frac{1}{2^{50}} \frac{50!}{(30!)(20!)} = 0.042.$$

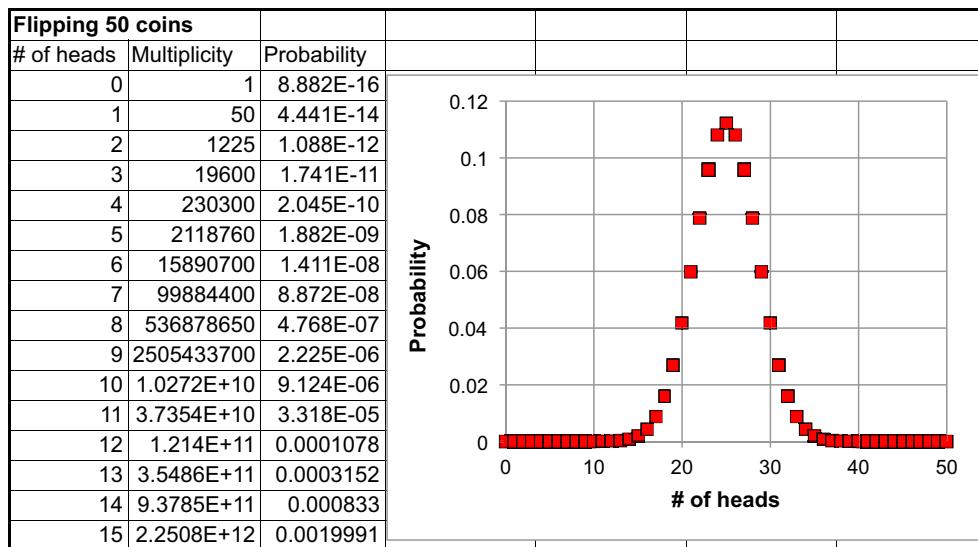
- e) The probability of getting 40 heads would be

$$\mathcal{P}(40) = \frac{\Omega(40)}{2^{50}} = \frac{1}{2^{50}} \frac{50!}{(40!)(10!)} = 0.00000091.$$

- f) There's only one way to get 50 heads, so the probability would be simply

$$\mathcal{P}(50) = \frac{1}{2^{50}} = 8.88 \times 10^{-16}.$$

- g) You can sketch the probability graph pretty well from the points computed in parts (c) through (f). Another option, though, is to use a computer spreadsheet. Shown below are the first several rows of a spreadsheet that computes the multiplicity and probability for any number of heads from 0 through 50. I plotted the third column vs. the first to obtain the graph at right.



Problem 2.4. The number of ways of choosing five cards from 52 is simply

$$\binom{52}{5} = \frac{52!}{(5!)(47!)} = 2.6 \times 10^6,$$

or 2.6 million. Of all of these possible hands, only four are royal flushes, so the probability of getting a royal flush on the first deal is

$$\frac{4}{2.6 \times 10^6} = 1.54 \times 10^{-6},$$

that is, somewhat better than one in a million.

Problem 2.5. (Microstates of a small Einstein solid.) To represent each microstate I'll use a sequence of digits, for the number of energy units in the first, second, and third oscillators, respectively.

a) $N = 3, q = 4$:

400	310	031	220	211
040	301	103	202	121
004	130	013	022	112

I count 15 microstates. And according to the formula, there should be

$$\binom{4+3-1}{4} = \frac{6!}{4! 2!} = \frac{6 \cdot 5}{2} = 15.$$

b) $N = 3, q = 5$:

500	410	041	320	032	311	221
050	401	104	302	203	131	212
005	140	014	230	023	113	122

I count 21 microstates. And according to the formula, there should be

$$\binom{5+3-1}{5} = \frac{7!}{5! 2!} = \frac{7 \cdot 6}{2} = 21.$$

c) $N = 3, q = 6$:

600	501	015	042	141	033	132
060	150	420	204	114	321	213
006	051	402	024	330	312	123
510	105	240	411	303	231	222

I count 28 microstates. And according to the formula, there should be

$$\binom{6+3-1}{6} = \frac{8!}{6! 2!} = \frac{8 \cdot 7}{2} = 28.$$

d) $N = 4, q = 2$:

2000	0020	1100	1001	0101
0200	0002	1010	0110	0011

I count 10 microstates. And according to the formula, there should be

$$\binom{2+4-1}{2} = \frac{5!}{2!3!} = \frac{5 \cdot 4}{2} = 10.$$

e) $N = 4, q = 3$:

3000	2100	0210	0021	1110
0300	2010	0201	1002	1101
0030	2001	1020	0102	1011
0003	1200	0120	0012	0111

I count 20 microstates. And according to the formula, there should be

$$\binom{3+4-1}{3} = \frac{6!}{3!3!} = \frac{6 \cdot 5 \cdot 4}{3 \cdot 2} = 20.$$

f) If $N = 1$, then all the energy must belong to the one and only oscillator, so there's only one microstate, which we would denote simple “q”. And according to the formula, the multiplicity should be

$$\binom{q+1-1}{q} = \frac{q!}{q!} = 1.$$

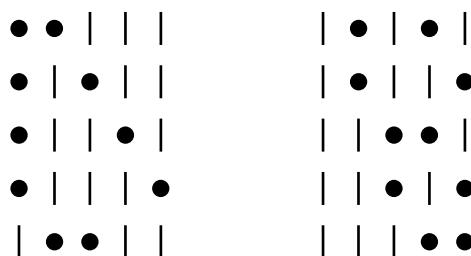
g) If $q = 1$, then there's only one unit of energy to distribute among the N oscillators, so the allowed states would be 1000, 0100, 0010, and so on up to 0001. There are N places to put the unit of energy, so the number of possible microstates is N . And indeed, according to the formula,

$$\Omega(N, 1) = \binom{1+N-1}{1} = \frac{N!}{1!(N-1)!} = N.$$

Problem 2.6. For $N = 30$ and $q = 30$, the number of microstates should be

$$\Omega(30, 30) = \binom{30+30-1}{30} = \frac{59!}{(30!)(29!)} = 5.91 \times 10^{16}.$$

Problem 2.7. To represent a system with four oscillators, we need three vertical lines (partitions between the oscillators). We also need two dots, to represent the two units of energy. So we want to draw all possible sequences of three lines and two dots. Here they are:



These ten microstates are, of course, the same as those enumerated in Problem 2.5(d).

Problem 2.8. (Two small Einstein solids.)

- a) Of the 20 units of energy, anywhere from 0 to 20 could be in solid *A*. Each possibility from 0 to 20 defines a different macrostate, so there are 21 macrostates in total.
- b) The combined system has 20 oscillators and 20 units of energy, so the total number of microstates is

$$\Omega(20, 20) = \binom{20+20-1}{20} = \frac{39!}{(20!)(19!)} = 6.89 \times 10^{10}.$$

- c) For the macrostate with all the energy in solid *A*, the multiplicity of solid *A* is

$$\Omega(10, 20) = \binom{20+10-1}{20} = \frac{29!}{(20!)(9!)} = 1.00 \times 10^7,$$

while the multiplicity of solid *B* is 1. Assuming that the system is in equilibrium, all microstates are equally probable, so the probability of this macrostate is

$$\text{Probability} = \frac{\Omega(\text{this state})}{\Omega(\text{total})} = \frac{1.00 \times 10^7}{6.89 \times 10^{10}} = 1.45 \times 10^{-4}.$$

- d) For the macrostate with half the energy in each solid, the multiplicity of the combined system is

$$\Omega = \Omega_A \Omega_B = \binom{10+10-1}{10} \binom{10+10-1}{10} = \left(\frac{19!}{(10!)(9!)} \right)^2 = 8.534 \times 10^9,$$

so the probability (in equilibrium) is

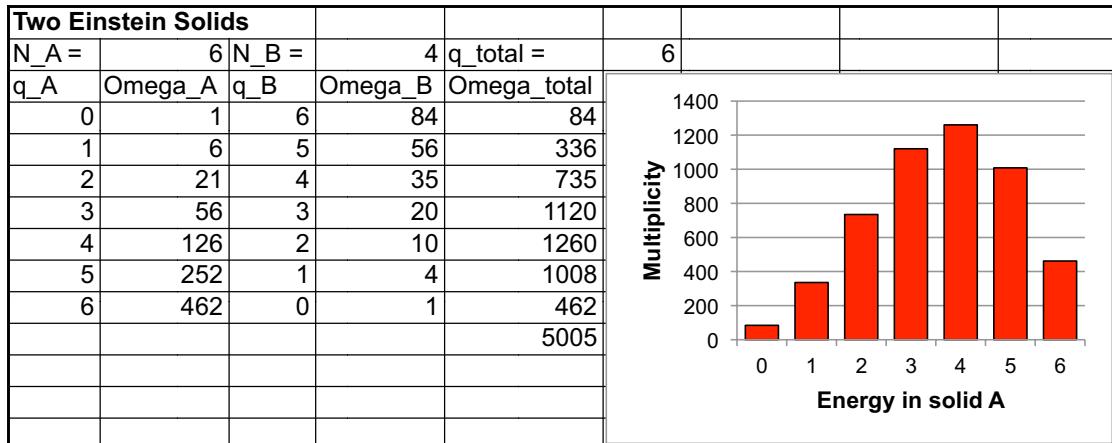
$$\text{Probability} = \frac{8.53 \times 10^9}{6.89 \times 10^{10}} = 0.124.$$

- e) The probability of the energy being evenly distributed is greater than that of all the energy being in *A* by a factor of nearly 1000. So if this system started out with all (or nearly all) of the energy in one solid or the other, then we could be pretty sure that it would evolve toward a state with energy more evenly distributed. And if it started out with the energy evenly distributed, we could be pretty sure that at some later time we wouldn't find all the energy on one side or the other—this would happen less than one time in a thousand. So the evolution from the unlikely state to the likely one is sort of irreversible, but not exactly since the process does occasionally happen in reverse.

Problem 2.9. I used the Excel spreadsheet program. Here are the formulas that reproduce the table in Figure 2.4:

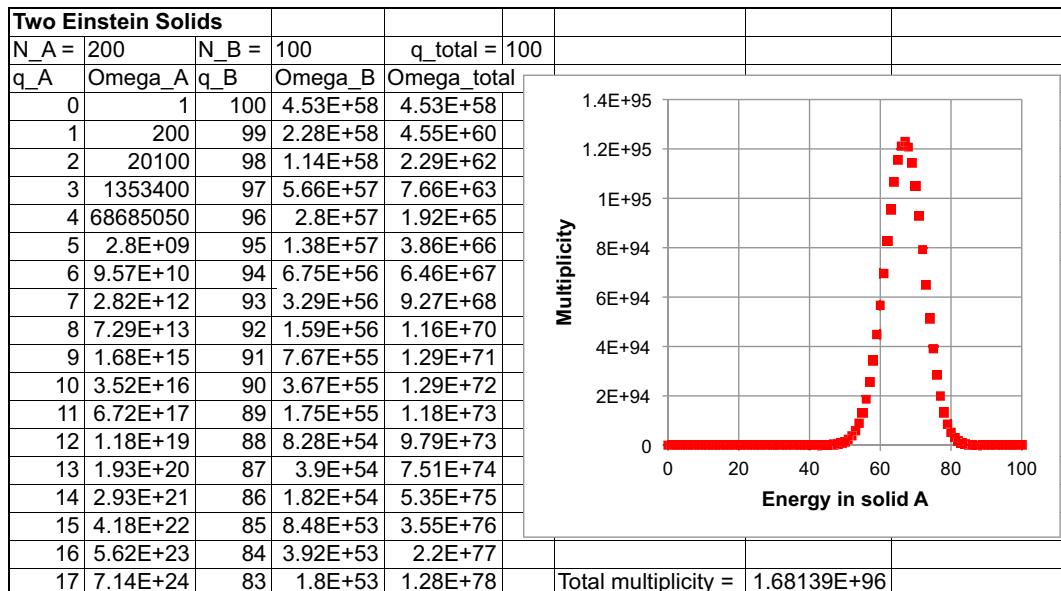
	A	B	C	D	E	F
1	Two	Einstein	Solids			
2	N_A =	3	N_B =	3	q_total =	6
3	q_A	Omega_A	q_B	Omega_B	Omega_total	
4	0	=COMBIN(A4+\$B\$2-1,A4)	=\$F\$2-A4	=COMBIN(C4+\$D\$2-1,C4)	=B4*D4	
5	=A4+1	=COMBIN(A5+\$B\$2-1,A5)	=\$F\$2-A5	=COMBIN(C5+\$D\$2-1,C5)	=B5*D5	
6	=A5+1	=COMBIN(A6+\$B\$2-1,A6)	=\$F\$2-A6	=COMBIN(C6+\$D\$2-1,C6)	=B6*D6	
7	=A6+1	=COMBIN(A7+\$B\$2-1,A7)	=\$F\$2-A7	=COMBIN(C7+\$D\$2-1,C7)	=B7*D7	
8	=A7+1	=COMBIN(A8+\$B\$2-1,A8)	=\$F\$2-A8	=COMBIN(C8+\$D\$2-1,C8)	=B8*D8	
9	=A8+1	=COMBIN(A9+\$B\$2-1,A9)	=\$F\$2-A9	=COMBIN(C9+\$D\$2-1,C9)	=B9*D9	
10	=A9+1	=COMBIN(A10+\$B\$2-1,A10)	=\$F\$2-A10	=COMBIN(C10+\$D\$2-1,C10)	=B10*D10	
11					=SUM(E4:E10)	

Then I changed the values in cells B2 and D2 to obtain the following table:



The most probable macrostate is $q_A = 4, q_B = 2$, with probability $1260/5005 = 25.2\%$. The least probable macrostate is $q_A = 0, q_B = 6$, with probability $84/5005 = 1.7\%$.

Problem 2.10. Here's an Excel spreadsheet showing the case $N_A = 200$, $N_B = 100$, and $q_{\text{total}} = 100$:

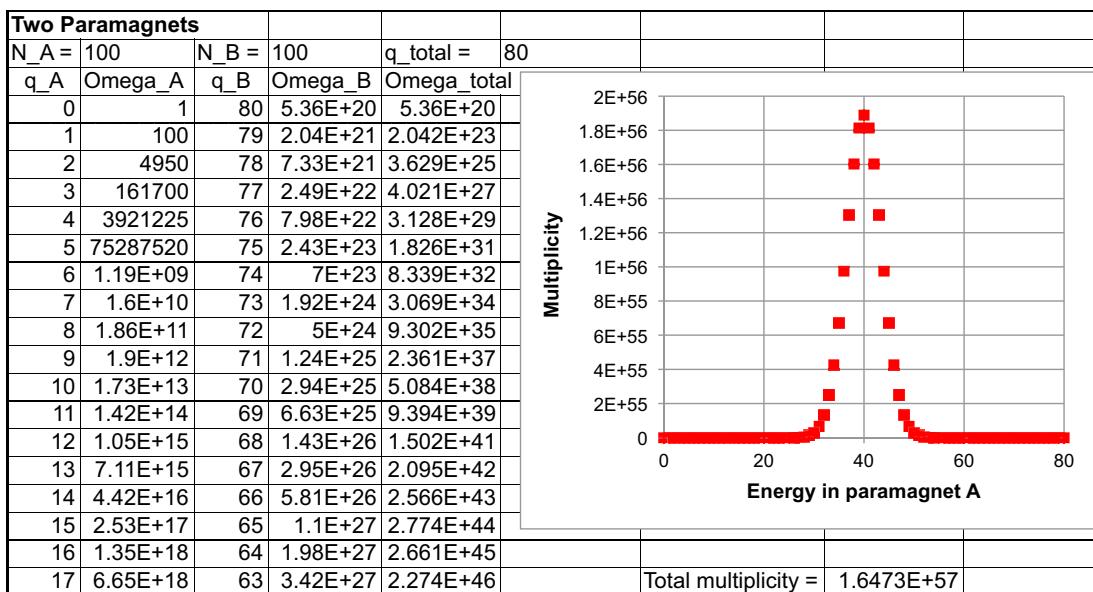


(To save space I've shown only the first 18 of the 101 rows.) The most probable macrostate is $q_A = 67$, $q_B = 33$, with probability $1.23 \times 10^{95} / 1.68 \times 10^{96} = 7.3\%$ (not terribly large). The least probable macrostate is $q_A = 0$, $q_B = 100$, with probability $4.53 \times 10^{58} / 1.68 \times 10^{96} = 2.7 \times 10^{-38}$ (tiny!).

Problem 2.11. The main difference between this system and the system of two Einstein solids considered in the text (and in the previous three problems) is that for a two-state paramagnet with N elementary dipoles and q units of energy (equal to the number of dipoles pointing down), the multiplicity is simply

$$\Omega(N, q) = \binom{N}{q}.$$

This formula therefore appears in the second and fourth columns of the spreadsheet. For example, the formula in Cell B4 is “=COMBIN(\$B\$2,A4)”. With $q_{\text{total}} = 80$, the main body of the spreadsheet contains 81 rows, the first several of which are as follows:



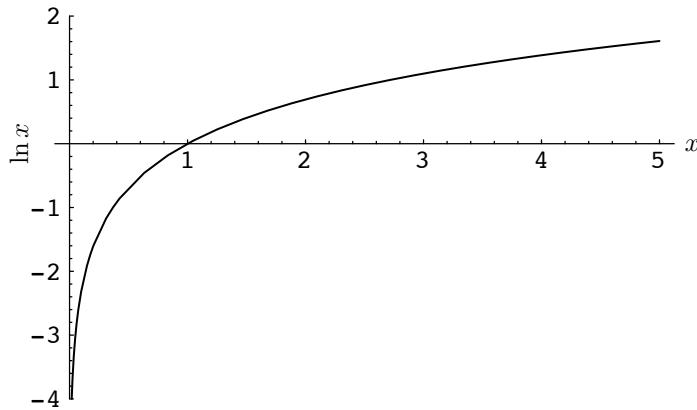
Although the graph of Ω_{total} looks very similar to the case of two identical Einstein solids, it is interesting to note that the multiplicities of the *individual* paramagnets are maximized when $q = 50$, that is, when half the dipoles point up and half point down; the consequences of this behavior are explored in Section 3.3.

Since the two paramagnets are the same size, the most probable macrostate is the one with the energy evenly distributed: $q_A = q_B = 40$, with $\Omega_{\text{total}} = 1.9 \times 10^{56}$ and probability 11.4%. The least likely macrostates are the two at the extremes, with all the energy on one side or the other: $q_A = 0$ and $q_B = 80$ (or vice-versa), with $\Omega_{\text{total}} = 5.4 \times 10^{20}$ and probability 3.3×10^{-37} .

Problem 2.12. (Properties of the natural log function.)

- a) From the definition $e^{\ln x} = x$ we can see that $\ln x$ is defined only for positive x , and that it is an increasing function of x . A few particular values are $\ln 1 = 0$, $\ln e = 1$, and $\ln(1/e) = -1$. Starting from these values it's easy to sketch the graph. For this official solution, however, I plotted a precise graph using *Mathematica*, with the instruction

`Plot[Log[x],{x,0,5},PlotRange->{-4,2}]:`



- b) To prove that $\ln ab = \ln a + \ln b$, start with the exponential of the left-hand side:

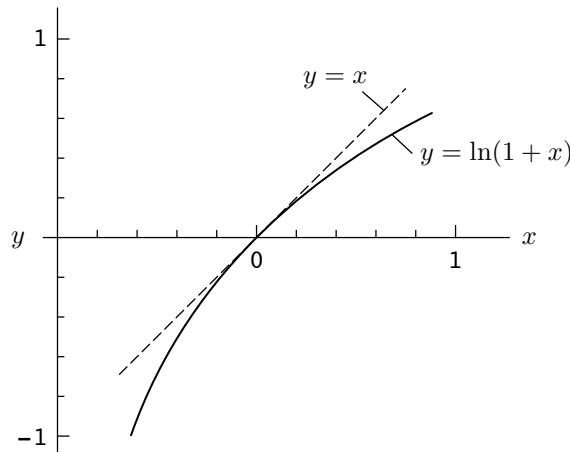
$$e^{\ln ab} = ab = e^{\ln a}e^{\ln b} = e^{\ln a + \ln b},$$

where the last step follows from the properties of exponents. Undoing the exponentiation now gives the desired identity. Similarly,

$$e^{\ln a^b} = a^b = (e^{\ln a})^b = e^{b \ln a},$$

so we can conclude that $\ln a^b = b \ln a$.

- c) Let $y = \ln x$, so that $e^y = x$. Differentiating the latter equation gives $dx/dy = e^y$, and taking the reciprocal of this result gives $dy/dx = 1/e^y = 1/x$, in other words, the derivative of $\ln x$ is $1/x$.
- d) You can derive this approximation, and improvements to it, using a Taylor series. But it's simpler to just approximate $\ln(1+x)$ by the best straight line near the point $x=0$, that is, where the argument of the log function equals 1:



At this point, the derivative of the natural log function is $1/1 = 1$. Therefore, if you imagine zooming in on a tiny part of the graph around this point, it will look

like a straight line with a slope of 1. The equation of this line is $y = x$, so we can approximate $\ln(1 + x) \approx x$. For $x = 0.1$, $\ln(1 + x) = 0.0953$, off by about 5%. For $x = 0.01$, $\ln(1 + x) = 0.00995$, off by only 0.5%.

Problem 2.13. (Fun with logarithms.)

- a) $e^{a \ln b} = (e^{\ln b})^a = b^a$.
- b) $\ln(a + b) = \ln\left[a\left(1 + \frac{b}{a}\right)\right] = \ln a + \ln\left(1 + \frac{b}{a}\right)$. The second logarithm can be simplified using the approximation $\ln(1 + x) \approx x$, which is valid when $|x| \ll 1$. In this case the logarithm is just b/a , so $\ln(a + b) \approx \ln a + (b/a)$.

Problem 2.14. We want to solve the equation

$$e^{10^{23}} = 10^x$$

for x . A good first step is to take the natural log of both sides. Then the left-hand side becomes simply 10^{23} , while the right-hand side becomes $\ln 10^x = x \ln 10$. Therefore,

$$x = \frac{10^{23}}{\ln 10} = 4.34 \times 10^{22}.$$

So $e^{10^{23}} = 10^{4.34 \times 10^{22}}$.

Problem 2.15. According to my calculator, $50! = 3.0414 \times 10^{64}$. Stirling's approximation, however, gives

$$50! \approx 50^{50} e^{-50} \sqrt{2\pi}^{50} = 3.0363 \times 10^{64},$$

off by about 0.2%. The natural logarithm of $50!$ is 148.5, while the simplified form of Stirling's approximation gives

$$\ln 50! \approx 50 \ln 50 - 50 = 145.6,$$

off by about 2%.

Problem 2.16. First note that for 1000 coins, the total number of possible outcomes (microstates) is 2^{1000} .

- a) The number of ways of getting exactly 500 heads and 500 tails is

$$\Omega(500) = \binom{1000}{500} = \frac{1000!}{(500!)^2} \approx \frac{1000^{1000} e^{-1000} \sqrt{2\pi}^{1000}}{(500^{500} e^{-500} \sqrt{2\pi}^{500})^2} = \frac{2^{1000}}{\sqrt{500\pi}}.$$

The probability is this divided by 2^{1000} , or simply $1/\sqrt{500\pi} = .025$. So the chance of getting exactly 500 heads is about 2.5%, or 1 in 40.

- b) The number of ways of getting exactly 600 heads and 400 tails is

$$\begin{aligned} \Omega(600) &= \binom{1000}{600} = \frac{1000!}{600! 400!} \approx \frac{1000^{1000} e^{-1000} \sqrt{2\pi}^{1000}}{600^{600} e^{-600} \sqrt{2\pi}^{600} 400^{400} e^{-400} \sqrt{2\pi}^{400}} \\ &= \frac{1000^{1000}}{600^{600} 400^{400} \sqrt{480\pi}}. \end{aligned}$$

Again, the probability is this divided by 2^{1000} :

$$P(600) = \frac{500^{1000}}{600^{600} 400^{400} \sqrt{480\pi}} = \frac{500^{600} 500^{400}}{600^{600} 400^{400} \sqrt{480\pi}} = \left(\frac{5}{6}\right)^{600} \left(\frac{5}{4}\right)^{400} \frac{1}{\sqrt{480\pi}}.$$

Now all the factors can be evaluated on a calculator. The result is $P(600) = 4.6 \times 10^{-11}$, much smaller than $P(500)$.

Problem 2.17. To simplify Ω in the limit $q \ll N$ (with both q and N large), we can start by repeating exactly the same steps as in equations 2.17 and 2.18 to obtain

$$\ln \Omega \approx (N+q) \ln(N+q) - q \ln q - N \ln N.$$

Now expand the first logarithm in the limit $q \ll N$:

$$\ln(N+q) = \ln\left[N\left(1 + \frac{q}{N}\right)\right] = \ln N + \ln\left(1 + \frac{q}{N}\right) \approx \ln N + \frac{q}{N}.$$

Plugging this result into the previous equation and canceling the $N \ln N$ terms, we obtain

$$\ln \Omega \approx q \ln N + q + \frac{q^2}{N} \quad q \ln q \approx q \ln \frac{N}{q} + q,$$

where in the last step I've dropped the q^2/N since it's much smaller than the others. Exponentiating now gives

$$\Omega \approx e^{q \ln(N/q)} e^q = \left(\frac{N}{q}\right)^q e^q = \left(\frac{eN}{q}\right)^q.$$

Since the original formula for Ω is symmetrical under the interchange of q and N (after the initial approximation in equation 2.17), we could have obtained this result simply by interchanging q and N in equation 2.21.

Problem 2.18. First note that $(N-1)! = N!/N$, since dividing by N cancels the final factor in $N!$, leaving just the first $N-1$ factors. Similarly, $(q+N-1)! = (q+N)!/(q+N)$. Thus, as the hint says,

$$\Omega(N, q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} = \frac{(q+N)!}{q!N!} \frac{N}{q+N}.$$

Now apply Stirling's approximation to each of the factorials and cancel as many factors as possible:

$$\Omega(N, q) \approx \frac{(q+N)^{q+N} e^{-(q+N)} \sqrt{2\pi(q+N)}}{q^q e^{-q} \sqrt{2\pi q} N^N e^{-N} \sqrt{2\pi N}} \frac{N}{q+N} = \frac{(q+N)^{q+N}}{q^q N^N} \sqrt{\frac{N}{2\pi q(q+N)}}.$$

Finally, write $(q+N)^{q+N}$ as $(q+N)^q (q+N)^N$, to obtain

$$\Omega(N, q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \sqrt{\frac{N}{2\pi q(q+N)}}.$$

Problem 2.19. The multiplicity of a two-state paramagnet is

$$\Omega = \binom{N}{N_{\downarrow}} = \frac{N!}{N_{\downarrow}! (N - N_{\downarrow})!}.$$

Applying Stirling's approximation to each of the factorials gives

$$\Omega \approx \frac{(N/e)^N}{(N_{\downarrow}/e)^{N_{\downarrow}} ((N - N_{\downarrow})/e)^{N - N_{\downarrow}}} = \frac{N^N}{N_{\downarrow}^{N_{\downarrow}} (N - N_{\downarrow})^{N - N_{\downarrow}}},$$

up to factors that are merely large. Taking the logarithm of both sides gives

$$\ln \Omega \approx N \ln N - N_{\downarrow} \ln N_{\downarrow} - (N - N_{\downarrow}) \ln(N - N_{\downarrow}).$$

The final logarithm can be written $\ln[N(1 - N_{\downarrow}/N)] = \ln N + \ln(1 - N_{\downarrow}/N)$. In the limit $N_{\downarrow} \ll N$, the second term is approximately $-N_{\downarrow}/N$, so

$$\ln \Omega \approx N \ln N - N_{\downarrow} \ln N_{\downarrow} - (N - N_{\downarrow}) \left(\ln N - \frac{N_{\downarrow}}{N} \right).$$

The $N \ln N$ terms cancel, while the term N_{\downarrow}^2/N is negligible compared to the others. Gathering the remaining terms gives

$$\ln \Omega \approx N_{\downarrow} \ln \frac{N}{N_{\downarrow}} + N_{\downarrow} = N_{\downarrow} \ln \frac{Ne}{N_{\downarrow}} = \ln \left(\frac{Ne}{N_{\downarrow}} \right)^{N_{\downarrow}},$$

so in this limit the multiplicity is approximately

$$\Omega \approx \left(\frac{Ne}{N_{\downarrow}} \right)^{N_{\downarrow}}.$$

This is the same result as in Problem 2.17, but with q replaced by N_{\downarrow} . The difference between the two systems is that each particle in the paramagnet can hold at most one unit of energy (obtained by flipping the dipole from up to down), while each oscillator in the Einstein solid can hold arbitrarily many units of energy. Apparently, in the limit where the total number of energy units is much less than the number of particles, the states of the Einstein solid in which some oscillators contain more than one unit of energy (each) are insignificant; they contribute a factor to the multiplicity that is merely large.

Problem 2.20. To shrink Figure 2.7 to fit on the page, we would have to reduce the full scale of 100,000 km down to about 20 cm. That's a reduction factor of

$$\frac{100,000 \text{ km}}{20 \text{ cm}} = \frac{10^8 \text{ m}}{0.2 \text{ m}} = 5 \times 10^8.$$

The width of the peak would therefore be reduced by this same factor, from 1 cm down to

$$\frac{1 \text{ cm}}{5 \times 10^8} = 2 \times 10^{-11} \text{ m} = 0.2 \text{ \AA},$$

a few times smaller than the size of an atom(!).

Problem 2.21. First let's check the algebra in the problem. Defining $z = q_A/q$, we have

$$1 - z = 1 - \frac{q_A}{q} = \frac{q - q_A}{q} = \frac{q_B}{q},$$

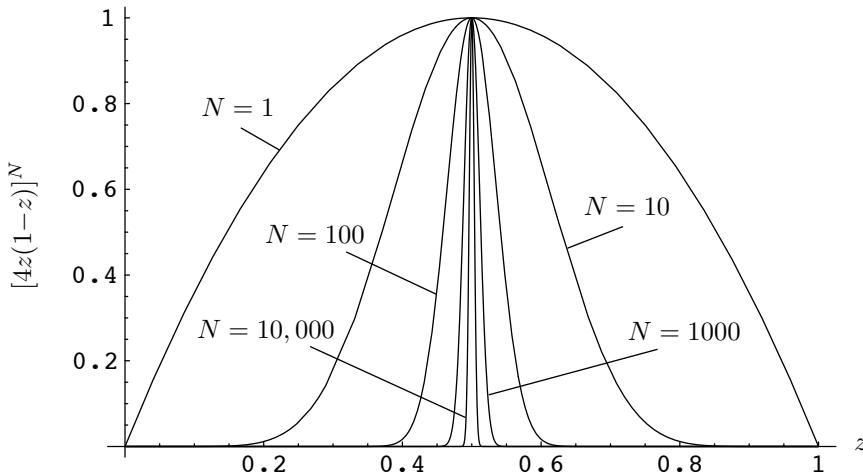
as claimed. We can therefore rewrite equation 2.22 as

$$\Omega = \left(\frac{e}{N}\right)^{2N} [qz - q(1 - z)]^N = \left(\frac{qe}{N}\right)^{2N} [z(1 - z)]^N = \left(\frac{qe}{2N}\right)^{2N} [4z(1 - z)]^N.$$

The first factor is just the height of the peak, Ω_{\max} (see equation 2.23). Dividing by this factor should give a function of the same shape, but scaled so that its maximum value is 1. To plot this formula for several values of N , I used the *Mathematica* instruction

```
Plot[Evaluate[Table[(4z(1-z))^(10^p), {p, 0, 4}]], {z, 0, 1}, PlotRange->All];
```

This produced the following graph, showing how the peak gets skinnier as N increases:



Problem 2.22. (Estimating the width of the multiplicity peak.)

- a) The number of energy units in Solid A can be 0, 1, 2, etc., up to $2N$, so the total number of macrostates is $2N + 1$.
- b) According to Problem 2.18, the multiplicity of any large Einstein solid is

$$\Omega(N, q) = \left(\frac{q + N}{q}\right)^q \left(\frac{q + N}{N}\right)^N \sqrt{\frac{N}{2\pi q(q + N)}}.$$

Here we want to substitute $2N$ for both N and q , so the multiplicity reduces to

$$\Omega_{\text{total}} = \left(\frac{2N+2N}{2N}\right)^{2N} \left(\frac{2N+2N}{2N}\right)^{2N} \sqrt{\frac{2N}{2\pi \cdot 2N(2N+2N)}} = 2^{2N} 2^{2N} \sqrt{\frac{1}{8\pi N}} = \frac{2^{4N}}{\sqrt{8\pi N}}.$$

- c) The multiplicity of just Solid A, when it has exactly half of the energy ($q = N$), is

$$\Omega_A = \left(\frac{N+N}{N}\right)^N \left(\frac{N+N}{N}\right)^N \sqrt{\frac{N}{2\pi N(N+N)}} = 2^N 2^N \sqrt{\frac{1}{4\pi N}} = \frac{2^{2N}}{\sqrt{4\pi N}}.$$

Since the multiplicity of Solid B is the same, the multiplicity of the composite system in this macrostate is just the square of Ω_A ,

$$\Omega_{\text{most likely}} = \frac{2^{4N}}{4\pi N}.$$

- d) Since the height of the peak is $\Omega_{\text{most likely}}$ while the area under the peak is Ω_{total} , the width of the peak must be roughly

$$\frac{\Omega_{\text{total}}}{\Omega_{\text{most likely}}} = \frac{2^{4N}/\sqrt{8\pi N}}{2^{4N}/4\pi N} = \frac{4\pi N}{\sqrt{8\pi N}} = \sqrt{2\pi N}.$$

This is fairly large, but the width of the entire graph of Ω vs. q_A is $2N + 1$, so the fractional width of the peak is $\sqrt{2\pi N}/(2N) = \sqrt{\pi/(2N)} \sim 1/\sqrt{N}$. This is quite small: when $N = 10^{23}$, the fractional width is less than 10^{-11} , or one part in 100 billion.

Problem 2.23. (A large two-state paramagnet.)

- a) With N dipoles of which exactly $N/2$ point up, the multiplicity of the paramagnet is

$$\Omega = \binom{N}{N/2} = \frac{N!}{[(N/2)!]^2} \approx \frac{N^N e^{-N} \sqrt{2\pi N}}{[(N/2)^{N/2} e^{-N/2} \sqrt{\pi N}]^2} = 2^N \sqrt{\frac{2}{\pi N}}.$$

For $N = 10^{23}$, then, the multiplicity is roughly $2^{10^{23}}/(4 \times 10^{11})$. Since the denominator is merely large, we could just as well neglect it and say that $\Omega = 2^{10^{23}}$, which is the number of microstates if we allow any number of dipoles to be pointing up.

- b) A year is about 3×10^7 seconds, so ten billion years is 3×10^{17} seconds or 3×10^{26} nanoseconds. If the microstate of the system changes once per nanosecond, this is how many microstates the system will explore in the age of the universe. But this is a *tiny* fraction of the total number of microstates—so small a fraction that the ratio of states not explored to states explored is, to within the limits of compact notation, $2^{10^{23}}$.
- c) Even if we wait for the age of the universe, the fraction of all “accessible” microstates that are actually explored by this system is so tiny that it might be more accurate to say that the system explores *none* of its “accessible” microstates. When we call a microstate “accessible,” therefore, we should not think that the system will ever actually be in that microstate. So what *do* we mean? I think the best interpretation is in terms of our ignorance of which microstates the system will actually explore in the future. *For all we know*, the system might soon be found in any of its “accessible” microstates, even though the probability of its being found in any one of them is Vanishingly small.

Problem 2.24. (Multiplicity of a large two-state paramagnet.)

- a) The most likely macrostate is $N_\uparrow = N_\downarrow = N/2$. At this point the multiplicity is

$$\Omega_{\max} = \frac{N!}{N_\uparrow!N_\downarrow!} = \frac{N!}{(\frac{N}{2}!)^2} \approx \frac{N^N e^{-N} \sqrt{2\pi N}}{(\frac{N}{2})^{N/2} e^{-N/2} \sqrt{2\pi N/2})^2} = 2^N \sqrt{\frac{2}{\pi N}}.$$

- b) By Stirling's approximation, the multiplicity is

$$\Omega = \frac{N!}{N_\uparrow!N_\downarrow!} \approx \frac{N^N e^{-N} \sqrt{2\pi N}}{N_\uparrow^{N_\uparrow} e^{-N_\uparrow} \sqrt{2\pi N_\uparrow} N_\downarrow^{N_\downarrow} e^{-N_\downarrow} \sqrt{2\pi N_\downarrow}} = \frac{N^N}{N_\uparrow^{N_\uparrow} N_\downarrow^{N_\downarrow}} \sqrt{\frac{N}{2\pi N_\uparrow N_\downarrow}}.$$

If we set $N_\uparrow = (N/2) + x$, then $N_\downarrow = (N/2) - x$, and the multiplicity can be written

$$\begin{aligned} \Omega &\approx \frac{N^N}{\left(\frac{N}{2} + x\right)^{\frac{N}{2}+x} \left(\frac{N}{2} - x\right)^{\frac{N}{2}-x}} \sqrt{\frac{N}{2\pi \left(\frac{N}{2} + x\right) \left(\frac{N}{2} - x\right)}} \\ &= \frac{N^N}{\left[\left(\frac{N}{2}\right)^2 - x^2\right]^{N/2} \left(\frac{N}{2} + x\right)^x \left(\frac{N}{2} - x\right)^x} \sqrt{\frac{N}{2\pi \left[\left(\frac{N}{2}\right)^2 - x^2\right]}}. \end{aligned}$$

At this point it becomes simpler to work with the logarithm of the multiplicity:

$$\begin{aligned} \ln \Omega &= N \ln N - \frac{N}{2} \ln \left[\left(\frac{N}{2} \right)^2 - x^2 \right] - x \ln \left(\frac{N}{2} + x \right) + x \ln \left(\frac{N}{2} - x \right) \\ &\quad + \ln \sqrt{\frac{N}{2\pi}} - \frac{1}{2} \ln \left[\left(\frac{N}{2} \right)^2 - x^2 \right] \end{aligned}$$

So far I haven't assumed anything about the size of x relative to N . But if $x \ll N$, we can expand each of the logarithms containing two terms. For example,

$$\ln \left[\left(\frac{N}{2} \right)^2 - x^2 \right] = \ln \left(\frac{N}{2} \right)^2 + \ln \left[1 - \left(\frac{2x}{N} \right)^2 \right] \approx 2 \ln \left(\frac{N}{2} \right) - \left(\frac{2x}{N} \right)^2.$$

Similarly,

$$\ln \left(\frac{N}{2} \pm x \right) = \ln \left(\frac{N}{2} \right) + \ln \left[1 \pm \frac{2x}{N} \right] \approx \ln \left(\frac{N}{2} \right) \pm \frac{2x}{N}.$$

With these approximations, the logarithm of the multiplicity becomes

$$\begin{aligned} \ln \Omega &= N \ln N - N \ln \frac{N}{2} + \frac{2x^2}{N} - x \ln \frac{N}{2} - \frac{2x^2}{N} + x \ln \frac{N}{2} - \frac{2x^2}{N} \\ &\quad + \ln \sqrt{\frac{N}{2\pi}} - \ln \frac{N}{2} + \frac{2x^2}{N^2} \\ &= N \ln 2 - \frac{2x^2}{N} + \ln \sqrt{\frac{2}{\pi N}} - \frac{2x^2}{N^2}. \end{aligned}$$

The last term is much smaller than the others and can be neglected. Exponentiating the remaining terms gives

$$\Omega = 2^N \sqrt{\frac{2}{\pi N}} e^{-2x^2/N} \quad (\text{for } x \ll N).$$

This is a Gaussian function, peaked at $x = 0$, where its value agrees with the result of part (a).

- c) The Gaussian function falls off to $1/e$ of its peak value when $2x^2/N = 1$ or $x = \sqrt{N/2}$. So the full width of the peak would be twice this, or $\sqrt{2N}$.
- d) For $N = 10^6$, the half-width of the peak in the multiplicity function would be $\sqrt{500,000}$ or about 700. So an excess of 1000 heads puts us only a little beyond the point where the Gaussian has fallen off to $1/e$ of its maximum value. I wouldn't be surprised to obtain *approximately* this many heads, though I might be surprised to get an excess of *exactly* 1000. On the other hand, an excess of 10,000 heads lies far outside of the peak in the multiplicity function. At this point the Gaussian has fallen off to $e^{-200} \approx 10^{-87}$ of its maximum value. If I got a result anywhere close to this, I would be quite certain that the coins were not fair.

Problem 2.25. (Random walk.)

- a) Since each step of a random walk is equally likely to be forward or backward, the *most* likely ending place is right where I start—after an equal number of forward and backward steps.
- b) The distribution of possible ending places is the same as the probability distribution for coin tosses, as treated in the previous problem. For a large number of steps, this distribution is a Gaussian of the form $e^{-2x^2/N}$, where N is the total number of steps and x is the *excess* of forward steps over $N/2$. If each step has size ℓ (the mean free path), then the net distance traveled is ℓ times the difference between the numbers of forward and backward steps, that is, $2x\ell$. In this problem I'd rather use the symbol x for this net distance traveled, so let me substitute $x \rightarrow x/2\ell$ in the formula and write

$$\text{Distribution of ending positions} \propto e^{-x^2/2\ell^2 N}.$$

The half-width of this distribution (where it falls off to $1/e$ of its peak value) is $\sqrt{2N}\ell$, or $\sqrt{2N}$ step lengths. For $N = 10,000$, the half-width is about 140 steps, meaning that there's a good chance I'll end up within about 140 steps (in either direction) of my starting place. The chance of getting farther than about five hundred steps is negligible.

- c) As computed on page 42, the mean free path (ℓ) in air under atmospheric conditions is approximately 150 nm, and the average collision time ($\bar{\Delta t}$) is about 3×10^{-10} s. So in one second, the number of steps is about $N = 3 \times 10^9$, and therefore the expected net distance traveled is about $\sqrt{2N} = 80,000$ steps, or 12 million nanometers, or 12 mm. If we wait longer, the number of steps increases in proportion to t , but the average net distance traveled increases only in proportion to \sqrt{t} . At higher temperatures (but fixed pressure), the mean free path, which is proportional to V/N , would increase in

proportion to T . But the molecules are also moving faster, in proportion to \sqrt{T} , so the collision time, $\overline{\Delta t} = \ell/\bar{v}$, increases only in proportion to \sqrt{T} . The number of steps taken per second is therefore less, proportional to $1/\sqrt{T}$. The expected net distance traveled, measured as a number of steps, is proportional to $\sqrt{N} \propto T^{1/4}$. Multiply this by the step size, which is proportional to T , and we finally find that the expected net distance increases in proportion to $T^{3/4}$.

Comparison to Section 1.7: In Problem 1.69 we found that a localized concentration of particles diffuses with time according to the Gaussian distribution

$$\text{Excess concentration} \propto e^{-x^2/4Dt},$$

where D is the diffusion coefficient. And in Problem 1.70, we found that the diffusion coefficient is roughly

$$D \approx \frac{1}{2}\ell\bar{v},$$

where ℓ is the mean free path and \bar{v} is the average thermal velocity, equal to ℓ divided by the average collision time $\overline{\Delta t}$. Therefore the distribution of excess concentration can be written

$$\text{Excess concentration} \propto e^{-x^2/2\ell\bar{v}t} = e^{-x^2-t/2\ell^2t}.$$

But $t/\overline{\Delta t}$ is just the total number of steps that a molecule can take in time t . Therefore this distribution agrees exactly with result of the present analysis in terms of a random walk. The only difference is that here we're talking about the statistical distribution in the position of a single particle, whereas in Section 1.7 we thought in terms of a large number of particles spreading out simultaneously.

Problem 2.26. For a single atom confined to an area A , we would expect the multiplicity to be proportional to A/A_p , in analogy to equation 2.29. The constraint that determines the allowed region of momentum space is simply $p_x^2 + p_y^2 = 2mU$, and the constant of proportionality is $1/h^2$, since the number of distinct states for each dimension is still LL_p/h . Putting all these factors together gives $\Omega_1 = AA_p/h^2$. For a gas of N atoms we more or less raise this expression to the N th power, as in the three-dimensional case. Again, however, there is a factor of $1/N!$ to compensate for multiple counting of states with particles interchanged. And the momentum-space factor is the “surface area” of a hypersphere of dimension $2N$ (and radius $\sqrt{2mU}$ as before). Thus the multiplicity of the flatland gas is

$$\Omega(N, U, A) = \frac{1}{N!} \frac{A^N}{h^{2N}} \frac{\pi^N}{N!} (2mU)^N.$$

As in equation 2.40, I've omitted a few factors that are merely large.

Problem 2.27. The probability of finding any particular gas molecule in the leftmost 99% of a container is 99%. So the probability of finding all 100 molecules in the leftmost 99% would be

$$(0.99)^{100} = 0.366;$$

in other words, the rightmost 1% of the container will be empty about a third of the time. If instead there are 10,000 molecules, however, the probability drops to

$$(0.99)^{10,000} = (0.366)^{100} = 2.25 \times 10^{-44};$$

so this will “never” happen. And if there are 10^{23} molecules, the probability would be unimaginably small,

$$(0.99)^{10^{23}} = 10^{-4.4 \times 10^{20}}.$$

Problem 2.28. There are 52 possible cards that could be on top, and for each of these choices there are 51 possibilities for the next card, then 50 for the next, and so on down to 1 choice for the bottom card. So the total number of arrangements is just $52! = 8.06 \times 10^{67}$. If all arrangements are accessible, then the entropy is

$$\frac{S}{k} = \ln 52! = 156; \quad S = 156k = 2.16 \times 10^{-21} \text{ J/K.}$$

This is then the amount of entropy created by shuffling the cards, and it's *tiny* compared to the entropy associated with thermal motions, which is typically a large number (proportional to the number of particles) in fundamental units and a number of order 1 when multiplied by Boltzmann's constant.

Problem 2.29. For the most likely macrostate (with $q_A = 60$),

$$\frac{S}{k} = \ln(6.9 \times 10^{114}) = \ln 6.9 + 114 \ln 10 = 264.4.$$

And for the least likely macrostate ($q_A = 0$),

$$\frac{S}{k} = \ln(2.8 \times 10^{81}) = 187.5.$$

Even though the most likely macrostate is 10^{33} times more probable than the least likely macrostate, its entropy is larger by less than 80 units.

Over long time scales, where all macrostates are allowed, the entropy is

$$\frac{S}{k} = \ln(9.3 \times 10^{115}) = \ln 9.3 + 115 \ln 10 = 267.0,$$

only slightly larger than the entropy of the most likely macrostate.

Problem 2.30. (Entropy of two large interacting Einstein solids.)

a) When all microstates are allowed, the entropy is

$$\frac{S}{k} = \ln \frac{2^{4N}}{\sqrt{8\pi N}} = 4N \ln 2 - \ln \sqrt{8\pi N} = 2.77 \times 10^{23} \quad 28.1$$

for $N = 10^{23}$.

- b) For the most likely macrostate,

$$\frac{S}{k} = \ln \frac{2^{4N}}{4\pi N} = 4N \ln 2 \quad \ln(4\pi N) = 2.77 \times 10^{23} \quad 55.5.$$

- c) Notice that the $4N \ln 2$ terms are the same in both cases above, so the difference between these two entropies is only $55.5 - 28.1 = 27.4$ units, utterly negligible compared to either of the values themselves. Therefore the issue of time scales is quite irrelevant for such a large system.
- d) Inserting the partition causes the entropy to decrease by about 27 units out of 2.8×10^{23} , or about one part in 10^{22} . I would call this “violation” of the second law insignificant; no, I wouldn’t lose any sleep over it.

Problem 2.31. Starting from equation 2.40 for the multiplicity, we have for the entropy of an ideal gas

$$\begin{aligned} \frac{S}{k} &= \ln \left(\frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (2mU)^{3N/2} \right) = \ln V^N + \ln \left(\frac{2\pi m U}{h^2} \right)^{3N/2} - \ln N! - \ln[(3N/2)!] \\ &= N \ln V + N \ln \left(\frac{2\pi m U}{h^2} \right)^{3/2} - N \ln N + N - \frac{3N}{2} \ln \left(\frac{3N}{2} \right) + \frac{3N}{2} \\ &= N \left[\ln \frac{V}{N} + \ln \left(\frac{2\pi m U}{h^2} \right)^{3/2} - \ln \left(\frac{3N}{2} \right)^{3/2} + \frac{5}{2} \right] = N \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]. \end{aligned}$$

In the second line I’ve used Stirling’s approximation twice, in the form of equation 2.16 which omits the merely “large” factor of $\sqrt{2\pi N}$. The final expression is the Sackur-Tetrode result, equation 2.49.

Problem 2.32. Taking the logarithm of the result of Problem 2.26 and using Stirling’s approximation, we have

$$\begin{aligned} \frac{S}{k} &= \ln \left(\frac{1}{(N!)^2} \left(\frac{2\pi m U A}{h^2} \right)^N \right) = N \ln \left(\frac{2\pi m U A}{h^2} \right) - 2(N \ln N - N) \\ &= N \left[\ln \left(\frac{2\pi m U A}{N^2 h^2} \right) + 2 \right] = N \left[\ln \left(\frac{A}{N} \frac{2\pi m U}{Nh^2} \right) + 2 \right]. \end{aligned}$$

Problem 2.33. For argon at room temperature and atmospheric pressure, the volume per molecule is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{10^5 \text{ N/m}^2} = 4.14 \times 10^{-26} \text{ m}^3,$$

while the energy per molecule is

$$\frac{U}{N} = \frac{3}{2} kT = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K})(300 \text{ K}) = 6.21 \times 10^{-21} \text{ J}.$$

The mass of an argon atom is 40 u or 6.64×10^{-26} kg, so the argument of the logarithm in the Sackur-Tetrode equation is

$$\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} = (4.14 \times 10^{-26} \text{ m}^3) \left(\frac{4\pi(6.64 \times 10^{-26} \text{ kg})(6.21 \times 10^{-21} \text{ J})}{3(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 1.02 \times 10^7.$$

The entropy of a mole of argon under these conditions is therefore

$$S = R[\ln(1.02 \times 10^7) + \frac{5}{2}] = R[18.64] = 155 \text{ J/K.}$$

The only relevant difference between argon and helium in this calculation is the larger mass of the argon atom, which increases the argument of the logarithm by a factor of $(40/4)^{3/2} = 31.6$. The reason why m matters is because for a given energy, a molecule with more mass has more momentum, resulting in a larger “hypersphere” of allowed momentum states for the gas and hence a larger multiplicity.

Problem 2.34. The increase in entropy during quasistatic isothermal expansion of an ideal gas is computed in equation 2.51 as

$$\Delta S = Nk \ln \frac{V_f}{V_i},$$

where V_i and V_f are the initial and final volumes. But the heat input during this process was computed in equation 1.31 as

$$Q = W = + \int_{V_i}^{V_f} \frac{NkT}{V} dV = NkT \ln \frac{V_f}{V_i}.$$

Dividing this expression by T gives the preceding expression for ΔS , so indeed, $\Delta S = Q/T$. For the free expansion process, however, ΔS is still given by the same expression but $Q = 0$; therefore ΔS is most definitely not equal to Q/T .

Problem 2.35. Writing $5/2$ as $\ln e^{5/2}$, the Sackur-Tetrode equation becomes

$$S = Nk \ln \left[\frac{V}{N} e^{5/2} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right].$$

We want to know when this quantity is negative, that is, when the argument of the logarithm is less than 1. So set it equal to 1 and use the equipartition theorem to write U in terms of T :

$$1 = \frac{V}{N} e^{5/2} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} = \frac{V}{N} e^{5/2} \left(\frac{2\pi mkT}{h^2} \right)^{3/2}.$$

Solving for T gives

$$T = \left(\frac{N}{V} \right)^{2/3} \frac{h^2}{2\pi e^{5/3} mk}.$$

We’re to assume that N/V is the same as at room temperature (T_0) and atmospheric pressure (P_0), so we can use the ideal gas law to write it as P_0/kT_0 , then plug in $P_0 = 10^5$ Pa and $T_0 = 300$ K. The mass of a helium atom is 4 u, where 1 u = 1.66×10^{-27} kg. Plugging in all these numbers, I get $T \approx 0.01$ K. Below this temperature, the methods of Chapter 7 become necessary.

Problem 2.36. A kilogram of carbon is about 100 moles, so the entropy of the book in fundamental units should be something on the order of 10^{26} . In conventional units, $S \sim Nk \sim 10^{26} \cdot 10^{-23} \text{ J/K} = 1000 \text{ J/K}$.

A kilogram of water would be about 50 moles, so a 400-kg moose would contain roughly 20,000 moles of particles. Its entropy in fundamental units would therefore be on the order of $(2 \times 10^4)(6 \times 10^{23}) \sim 10^{28}$, or perhaps 10^{29} if the “small” coefficient on Nk is on the order of 10 for a material that’s mostly liquid. In conventional units, $S \sim 10^{29} \cdot 10^{-23} \text{ J/K} = 10^6 \text{ J/K}$.

A mole of hydrogen has a mass of only a gram, and when ionized actually contains two moles of particles. The sun, therefore, contains roughly 4×10^{33} moles of particles, or 24×10^{56} particles. I would guess that its entropy in fundamental units is this number times a coefficient of at least 20 (given the high temperature compared to the room-temperature gas considered in the text), so I’ll guess a fundamental entropy on the order of 10^{59} . In conventional units, that would be about 10^{36} J/K .

Problem 2.37. The number of B molecules is xN . When the partition is removed, these molecules expand to fill a volume that is greater by a factor of $1/x$, so their entropy increases by

$$\Delta S_B = (xN)k \ln \frac{1}{x} = Nk x \ln x$$

according to the Sackur-Tetrode equation. Similarly, the number of A molecules is $(1-x)N$ and these expand in volume by a factor of $1/(1-x)$, so

$$\Delta S_A = [(1-x)N]k \ln \frac{1}{1-x} = Nk(1-x) \ln(1-x).$$

The total entropy increase upon mixing is simply the sum,

$$\Delta S_{\text{mixing}} = \Delta S_A + \Delta S_B = Nk[x \ln x + (1-x) \ln(1-x)].$$

When $x = 1/2$, this expression reduces to

$$\Delta S_{\text{mixing}} = Nk\left[\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2}\right] = Nk \ln \frac{1}{2} = Nk \ln 2.$$

Since this N is the *total* number of molecules, which is called $2N$ in equation 2.54, the results are in agreement.

Problem 2.38. In the unmixed state, this system could have quite a bit of entropy due to molecular energies and (for fluids) configurations. When we allow the system to mix, assuming that the mixture is ideal, the only change is that molecules of different types can now switch places with each other at random (with no inherent tendency to prefer like or unlike neighbors). Therefore, to compute the mixing entropy, we can ignore the initial entropy and pretend that the molecules are initially frozen in place. Upon mixing, molecules randomly switch places with each other but still occupy the same collection of N fixed sites. The increase in multiplicity due to mixing, therefore, is the number of ways

of assigning the two species of molecules to the N sites, that is, the number of ways of choosing N_A of the sites to be occupied by molecules of type A :

$$\Omega_{\text{mixing}} = \binom{N}{N_A}.$$

The entropy of mixing is then k times the natural log of this expression:

$$\Delta S_{\text{mixing}} = k \ln \left(\frac{N}{N_A} \right) = k \ln \left(\frac{N!}{N_A! N_B!} \right).$$

Assuming that both N_A and N_B are large, we can approximate the factorials using Stirling's approximation:

$$\begin{aligned}\Delta S_{\text{mixing}} &\approx k [N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B] \\ &= k [N \ln N - N_A \ln N_A - N_B \ln N_B].\end{aligned}$$

Now substitute $N_A = (1-x)N$ and $N_B = xN$:

$$\begin{aligned}\Delta S_{\text{mixing}} &= k [N \ln N - (1-x)N \ln[(1-x)N] - xN \ln[xN]] \\ &= Nk [\ln N - (1-x) \ln(1-x) - (1-x) \ln N - x \ln x - x \ln N].\end{aligned}$$

The $\ln N$ terms now cancel, leaving us with the same expression as in Problem 2.37,

$$\Delta S_{\text{mixing}} = Nk [x \ln x + (1-x) \ln(1-x)].$$

Problem 2.39. Rather than computing the entropy from scratch using equation 2.57, I'll take advantage of the calculation of the actual entropy of a mole of helium at the top of page 78. There I found that the argument of the logarithm was 330,000. Here, however, the argument of the logarithm lacks a factor of N in the denominator, so it is larger by a factor of Avogadro's number. The logarithm itself is therefore

$$\ln[(6 \times 10^{23})(330,000)] = 67.5,$$

and so the entropy of this hypothetical system would be

$$S = Nk[67.5 + 1.5] = 69Nk = 573 \text{ J/K}.$$

That's four and a half times as large as the actual entropy of a mole of indistinguishable helium atoms.

Problem 2.40. (Irreversible processes.)

- a) When you stir salt into a pot of soup, the sodium and chlorine ions can roam throughout the entire volume of the liquid. They can then have many more possible arrangements than when they are locked into crystals. More arrangements means higher multiplicity and hence higher entropy. And as we all know, it's not at all easy to reverse the process and get the salt out of the soup.
- b) Scrambling an egg mixes the yolk with the white, so that creates mixing entropy as the "yolk molecules" and "white molecules" can mix among each other. In addition, cooking the egg "denatures" the protein molecules, undoing their special folded patterns and stretching them out into long chains that can flop around randomly.
- c) Humpty Dumpty's fall itself is reversible (to a good approximation, neglecting air resistance), but when he lands and breaks into many pieces, his entropy suddenly increases because there are many more ways for him to be broken than whole. If the king's horses and the king's men just knew the second law of thermodynamics, they wouldn't have wasted their time trying to put him back together again!
- d) There are many more ways for the sand to be scattered about than for it to be sculpted into a sand castle, so the action of the wave most definitely increases the multiplicity and entropy of the sand.
- e) You can cut the tree in many places, at many angles, and it can fall in many directions, so there are many more ways for it to be cut down than for it to remain standing. Hence its entropy has increased. And of course, we all know that it's pretty much impossible to undo the cutting.
- f) When you burn gasoline, not only do you convert a smaller number of relatively large hydrocarbon molecules into a larger number of relatively small exhaust gas molecules, but you also release a great deal of thermal energy (converted from chemical energy) into the environment. This energy can arrange itself in many ways among the surrounding atoms, so the entropy of the environment increases a great deal as this thermal energy spreads farther and farther.

Problem 2.41. Several of *my* favorite irreversible processes are described in the previous problem. Another familiar one is spilling a pail of milk (more ways for the milk to be splattered on the ground than contained in the pail), which you shouldn't cry over because crying won't make the process any less irreversible. Then there are geological processes such as erosion by streams and landslides; these convert gravitational energy into thermal energy and also often break large rocks into smaller pieces, with more arrangements possible for the final state either way. Finally, the process of feeding hay to a horse is irreversible (metabolism converts chemical energy to thermal energy with more possible arrangements), as is implied by a paraphrase of the second law that I read in Nordstrom and Munoz (1994): "You can't shovel manure into the rear end of a horse and expect hay to come out of its mouth."

Problem 2.42. (Entropy of a black hole.)

- a) In the SI system, the units of G are $\text{N m}^2/\text{kg}^2$. But a newton is a kg m/s^2 , so the units of G can also be written as $\text{m}^3/\text{kg s}^2$. Meanwhile M has units of kg and c has units of m/s. We want a combination of these three quantities that has units of meters. We can get meters from either G or c , but each also involves seconds; the only way to make the seconds cancel is to take the combination G/c^2 , which has units of m/kg . Now we have meters to the first power as desired. To cancel the kg in the denominator, just multiply by M : radius $\sim GM/c^2$ (up to a purely numerical factor). For $M = 2 \times 10^{30}$ kg this evaluates to 1500 m, or about a mile.
- b) Ordinarily, the entropy of a system is of the same order as the number of particles in the system. If we take a system of N particles and compress it to form a black hole, the second law requires that when we're done, the entropy of the black hole is still at least of order N . But since the end result is the same whether we start with a lot of particles or a few (with the same total mass), the final entropy must in fact be of the order of the *maximum* N , the largest possible number of particles that it could have been formed from. (To maximize N , we want long-wavelength, massless particles.)
- c) Suppose we start with N photons, each of which has a wavelength equal to the size of the black hole: $\lambda = GM/c^2$. Each photon has an energy $\epsilon = hc/\lambda$, and the total energy of all of them must equal Mc^2 :

$$Mc^2 = N\epsilon = \frac{Nhc}{\lambda} = \frac{Nhc^3}{GM}.$$

Solving for N gives

$$N = \frac{GM^2}{hc},$$

and so the entropy in conventional units must be of order

$$S \sim \frac{GM^2 k}{hc}.$$

- d) For a one-solar-mass black hole,

$$\frac{S}{k} = \frac{8\pi^2(6.67 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(2 \times 10^{30} \text{ kg})^2}{(6.63 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m/s})} = 1.06 \times 10^{77},$$

or in conventional units,

$$S = (1.06 \times 10^{77})(1.38 \times 10^{-23} \text{ J/K}) = 1.5 \times 10^{54} \text{ J/K}.$$

This is an *enormous* entropy. For comparison, an ordinary star like the sun contains of order 10^{57} particles, so its entropy is something like $10^{57}k$. To equal the entropy of a single one-solar-mass black hole, you would need 10^{20} ordinary stars, or enough to populate a billion (10^9) Milky Way galaxies. Furthermore, since the entropy of a black hole is proportional to the *square* of its mass, a million-solar-mass black hole (as may exist at the center of our galaxy) would have a trillion (10^{12}) times the entropy of a one-solar-mass black hole.

3 Interactions and Implications

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Problem 3.1. In each case I'll use a centered-difference approximation, taking a difference of values just above and just below the point where I want the derivative. When $q_A = 1$,

$$T_A = \frac{\Delta U_A}{\Delta S_A} = \frac{2\epsilon - 0\epsilon}{10.7k - 0k} = .19 \frac{\epsilon}{k} = 220 \text{ K},$$

where the last value is for $\epsilon = .1 \text{ eV}$ (so that $\epsilon/k = (.1 \text{ eV})/(8.62 \times 10^{-5} \text{ eV/K}) = 1160 \text{ K}$). Similarly,

$$T_B = \frac{\Delta U_B}{\Delta S_B} = \frac{100\epsilon - 98\epsilon}{187.5k - 185.3k} = .91 \frac{\epsilon}{k} = 1060 \text{ K}.$$

As expected, Solid B is much hotter when it has nearly all of the energy. However, at $q_A = 60$,

$$T_A = \frac{61\epsilon - 59\epsilon}{160.9k - 157.4k} = .57 \frac{\epsilon}{k} = 660 \text{ K},$$

while

$$T_B = \frac{41\epsilon - 39\epsilon}{107.0k - 103.5k} = .57 \frac{\epsilon}{k} = 660 \text{ K}.$$

At this point the temperatures are essentially the same.

Problem 3.2. If A is in thermal equilibrium with B, then $T_A = T_B$ and therefore

$$\left(\frac{\partial S}{\partial U} \right)_A = \left(\frac{\partial S}{\partial U} \right)_B,$$

where it is understood that N and V are fixed in each derivative, and the subscripts merely indicate which system. Similarly, if B is in thermal equilibrium with C, then $T_B = T_C$ and therefore

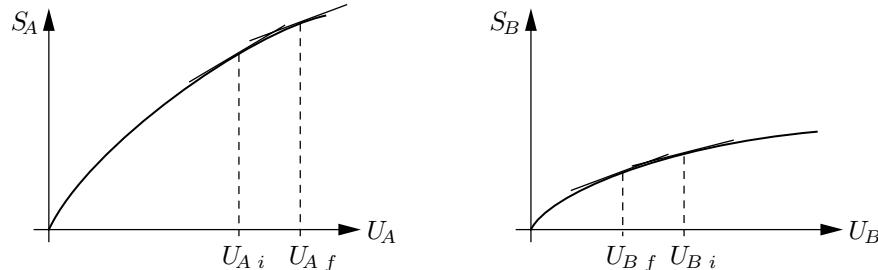
$$\left(\frac{\partial S}{\partial U} \right)_B = \left(\frac{\partial S}{\partial U} \right)_C.$$

But these two equations together imply that

$$\left(\frac{\partial S}{\partial U} \right)_A = \left(\frac{\partial S}{\partial U} \right)_C,$$

which says that $T_A = T_C$, which means that A is in thermal equilibrium with C. Basically, all we need to know for this proof is that “thermal equilibrium” implies equal temperatures, and that temperature is a property that has a numerical value and therefore obeys the “transitive” law of mathematical equality. Not a very interesting proof, in my opinion.

Problem 3.3. Look at the slopes of the tangent lines at the initial energy values:



Since the slope of graph A is steeper than the slope of graph B , a transfer of energy from B to A will cause A to gain more entropy than B loses; therefore this will happen spontaneously. Energy flows from B to A until the slopes of the entropy graphs become equal, at the points marked $U_{A,f}$ and $U_{B,f}$.

Problem 3.4. A “miserly” system (A) can certainly be in thermal equilibrium with another system (B)—they just need to be at the same temperature. Usually, however, the equilibrium will not be stable. If system B is also “miserly,” then any small flow of energy from B to A will cause the temperature of B to increase while the temperature of A decreases. We then get a run-away effect, as more and more energy spontaneously flows from B to A . And if the initial fluctuation results in energy flowing from A to B , the run-away effect goes in the opposite direction. (This instability is sometimes offered as a proof that miserly systems cannot even exist. Imagine splitting a single miserly system into two parts, A and B ; then since A and B cannot be in stable equilibrium with each other, the system as a whole is unstable. However, this “proof” has a loophole: If there are long-range forces between the particles in the original system, then we cannot mentally divide it into two miserly subsystems that interact only thermally. Gravitationally bound systems like stars can be miserly precisely because of the long-range gravitational forces between the particles.) But what if system B is not “miserly”? If it is a large “reservoir” whose temperature doesn’t change significantly when it absorbs or emits energy, then again any small transfer of energy from B to A will result in A becoming colder than B so we get a run-away effect. The only way for the equilibrium to be stable is if system B is “normal” and sufficiently small (more precisely, has a sufficiently low heat capacity) that a spontaneous transfer of energy from B to A causes B to cool off *more* than A does. Then A will become a bit hotter than B and the energy will spontaneously flow back.

Problem 3.5. The result of Problem 2.17 was

$$\Omega = \left(\frac{eN}{q} \right)^q,$$

for an Einstein solid in the “low-temperature” limit $q \ll N$. Therefore the entropy in this limit is

$$S = k \ln \left(\frac{eN}{q} \right)^q = kq \ln \left(\frac{eN}{q} \right) = kq [\ln e + \ln N - \ln q] = kq [\ln N - \ln q + 1].$$

But $U = q\epsilon$, where ϵ is the size of each energy unit, so

$$S = \frac{kU}{\epsilon} [\ln N - \ln U + \ln \epsilon + 1].$$

Differentiating with respect to U now gives

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k}{\epsilon} [\ln(N\epsilon/U) + 1] + \frac{kU}{\epsilon} \left(-\frac{1}{U} \right) = \frac{k}{\epsilon} \ln\left(\frac{N\epsilon}{U}\right).$$

Solving for U is now just a couple of steps:

$$\frac{\epsilon}{kT} = \ln\left(\frac{N\epsilon}{U}\right) \quad \Rightarrow \quad e^{\epsilon/kT} = \frac{N\epsilon}{U} \quad \Rightarrow \quad U = N\epsilon e^{-\epsilon/kT}.$$

Note that as $T \rightarrow 0$, the energy goes to zero as expected.

Problem 3.6. We're given that the multiplicity of the system has the form

$$\Omega = A U^{Nf/2},$$

where A is some constant that's independent of U . The entropy, therefore, is

$$S = k \ln \Omega = k \ln A + \frac{Nfk}{2} \ln U.$$

Differentiating with respect to U gives the temperature,

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{kNf}{2} \frac{1}{U},$$

and solving for U gives simply

$$U = \frac{NfkT}{2}.$$

This is the equipartition theorem: Each degree of freedom gets an average energy of $kT/2$, and the total energy is this times the number of degrees of freedom, Nf . The theorem is valid whenever our original formula for the multiplicity is valid, that is, when all the energy is in quadratic degrees of freedom and the number of energy units is much larger than the number of degrees of freedom (high-temperature limit). But the theorem cannot be valid for arbitrarily small values of U , because as $U \rightarrow 0$, its logarithm goes to $-\infty$ and therefore the entropy becomes negative, which is impossible.

Problem 3.7. From Problem 2.42, the entropy of a black hole is

$$S = \frac{8\pi^2 GM^2 k}{hc} = \frac{8\pi^2 G(Mc^2)^2 k}{hc^5} = \frac{8\pi^2 GU^2 k}{hc^5},$$

where U is the black hole's energy. To find the temperature, just differentiate with respect to U :

$$\frac{1}{T} = \frac{dS}{dU} = \frac{16\pi^2 GUk}{hc^5} = \frac{16\pi^2 GMk}{hc^3},$$

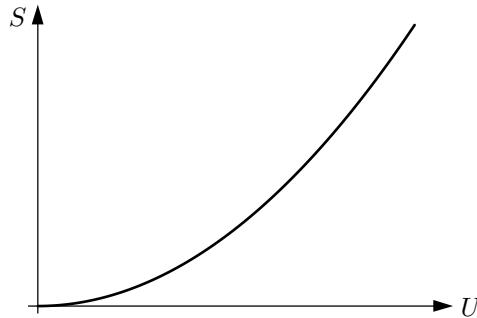
or

$$T = \frac{hc^3}{16\pi^2 GMk}.$$

For $M = 2 \times 10^{30}$ kg (our sun's mass), this evaluates to

$$T = \frac{(6.63 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m})^3}{16\pi^2(6.67 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(2 \times 10^{30} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} = 6.1 \times 10^{-8} \text{ K},$$

a temperature so tiny that for most purposes it may as well be zero. Notice also that as M (or U) increases, T decreases. Because $S \propto U^2$, a graph of S vs. U is an upward-opening parabola:

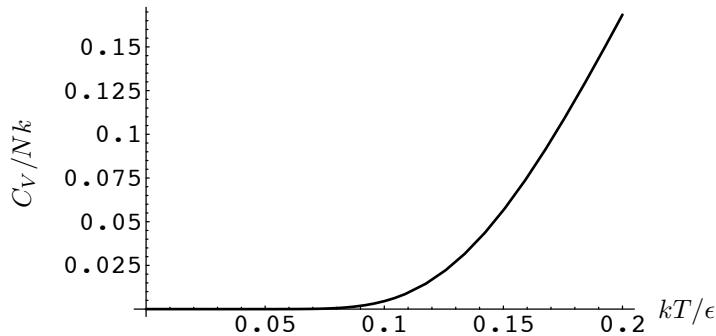


The concave-up shape indicates that as energy is added to this system, its tendency to absorb energy *increases*—it becomes more and more “greedy,” or less “generous,” that is, colder. In the language of Figure 3.2, this is a “miserly” system.

Problem 3.8. For an Einstein solid in the low-temperature limit, $U = N\epsilon e^{-\epsilon/kT}$ and therefore

$$C_V = N\epsilon \frac{d}{dT} e^{-\epsilon/kT} = N\epsilon \left(\frac{\epsilon}{kT^2}\right) e^{-\epsilon/kT} = Nk \left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT}.$$

Even though the prefactor ϵ/kT blows up as $T \rightarrow 0$, the whole expression goes to zero because of the exponentially small exponential factor. To plot the heat capacity I gave the instruction `Plot[(1/t)^2*Exp[-1/t],{t,0,.2},PlotRange->All]` to *Mathematica*, and it produced the graph below, showing the exponentially suppressed heat capacity as $T \rightarrow 0$.



Problem 3.9. If each of the N CO molecules has two equally-likely orientations, then the multiplicity of the system would be 2^N , and the associated entropy is simply

$$S = k \ln \Omega = k \ln(2^N) = Nk \ln 2.$$

For one mole $N = 6 \times 10^{23}$, this evaluates to 4.2×10^{23} units of entropy (S/k), or a conventional entropy of 5.8 J/K.

Problem 3.10. (Melting an ice cube.)

- a) As the ice melts into water, its entropy increases by

$$\Delta S = \frac{Q}{T} = \frac{mL}{T} = \frac{(30 \text{ g})(333 \text{ J/g})}{273 \text{ K}} = 36.6 \text{ J/K.}$$

- b) As the water's temperature rises, its entropy increases by

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T} = C \ln \frac{T_f}{T_i} = (30 \text{ g})(4.186 \text{ J/g K}) \ln \frac{298 \text{ K}}{273 \text{ K}} = 11.0 \text{ J/K.}$$

- c) The heat lost by the kitchen is the same as the heat gained by the ice/water, $mL + mc\Delta T$. So the change in the kitchen's entropy is

$$\Delta S = \frac{Q}{T} = \frac{(30 \text{ g})(333 \text{ J/g}) - (30 \text{ g})(4.186 \text{ J/g K})(25 \text{ K})}{298 \text{ K}} = 44.1 \text{ J/K.}$$

- d) The net change in the entropy of the universe due to these events is

$$\Delta S_{\text{total}} = 36.6 \text{ J/K} + 11.0 \text{ J/K} - 44.1 \text{ J/K} = 3.5 \text{ J/K.}$$

Since this is an irreversible process, the entropy of the universe has increased (but only slightly, since the temperatures of the ice and the kitchen differed by less than 10%).

Problem 3.11. The difference in temperature between the hot water and the cold water is 45°C, but there's twice as much hot water than cold, so the cold water will go up in temperature twice as much as the hot water comes down. This implies that the final temperature is 15°C less than the initial temperature of the hot water, that is, the final temperature is 40°C. Knowing this, we can calculate the change in entropy of the cold water,

$$\Delta S_{\text{cold}} = (25 \text{ kg})(4186 \text{ J/kg K}) \int_{283 \text{ K}}^{313 \text{ K}} \frac{dT}{T} = (104,650 \text{ J/K}) \ln \frac{313}{283} = 10,550 \text{ J/K,}$$

and the change in entropy of the hot water,

$$\Delta S_{\text{hot}} = (50 \text{ kg})(4186 \text{ J/kg K}) \int_{328 \text{ K}}^{313 \text{ K}} \frac{dT}{T} = (209,300 \text{ J/K}) \ln \frac{313}{328} = -9800 \text{ J/K.}$$

The total change in the entropy of the system is, of course, positive:

$$\Delta S_{\text{total}} = 10,550 \text{ J/K} - 9800 \text{ J/K} = +750 \text{ J/K.}$$

Problem 3.12. In Problem 1.59 I estimated that the rate of heat loss from my home in January is about 3.7 kW, so the total heat loss in one day would be roughly 3×10^8 J. The indoor temperature is about 65°F or 291 K, while the average outdoor temperature is 33°F or 274 K. Therefore, the entropy gained by the outdoors is

$$\Delta S_{\text{outside}} = \frac{Q}{T} = \frac{3 \times 10^8 \text{ J}}{274 \text{ K}} = 1.09 \times 10^6 \text{ J/K},$$

while the entropy lost by the interior is

$$\Delta S_{\text{inside}} = \frac{Q}{T} = \frac{3 \times 10^9 \text{ J}}{291 \text{ K}} = -1.03 \times 10^6 \text{ J/K}.$$

The net change in the entropy of the universe due to this heat flow is therefore

$$\Delta S_{\text{net}} = (1.09 \times 10^6 \text{ J/K}) - (1.03 \times 10^6 \text{ J/K}) = 6 \times 10^4 \text{ J/K}.$$

In fundamental units, that's about 4×10^{27} units of entropy.

Problem 3.13. (Entropy generation by solar heating.)

- a) Assuming an average of eight hours of high-quality sunlight per day, a square meter of earth's surface receives in one year a total energy of

$$(1000 \text{ J/s})(3600 \text{ s/hr})(8 \text{ hrs/day})(365 \text{ days}) = 1.05 \times 10^{10} \text{ J}.$$

The entropy gained by the earth upon receiving this much energy is

$$\Delta S_{\text{earth}} = \frac{Q}{T} = \frac{1.05 \times 10^{10} \text{ J}}{300 \text{ K}} = 3.5 \times 10^7 \text{ J/K}.$$

The entropy lost by the sun upon emitting this much energy is 20 times smaller than this, since the sun's surface is 20 times hotter than the earth's. The net change in entropy due to this process is therefore 19/20 of the preceding result; I'll just round it down to $3 \times 10^7 \text{ J/K}$.

- b) On a square meter of earth, in one year, you might be able to grow a few kilograms of grass, containing perhaps 1000 moles of carbon and other atoms. Even if this grass has zero entropy, the net reduction in entropy upon assembling it out of smaller molecules would only be of order

$$Nk = nR \approx (1000 \text{ moles})(8.3 \text{ J/mol K}) \sim 10^4 \text{ J/K},$$

about 3000 times less than the entropy created by sunlight warming this patch of ground. So there's no violation of the second law here: The growth of the grass merely reduces the *increase* in entropy by a small fraction of a percent. A similar analysis could be applied to the growth of any other living thing, as well as to the process of evolution, which is claimed (by the so-called "scientific creationists") to violate the second law.

Problem 3.14. As the temperature of the aluminum increases from 0 to some final value T_f , its entropy increases by

$$\Delta S = \int_0^{T_f} \frac{C_V dT}{T} = \int_0^{T_f} \frac{aT + bT^3}{T} dT = \int_0^{T_f} (a + bT^2) dT = aT_f + \frac{b}{3}T_f^3.$$

Assuming that the aluminum has no entropy at 0 K, this formula gives its absolute entropy at temperature T_f . Setting $T_f = 1$ K and plugging in the given values of a and b gives

$$S(1 \text{ K}) = (.00135 \text{ J/K}^2)(1 \text{ K}) + \frac{1}{3}(.0000248 \text{ J/K}^4)(1 \text{ K})^3 = .00136 \text{ J/K}.$$

At this very low temperature, nearly all of the entropy comes from the linear term, that is, from the conduction electrons. At 10 K, however,

$$S(10 \text{ K}) = (.00135 \text{ J/K}^2)(10 \text{ K}) + \frac{1}{3}(.0000248 \text{ J/K}^4)(10 \text{ K})^3 = .0218 \text{ J/K},$$

so most of the entropy comes from the lattice vibrations. In fundamental units, these results become

$$\frac{S(1 \text{ K})}{k} = \frac{.00136 \text{ J/K}}{1.38 \times 10^{-23} \text{ J/K}} = 9.8 \times 10^{19}; \quad \frac{S(10 \text{ K})}{k} = \frac{.0218 \text{ J/K}}{1.38 \times 10^{-23} \text{ J/K}} = 1.58 \times 10^{21}.$$

So even at 1 K, the entropy is quite large. On the other hand, since most “degrees of freedom” are frozen out, the entropy is much smaller than the number of particles.

Problem 3.15. In Problem 1.55 I showed that the heat capacity of a gravitationally bound system is

$$C = \frac{3}{2}Nk,$$

where N is the number of particles. The entropy should therefore be

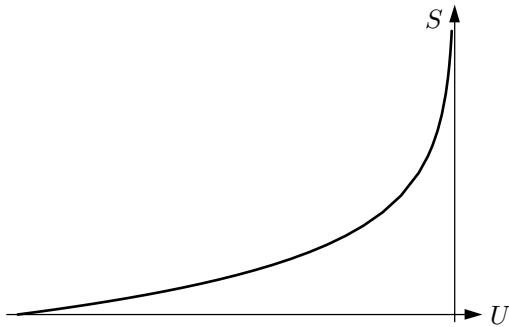
$$S = \int \frac{C}{T} dT = \frac{3}{2}Nk \int \frac{1}{T} dT = \frac{3}{2}Nk \ln T + \text{constant}.$$

Since the total energy is $U = \frac{3}{2}NkT$, the entropy can also be written

$$S = \frac{3}{2}Nk \ln\left(\frac{2U}{2Nk}\right) + \text{constant} = \frac{3}{2}Nk \ln(-U) + \text{constant},$$

where I’ve absorbed as much as possible into the constant in the final expression. To sketch the function $S(U)$, start with the natural logarithm function and then flip it both horizontally and vertically to take care of the two minus signs. To plot the function accurately, I used the *Mathematica* instruction `Plot[-Log[-u], {u, -1, 0}, PlotRange -> {0, 5}]`, which

produced the graph below. Notice that the curve is concave-up, indicating that this is a “miserly” system whose temperature decreases as you add energy.



Problem 3.16. (Thermodynamics of computing.)

- a) Before the memory was erased, it could have been in any one of $2^{2^{33}}$ different microstates (at least). After it is erased, its new microstate is completely specified and unrelated to the previous one, but somehow the whole system, including the hardware that did the erasing, must still have $2^{2^{33}}$ possible states, corresponding to the number of possible initial conditions. This multiplicity of possible states gives the system an entropy equal to

$$S = k \ln 2^{2^{33}} = k \cdot 2^{33} \ln 2 = k \cdot (6.0 \times 10^9) = 8.2 \times 10^{-14} \text{ J/K}.$$

- b) To dump this entropy into an environment at 300 K would require a heat transfer of at least

$$Q = T \Delta S = (300 \text{ K})(8.2 \times 10^{-14} \text{ J/K}) = 2.5 \times 10^{-11} \text{ J},$$

or 25 picojoules. Not a very significant amount. Of course, today’s computers are much less thermodynamically efficient, expelling a good deal more waste heat than this lower limit. But at the rate computer technology is progressing, who knows how long it will be before the thermodynamic limit becomes a significant constraint?

Problem 3.17. For $N = 100$ and $N_\uparrow = 98$, there are 98 dipoles pointing up, each with energy B , and two pointing down, each with energy $+B$, so the total energy is $96B$, as indicated in the second column of Table 3.2. The total magnetization is $+98 - 2 = 96$, so $M/N = 0.96$, as indicated in column 3. The multiplicity is the number of ways of choosing the two down-dipoles from among the total of 100, which is $(100)(99)/2 = 4950$ (column 4). The entropy in units of k is $\ln 4950 = 8.507$ (column 5). The temperature is

$$T = \frac{\Delta U}{\Delta S} = \frac{(-94B) - (-98B)}{11.99k - 4.61k} = \frac{4B}{7.38k} = 0.54 \frac{B}{k},$$

where I’ve used a centered-difference approximation, involving the two adjacent rows of values, to evaluate the derivative; this verifies the entry in column 6. Similarly, the heat capacity is

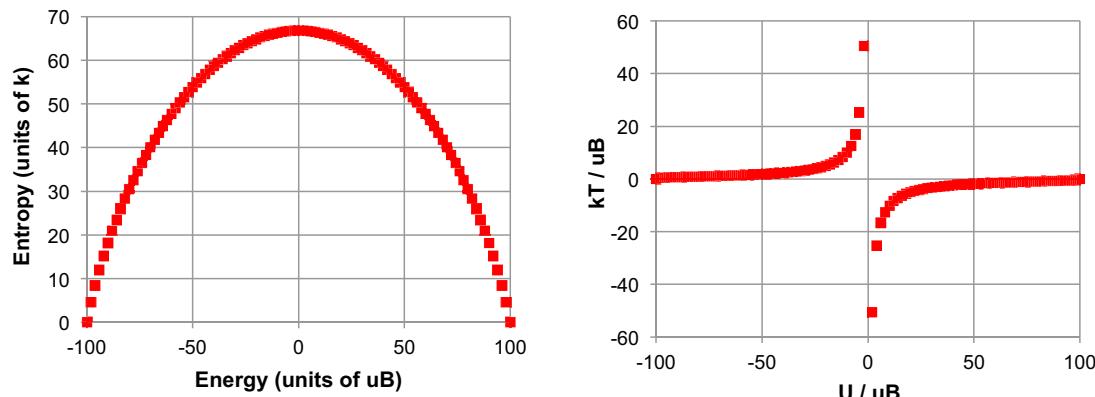
$$C = \frac{\Delta U}{\Delta T} = \frac{4B}{(.60B/k) - (.47B/k)} = 31k,$$

or $0.31k$ per dipole, verifying the entry in column 7.

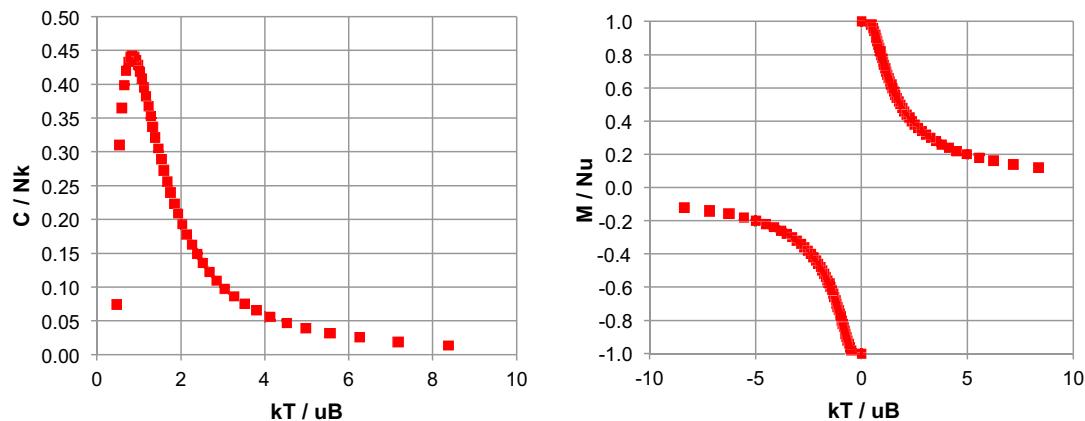
Problem 3.18. Here are the formulas from the first few rows of the Excel spreadsheet that I used to produce Table 3.2:

	A	B	C	D	E	F	G
1	Two-state paramagnet						
2	Nup	U/uB	M/Nu	Ω	S/k	kT/uB	C/Nk
3	100	=100 - 2*A3	=-B3/100	=COMBIN(100,A3)	=LN(D3)	0	
4	=A3 - 1	=100 - 2*A4	=-B4/100	=COMBIN(100,A4)	=LN(D4)	=4/(E5-E3)	=4/(F5-F3)/100
5	=A4 - 1	=100 - 2*A5	=-B5/100	=COMBIN(100,A5)	=LN(D5)	=4/(E6-E4)	=4/(F6-F4)/100
6	=A5 - 1	=100 - 2*A6	=-B6/100	=COMBIN(100,A6)	=LN(D6)	=4/(E7-E5)	=4/(F7-F5)/100
7	=A6 - 1	=100 - 2*A7	=-B7/100	=COMBIN(100,A7)	=LN(D7)	=4/(E8-E6)	=4/(F8-F6)/100
8	=A7 - 1	=100 - 2*A8	=-B8/100	=COMBIN(100,A8)	=LN(D8)	=4/(E9-E7)	=4/(F9-F7)/100
9	=A8 - 1	=100 - 2*A9	=-B9/100	=COMBIN(100,A9)	=LN(D9)	=4/(E10-E8)	=4/(F10-F8)/100
10	=A9 - 1	=100 - 2*A10	=-B10/100	=COMBIN(100,A10)	=LN(D10)	=4/(E11-E9)	=4/(F11-F9)/100

For the computed values, see the table as printed in the book. Here are spreadsheet-generated graphs of entropy and temperature vs. energy:



And here are graphs of heat capacity and magnetization vs. temperature:



Problem 3.19. Starting from equations 3.28 and 3.29, we have

$$\begin{aligned}\frac{1}{T} &= \frac{k}{2B} \frac{\partial}{\partial N_\uparrow} [N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow)] \\ &= \frac{k}{2B} \left[\ln N_\uparrow - \frac{N_\uparrow}{N_\uparrow} + \ln(N - N_\uparrow) + \frac{N - N_\uparrow}{N - N_\uparrow} \right] = \frac{k}{2B} \ln \frac{N_\uparrow}{N - N_\uparrow}.\end{aligned}$$

But from equation 3.25, $N_\uparrow = N/2 - U/2B$, so

$$\frac{1}{T} = \frac{k}{2B} \ln \left(\frac{N - U/B}{N + U/B} \right),$$

where I've canceled the factors of 1/2 in the numerator and denominator of the argument of the logarithm. To solve for U , first isolate the logarithm and then exponentiate both sides to obtain

$$\frac{N - U/B}{N + U/B} = e^{2B/kT}, \quad \text{or} \quad N - \frac{U}{B} = e^{2B/kT} \left(N + \frac{U}{B} \right).$$

Now gather the terms containing U 's:

$$\frac{U}{B} (1 + e^{2B/kT}) = N (1 - e^{2B/kT}), \quad \text{i.e.,} \quad U = N B \left(\frac{1 - e^{2B/kT}}{1 + e^{2B/kT}} \right).$$

To write this in terms of a tanh function, multiply the numerator and denominator by $e^{-B/kT}$:

$$U = N B \left(\frac{e^{-B/kT} - e^{-B/kT}}{e^{-B/kT} + e^{-B/kT}} \right) = N B \left(\frac{2 \sinh(B/kT)}{2 \cosh(B/kT)} \right) = N B \tanh \left(\frac{B}{kT} \right).$$

Finally, to evaluate the heat capacity, note that

$$\frac{d}{dx} \tanh x = \frac{d}{dx} \frac{\sinh x}{\cosh x} = \frac{\cosh^2 x - \sinh^2 x}{\cosh^2 x} = \frac{1}{\cosh^2 x},$$

where the last step follows from the identity $\cosh^2 x - \sinh^2 x = 1$ (which you can prove by brute-force reduction to exponential functions). The heat capacity is therefore

$$\begin{aligned}C_B &= \frac{\partial U}{\partial T} = N B \frac{\partial}{\partial T} \tanh \left(\frac{B}{kT} \right) = N B \frac{1}{\cosh^2(B/kT)} \left(\frac{B}{k} \right) (-T^{-2}) \\ &= N k \frac{(B/kT)^2}{\cosh^2(B/kT)}.\end{aligned}$$

Problem 3.20. For the numbers given, the quantity B/kT is

$$x = \frac{B}{kT} = \frac{(9.27 \times 10^{-24} \text{ J/T})(2.06 \text{ T})}{(1.38 \times 10^{-23} \text{ J/K})(2.2 \text{ K})} = 0.629.$$

The hyperbolic tangent of this number is 0.558, so

$$\frac{U}{N \cdot B} = \tanh x = 0.558; \quad \frac{M}{N} = \tanh x = 0.558.$$

To find the entropy, you could use the formula derived in Problem 3.23 below. Alternatively, note from equation 3.25 that the total energy determines the fractions of up and down dipoles:

$$\frac{N_{\uparrow}}{N} = \frac{1}{2} \left(1 - \frac{U}{N \cdot B} \right) = 0.779; \quad \frac{N_{\downarrow}}{N} = 1 - \frac{N_{\uparrow}}{N} = 0.221.$$

From equation 3.28, the maximum possible entropy is $Nk \ln 2$, and the ratio of the actual entropy to the maximum is

$$\frac{S}{S_{\max}} = \frac{1}{\ln 2} \left(\ln N - \frac{N_{\uparrow}}{N} \ln N_{\uparrow} - \frac{N_{\downarrow}}{N} \ln N_{\downarrow} \right) = \frac{1}{\ln 2} \left(\frac{N_{\uparrow}}{N} \ln \frac{N_{\uparrow}}{N} + \frac{N_{\downarrow}}{N} \ln \frac{N_{\downarrow}}{N} \right).$$

Plugging our numbers into this formula gives 0.76, meaning that the entropy is about 3/4 what it would be if half the dipoles pointed up and half pointed down.

To achieve 99% of the maximum magnetization, we would need $\tanh x = 0.99$ or $x = 2.65$, about 4.2 times greater than the value for our parameters. So we would need to increase the magnetic field to $4.2 \times 2.06 \text{ T} = 8.65 \text{ T}$, or decrease the temperature to $2.2 \text{ K}/4.2 = 0.52 \text{ K}$, or combine a somewhat smaller increase in the field strength with a somewhat smaller decrease in the temperature.

Problem 3.21. For these parameters,

$$\frac{B}{kT} = \frac{(5 \times 10^{-8} \text{ eV/T})(.63 \text{ T})}{(8.617 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 1.22 \times 10^{-6}.$$

Because this quantity is so small, I can use the linearized formula 3.35 for the magnetization:

$$\frac{M}{N} = \frac{B}{kT} = 1.22 \times 10^{-6},$$

or

$$\frac{M}{N} = (1.22 \times 10^{-6})(5 \times 10^{-8} \text{ eV/T}) = 6.1 \times 10^{-14} \text{ eV/T}.$$

The excess of up dipoles over down dipoles is only of order one part in a million. Furthermore, these nuclear dipoles are very weak to begin with. It's a wonder that Purcell and Pound were able to detect the magnetization. The energy difference between the two states of a dipole is

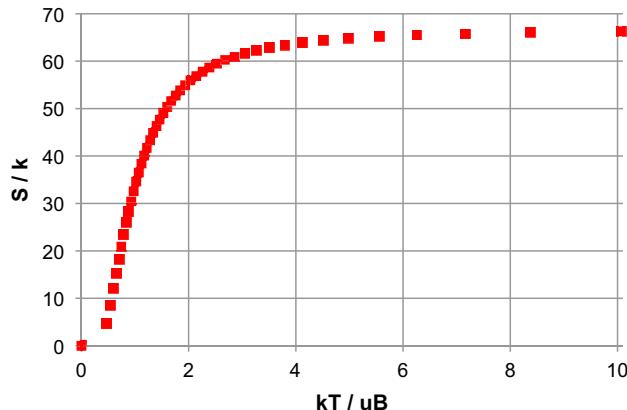
$$\epsilon = 2 \cdot B = 2(5 \times 10^{-8} \text{ eV/T})(.63 \text{ T}) = 6.3 \times 10^{-8} \text{ eV}.$$

A photon with this energy has a wavelength of

$$\lambda = \frac{hc}{\epsilon} = \frac{(4.14 \times 10^{-15} \text{ eV s})(3 \times 10^8 \text{ m/s})}{6.3 \times 10^{-8} \text{ eV}} = 19.7 \text{ meters}$$

or about 20 meters—in the radio wave portion of the electromagnetic spectrum.

Problem 3.22. From the numbers in Table 3.2 you can see that the entropy goes to zero as $T \rightarrow 0$, and goes to a constant value as $T \rightarrow \infty$. (If the number of dipoles is large, that constant value is $N \ln 2$, since the multiplicity is equal to 2^N up to a factor that is merely large.) To plot an accurate graph of $S(T)$, I used the same spreadsheet that generated Table 3.2:



Since the natural unit of temperature on this graph is B/k , increasing the value of B would increase the temperature scale over which the entropy rises. That is, when the field is strong, a higher temperature is required to reach a given entropy value. This makes sense, because in a stronger field there is more tendency of the dipoles to be aligned in an orderly way, hence less entropy (at a given temperature).

Problem 3.23. Equation 3.28 gives the entropy in terms of N_\uparrow and N_\downarrow ,

$$\frac{S}{k} = N \ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow,$$

while equation 3.25 gives N_\uparrow and N_\downarrow in terms of the energy U :

$$N_\uparrow = \frac{1}{2} \left(N - \frac{U}{B} \right); \quad N_\downarrow = N - N_\uparrow = \frac{1}{2} \left(N + \frac{U}{B} \right).$$

Finally, equation 3.31 gives U/B in terms of temperature:

$$\frac{U}{B} = N \tanh x, \quad \text{where } x = B/kT.$$

Therefore the number of up dipoles can be written

$$N_\uparrow = \frac{N}{2} (1 + \tanh x) = \frac{N}{2} \left(\frac{\cosh x + \sinh x}{\cosh x} \right) = \frac{Ne^x}{2 \cosh x},$$

where the last step follows from the definitions of cosh and sinh. Similarly, the number of down dipoles is

$$N_\downarrow = \frac{N}{2} (1 - \tanh x) = \frac{N}{2} \left(\frac{\cosh x - \sinh x}{\cosh x} \right) = \frac{Ne^{-x}}{2 \cosh x}.$$

Plugging these expressions into the entropy formula gives

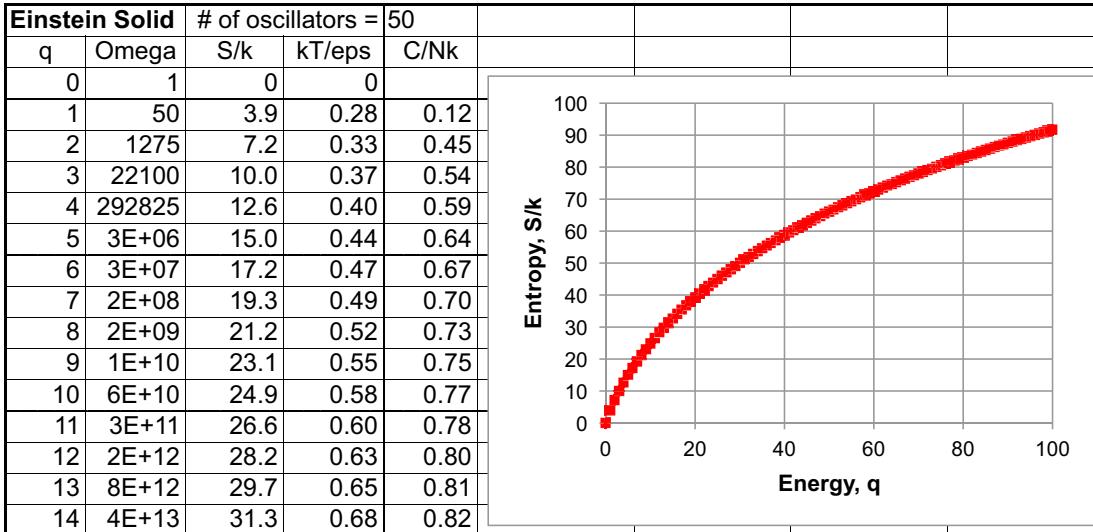
$$\begin{aligned}\frac{S}{Nk} &= \ln N - \frac{e^x}{2 \cosh x} \ln\left(\frac{Ne^x}{2 \cosh x}\right) - \frac{e^{-x}}{2 \cosh x} \ln\left(\frac{Ne^{-x}}{2 \cosh x}\right) \\ &= \ln N - \frac{e^x}{2 \cosh x} [\ln N + x - \ln(2 \cosh x)] - \frac{e^{-x}}{2 \cosh x} [\ln N - x - \ln(2 \cosh x)].\end{aligned}$$

The $\ln N$ terms now cancel, leaving

$$\begin{aligned}\frac{S}{Nk} &= x \left(\frac{e^x - e^{-x}}{2 \cosh x} \right) + \left(\frac{e^x + e^{-x}}{2 \cosh x} \right) \ln(2 \cosh x) \\ &= \ln(2 \cosh x) - x \tanh x.\end{aligned}$$

This function is plotted in Figure 4.14. As $T \rightarrow 0$, $x \rightarrow \infty$ so $\tanh x \rightarrow 1$ and $2 \cosh x \rightarrow e^x$. Therefore $S/Nk \rightarrow \ln e^x = x = x = 0$, as expected. As $T \rightarrow \infty$, $x \rightarrow 0$ so $\tanh x \rightarrow 0$ and $\cosh x \rightarrow 1$. Therefore $S/Nk \rightarrow \ln 2$, again as expected (since the multiplicity when $N_\uparrow = N/2$ differs from the total multiplicity of all macrostates, 2^N , by a factor that is merely large).

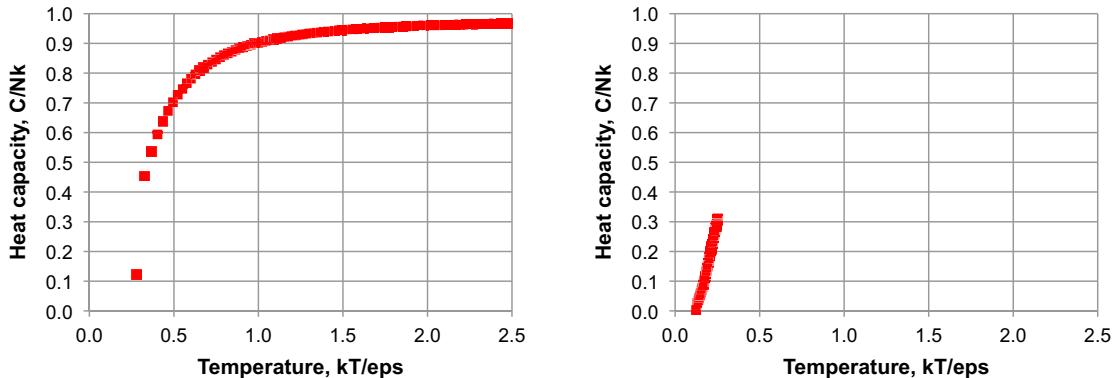
Problem 3.24. Here's an Excel spreadsheet showing the first 15 rows of the table and the entropy-energy graph for an Einstein solid with 50 oscillators:



Since the graph is increasing and concave-down, this system behaves "normally": its temperature is always positive and increases as energy is added.

The graph on the left below shows the heat capacity per oscillator as a function of T for $N = 50$. Note that in the high-temperature limit the heat capacity approaches the result predicted by the equipartition theorem, $C = Nk$ (since there are two degrees of freedom per oscillator). Below $kT = \epsilon$, however, the heat capacity falls dramatically. The low-temperature behavior is better shown on the graph at right, obtained simply by changing

the number of oscillators to 5000, to dilute the energy a hundred-fold.



The data in Figure 1.14 follow curves of similar shape, except that the heat capacity continues to rise gradually, exceeding the equipartition value, at high temperatures. As explained in the caption to Figure 1.14, this behavior is a feature of C_P but not C_V . The value of ϵ for each solid can be estimated by noting that the heat capacity reaches half its equipartition value at $kT \approx \epsilon/3$. For lead, this temperature is about 22 K, so $\epsilon = 3(8.6 \times 10^{-5} \text{ eV/K})(22 \text{ K}) = .0057 \text{ eV}$. For aluminum it's at about 100 K, so $\epsilon = .026 \text{ eV}$. And for diamond it's at about 460 K, so $\epsilon = .12 \text{ eV}$. Because ϵ is proportional to the frequency of each atomic oscillator, and stiff and/or light materials vibrate at higher frequencies, it makes sense that ϵ would be lowest for lead and highest for diamond.

Problem 3.25. (Einstein solid, analytic treatment.)

a) Starting with the formula given for Ω ,

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln \left(\frac{q+N}{q} \right)^q + k \ln \left(\frac{q+N}{N} \right)^N \\ &= kq \ln \left(\frac{q+N}{q} \right) + kN \ln \left(\frac{q+N}{N} \right). \end{aligned}$$

The omitted factors in Ω were of order \sqrt{N} or \sqrt{q} , merely “large”. The logarithm of such a factor is a small number, negligible compared to q or N .

b) It's easiest to first re-express the derivative using the chain rule:

$$\begin{aligned} \frac{1}{T} = \frac{\partial S}{\partial U} &= \frac{\partial q}{\partial U} \frac{\partial S}{\partial q} = \frac{1}{\epsilon} \frac{\partial S}{\partial q} \\ &= \frac{k}{\epsilon} \frac{\partial}{\partial q} \left[q \ln(q+N) - q \ln q + N \ln(q+N) - N \ln N \right] \\ &= \frac{k}{\epsilon} \left[\ln(q+N) + \frac{q}{q+N} \ln q - \frac{q}{q} + \frac{N}{q+N} + 0 \right] \\ &= \frac{k}{\epsilon} \left[\ln \left(\frac{q+N}{q} \right) + \frac{q+N}{q} - \frac{q}{q} \right] = \frac{k}{\epsilon} \ln \left(1 + \frac{N}{q} \right). \end{aligned}$$

So the temperature is

$$T = \frac{\epsilon}{k \ln(1 + N\epsilon/U)}.$$

- c) Solving for U yields

$$U = \frac{N\epsilon}{e^{\epsilon/kT} - 1}.$$

The heat capacity is therefore

$$C = \frac{\partial U}{\partial T} = \frac{N\epsilon}{(e^{\epsilon/kT} - 1)^2} \frac{\partial}{\partial T} e^{\epsilon/kT} = \frac{N\epsilon^2}{kT^2} \frac{e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2}.$$

- d) When $kT \gg \epsilon$ the exponential $e^{\epsilon/kT}$ is approximately $1 + \epsilon/kT$. In the numerator we can just keep the 1 term, but in the denominator we need to keep the next term as well since the 1 cancels. Thus,

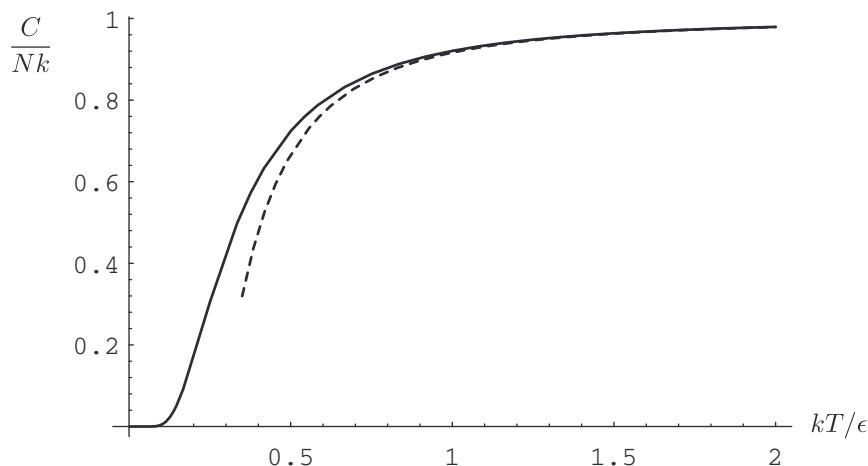
$$C \approx \frac{N\epsilon^2}{kT^2} \frac{1}{(\epsilon/kT)^2} = Nk.$$

This is just the prediction of the equipartition theorem, since each oscillator counts as two degrees of freedom (one kinetic, one potential).

- e) The function we want to plot is

$$\frac{C}{Nk} = \frac{e^{1/t}}{t^2(e^{1/t} - 1)^2}.$$

I like to do these kinds of graphs in *Mathematica*. In this case the instruction would be `Plot[Exp[1/t]/(t^2(Exp[1/t]-1)^2), {t, .001, 2}]`. This instruction generated the solid curve on the graph shown below. The dashed curve shows the approximate result of part (f).



Comparing the shape of this curve to the data in Figure 1.14, we see that it is generally similar but not exactly the same. We can neglect the discrepancy at high temperatures

where the measured heat capacities gradually rise above the equipartition prediction, because this is a feature of C_P , not C_V . At low temperatures, however, there is a subtle but significant difference: The curve predicted by the Einstein model is much flatter as it approaches the origin than the data. This discrepancy is discussed in Section 7.5. Neglecting these details, we can estimate the value of ϵ for each solid by noting that the heat capacity reaches half its equipartition value at $kT \approx \epsilon/3$. For lead, this temperature is about 22 K, so $\epsilon = 3(8.6 \times 10^{-5} \text{ eV/K})(22 \text{ K}) = .0057 \text{ eV}$. For aluminum it's at about 100 K, so $\epsilon = .026 \text{ eV}$. And for diamond it's at about 460 K, so $\epsilon = .12 \text{ eV}$. Because ϵ is proportional to the frequency of each atomic oscillator, and stiff and/or light materials vibrate at higher frequencies, it makes sense that ϵ would be lowest for lead and highest for diamond.

- f) First note that the exact expression can be written

$$\frac{C}{Nk} = \frac{x^2 e^x}{(e^x - 1)^2},$$

where $x = \epsilon/kT$. Now expand each exponential as $e^x \approx 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3$:

$$\frac{C}{Nk} \approx \frac{x^2(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3)}{(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 - 1)^2}.$$

Again the 1's in the denominator cancel, and the x^2 in the numerator then cancels two factors of x in the denominator:

$$\frac{C}{Nk} \approx \frac{1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3}{(1 + \frac{1}{2}x + \frac{1}{6}x^2)^2} \approx \frac{1 + x + \frac{1}{2}x^2}{1 + x + \frac{1}{4}x^2 + \frac{1}{3}x^2} = \frac{1 + x + \frac{1}{2}x^2}{1 + x + \frac{7}{12}x^2}.$$

In the second step I've squared out the denominator, keeping terms only through order x^2 since x^3 terms have already been dropped. I've also dropped the x^3 term in the numerator, for the same reason. Now just use long division to obtain the result

$$C = Nk \left[1 - \frac{1}{12}x^2 + \dots \right] = Nk \left[1 - \frac{1}{12} \left(\frac{\epsilon}{kT} \right)^2 + \dots \right].$$

So as the temperature is lowered, the heat capacity drops off from its asymptotic value. At $T = \epsilon/k$ the reduction is by only one part in 12, but below this temperature the fall-off becomes more dramatic (and the approximations made here become inaccurate).

Problem 3.26. As in the previous two problems, note that the heat capacity curve predicted by the Einstein model reaches half its maximum value at approximately $kT/\epsilon = 1/3$. From the vibrational portion of the hydrogen data in Figure 1.13, we see that this halfway point occurs at a temperature of somewhat less than 2000 K; I'll call it 1700 K. Therefore,

$$\frac{k}{\epsilon}(1700 \text{ K}) \approx \frac{1}{3} \quad \Rightarrow \quad \epsilon \approx 3(1700 \text{ K})(8.6 \times 10^{-5} \text{ eV/K}) = 0.44 \text{ eV}.$$

Problem 3.27. If $dS = 0$, then the thermodynamic identity becomes simply $dU = -P dV$, or

$$P = \left(\frac{\partial U}{\partial V} \right)_S.$$

This equation merely describes the work done during a “purely mechanical” compression (or expansion) that involves no change in entropy. When there’s no entropy change there can be no heat flow, since heat flow is caused by the tendency of entropy to increase. In this case, therefore, $dU = W$, the work done on the system, which is the force exerted times the displacement, or, multiplying and dividing by the area of the moving surface, the pressure times the change in volume. The minus sign indicates that the work done on the system is positive when its volume decreases.

Problem 3.28. For a diatomic gas such as air, $C_P = \frac{7}{2}nR$; in this case, $nR = PV/T = (10^5 \text{ N/m}^2)(10^{-3} \text{ m}^3)/(300 \text{ K}) = 1/3 \text{ J/K}$. Since the volume of the gas doubles but the pressure doesn’t change, the ideal gas law tells us that the temperature also doubles. Therefore,

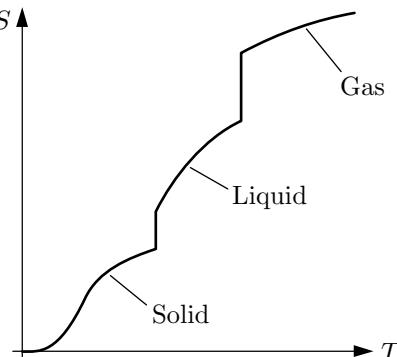
$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT = \frac{7}{2}nR \ln \frac{T_f}{T_i} = \frac{7}{2}\left(\frac{1}{3} \text{ J/K}\right) \ln 2 = 0.81 \text{ J/K}.$$

Problem 3.29. For an infinitesimal change at constant pressure, we can write

$$dS = \frac{Q}{T} = \frac{C_P dT}{T},$$

and therefore the slope of a graph of S vs. T should be

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}.$$



For a typical solid, C_P behaves as shown in Figure 1.14; the ratio C_P/T will also go strongly to zero at low temperature, so as $T \rightarrow 0$, the entropy graph should go to zero with a horizontal slope. The curve should then steepen until the ratio C_P/T peaks, then become gradually shallower as C_P becomes relatively constant. When the solid melts, however, there is a large heat input and hence a large ΔS with no change in temperature. At higher temperatures the slope takes on a new value, C_P/T with the new C_P value of the liquid (normally higher than that of the solid). Assuming that C_P for the liquid is relatively constant, the curve then becomes gradually shallower with increasing T until it jumps suddenly again at the liquid-gas phase transition. For water, at least, C_P of the gas is less than that of the liquid so above the transition the curve will be shallower than below. The graph above shows my attempt to correctly sketch all these features.

Problem 3.30. I used a ruler and pencil to extrapolate the heat capacity curve for diamond up to 500 K, using a straight line with a slope of 0.0414 J/K² and an intercept of -6.1 J/K. Writing the heat capacity as

$$C_P = aT - b,$$

we can integrate to obtain the change in entropy,

$$\Delta S = \int_{T_i}^{T_f} \frac{aT - b}{T} dT = a(T_f - T_i) - b \ln \frac{T_f}{T_i}.$$

Plugging in $T_i = 298$ K, $T_f = 500$ K, and my measured values of a and b give

$$S(500 \text{ K}) = S(298 \text{ K}) + (0.0414 \text{ J/K})(202 \text{ K}) - (6.1 \text{ J/K}) \ln \frac{500}{298} = S(298 \text{ K}) + 5.21 \text{ J/K}.$$

The table on page 404 gives $S(298 \text{ K}) = 2.38 \text{ J/K}$, so this estimate gives $S(500 \text{ K}) = 7.59 \text{ J/K}$.

Problem 3.31. To find the change in entropy, just divide C_P by T and integrate:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT = \int_{T_i}^{T_f} \frac{a + bT - cT^2}{T} dT = a \ln \frac{T_f}{T_i} + b(T_f - T_i) + \frac{c}{2} \left(\frac{1}{T_f^2} - \frac{1}{T_i^2} \right).$$

Plugging in our numbers gives

$$\begin{aligned} \Delta S &= (16.86 \text{ J/K}) \ln \frac{500}{298} + (.00477 \text{ J/K}^2)(202 \text{ K}) + \frac{8.54 \times 10^5 \text{ J K}}{2} \left(\frac{1}{(500 \text{ K})^2} - \frac{1}{(298 \text{ K})^2} \right) \\ &= (8.725 \text{ J/K}) + (0.964 \text{ J/K}) + (-3.100 \text{ J/K}) = 6.59 \text{ J/K}. \end{aligned}$$

The entropy at 298 K is given on page 404 as 5.74 J/K, so the entropy at 500 K should be approximately 12.33 J/K.

Problem 3.32. (A non-quasistatic compression.)

- a) The work I do is the force I exert times the displacement:

$$W = (2000 \text{ N})(.001 \text{ m}) = 2 \text{ J}.$$

- b) Absolutely no heat has been added. There was no spontaneous flow of energy from a hot object to a cold one.
 c) By the first law, $\Delta U = Q + W = 0 + 2 \text{ J} = 2 \text{ J}$.
 d) The change in volume is $\Delta V = (.01 \text{ m}^2)(.001 \text{ m}) = 10^{-5} \text{ m}^3$, so

$$\Delta S = \frac{1}{T} \Delta U + \frac{P}{T} \Delta V = \frac{2 \text{ J} + (10^5 \text{ N/m}^2)(-10^{-5} \text{ m}^3)}{300 \text{ K}} = \frac{2 \text{ J} - 1 \text{ J}}{300 \text{ K}} = \frac{1}{300} \text{ J/K}.$$

I've created entropy, because this is an irreversible, non-quasistatic compression; the force exerted on the piston from outside was twice as great as the force exerted by the gas from inside.

Problem 3.33. In a constant-volume process, the thermodynamic identity reduces to $dU = T dS$. Making this substitution for dU in the definition of C_V gives

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V.$$

To derive a similar formula for C_P , we need a “thermodynamic identity” for the enthalpy H . From its definition $H = U + PV$, we have

$$dH = dU + d(PV) = dU + P dV + V dP = T dS + V dP,$$

where the last step follows from the ordinary thermodynamic identity. In a constant-pressure process, therefore, $dH = T dS$, so

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P.$$

Problem 3.34. (Rubber band model.)

- a) Each link can point either left or right, so this system is mathematically the same as a collection of coins or a two-state paramagnet. The multiplicity is $\Omega = \binom{N}{N_R}$, so the entropy is

$$\begin{aligned} \frac{S}{k} &= \ln \Omega = k \ln \left(\frac{N}{N_R} \right) = k \ln \left(\frac{N!}{N_R!(N-N_R)!} \right) \\ &\approx N \ln N - N - (N_R \ln N_R - N_R) - [(N-N_R) \ln(N-N_R) - (N-N_R)] \\ &= N \ln N - N_R \ln N_R - (N-N_R) \ln(N-N_R), \end{aligned}$$

in analogy with equation 3.28.

- b) Each right-pointing link increases L by ℓ , while each left-pointing link decreases L by ℓ , so the net length must be

$$L = \ell(N_R - N_L) = \ell(2N_R - N), \quad \text{or} \quad N_R = \frac{1}{2} \left(\frac{L}{\ell} + N \right).$$

- c) If L is analogous to V and F is analogous to P , then the thermodynamic identity should be

$$dU = T dS + F dL.$$

The second term makes sense: It is the work (force times displacement) done on the system by quasistatically stretching it an amount dL .

- d) Imagine a process for which $dU = 0$. Then the thermodynamic identity says that $F dL = T dS$, or

$$F = T \left(\frac{\partial S}{\partial L} \right)_U.$$

For our system, it is convenient to express this partial derivative in terms of N_R , using the chain rule:

$$\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \frac{\partial N_R}{\partial L} = \frac{\partial S}{\partial N_R} \frac{1}{2\ell}.$$

Therefore, by the result of part (a),

$$F = \frac{kT}{2\ell} \left[\ln N_R - \frac{N_R}{N} + \ln(N - N_R) + \frac{N - N_R}{N - N_R} \right] = \frac{kT}{2\ell} \ln \left(\frac{N - N_R}{N_R} \right).$$

The result of part (b) can be used to write this in terms of L :

$$F = \frac{kT}{2\ell} \ln \left(\frac{2}{L/N\ell + 1} - 1 \right) = \frac{kT}{2\ell} \ln \left(\frac{1 - L/N\ell}{1 + L/N\ell} \right) = \frac{kT}{2\ell} \ln \left(\frac{1 + L/N\ell}{1 - L/N\ell} \right).$$

- e) When $L \ll N\ell$, the argument of the logarithm is approximately

$$\frac{1 + L/N\ell}{1 - L/N\ell} \approx (1 + L/N\ell)(1 + L/N\ell) \approx 1 + \frac{2L}{N\ell},$$

so the logarithm itself is approximately $2L/N\ell$ and therefore

$$F \approx \frac{kT}{2\ell} \frac{2L}{N\ell} = \frac{kTL}{N\ell^2}.$$

This expression is linear in L ; it has the form of Hooke's law, with the "spring constant" equal to $kT/N\ell^2$.

- f) The tension is proportional to T , so it's greater at high temperature than at low temperature. For a given tension, increasing T should cause the rubber band to contract: L must decrease to compensate. Although this behavior is opposite to that of an ideal gas, it *does* make sense if you think about it. At higher temperature there should be more randomness in the orientation of the links, causing the rubber band to contract.
- g) Under such an adiabatic stretching, the total entropy of the rubber band should be constant. Since stretching the rubber band decreases the configurational entropy computed in part (a), the vibrational entropy must increase to compensate. But this implies an increase in the number of units of vibrational energy, and therefore an increase in temperature. I tested this prediction with a real rubber band as suggested, and the effect is subtle but noticeable.

Problem 3.35. With three oscillators and four units of energy, the multiplicity is $\binom{4+3-1}{4} = 15$. If we now add an oscillator without removing any energy, the multiplicity increases to $\binom{4+4-1}{4} = 35$. If we remove one unit of energy, the multiplicity is then $\binom{3+4-1}{3} = 20$, still larger than what we started with. If we remove two units of energy, the multiplicity decreases to $\binom{2+4-1}{2} = 10$, which is too small. So apparently, to hold the multiplicity (and entropy) fixed while adding an oscillator, we need to remove somewhere between one and two units of energy (whatever that means), i.e., ϵ is somewhere between ϵ and 2ϵ .

Problem 3.36. (Chemical potential of a large Einstein solid.)

- a) We computed the entropy in Problem 3.25(a):

$$S = kq \ln\left(1 + \frac{N}{q}\right) + kN \ln\left(1 + \frac{q}{N}\right).$$

To compute the chemical potential, we need the derivative

$$\begin{aligned} \frac{\partial S}{\partial N} &= kq \left(\frac{1}{1+N/q} \right) \frac{1}{q} + k \ln\left(1 + \frac{q}{N}\right) + kN \left(\frac{1}{1+q/N} \right) \left(-\frac{q}{N^2} \right) \\ &= k \left(\frac{q}{q+N} \right) + k \ln\left(1 + \frac{q}{N}\right) - k \left(\frac{q}{N+q} \right) \\ &= k \ln\left(1 + \frac{q}{N}\right). \end{aligned}$$

The chemical potential is therefore

$$= T \frac{\partial S}{\partial N} = kT \ln\left(1 + \frac{q}{N}\right).$$

- b) In the limit $N \gg q$, the logarithm is approximately q/N , so $\approx kTq/N$. This says that when we add a “particle” to the system but no energy, the entropy in fundamental units increases by q/N , a number much less than 1. In the other limit, $N \ll q$, the logarithm is approximately $\ln(q/N)$, so $\approx kT \ln(q/N)$ and therefore, when we add a “particle” to the system but no energy, the entropy in fundamental units increases by $\ln(q/N)$ —a number somewhat larger than 1. This is a significantly larger increase than in the first case. In other words, when there’s already a large excess of particles over energy, adding yet another particle doesn’t increase the entropy by much. But when there’s an excess of energy units over particles, adding another particle gives a significant increase in entropy. Basically, the system “wants” to gain particles more in the second case than in the first.

Problem 3.37. (Ideal gas in a gravitational field.)

- a) The energy of the gas is

$$U = U_{\text{kinetic}} + Nmgz,$$

where the second term is the gravitational potential energy for the N molecules in the gas. The easiest way to compute the chemical potential is from the formula $= (\partial U / \partial N)_{S,V}$. The derivative of U_{kinetic} is not easy to work out, but we know that it *must* reduce to the formula given in the text for the chemical potential of a monatomic gas. (To prove this directly you would have to write U_{kinetic} in terms of entropy, then take the derivative, etc.) Meanwhile, the derivative of the potential energy term is just mgz . Thus the chemical potential is

$$= \left(\frac{\partial U}{\partial N} \right)_{S,V} = (z = 0) + mgz = kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + mgz.$$

Although it is a bit more difficult, we can also compute the chemical potential from the definition $\mu = T(\partial S/\partial N)_{U,V}$, using the Sackur-Tetrode equation (3.62) for the entropy. However, the U that appears in the Sackur-Tetrode equation represents only the kinetic energy; to see this, look back at the derivation in Section 2.5. In this problem, therefore, we should replace it by $U - Nmgz$:

$$S = Nk \left[\ln \left(V \left(\frac{4\pi m(U - Nmgz)}{2h^2} \right)^{3/2} \right) - \ln N^{5/2} + \frac{5}{2} \right].$$

Taking the derivative with respect to N , we get the same expression as in equation 3.63, plus an additional term from the derivative hitting the logarithm of $(U - Nmgz)$:

$$\begin{aligned} &= kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] - NkT \frac{\partial}{\partial N} \ln(U - Nmgz)^{3/2} \\ &= kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] - NkT \frac{3}{2} \frac{mgz}{U - Nmgz} \\ &= kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + NkT \frac{3}{2} \frac{mgz}{\frac{3}{2}NkT}. \end{aligned}$$

(In the last step I've again used the fact that the kinetic energy is $U - Nmgz$.) Canceling factors in the final term reduces this expression to the desired result.

- b) In equilibrium the two chemical potentials must be equal:

$$kT \ln \left[\frac{V}{N(z)} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + mgz = kT \ln \left[\frac{V}{N(0)} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right].$$

Each logarithm can be written as the log of a bunch of constants (including the volume and temperature which are the same for both) minus the logarithm of N . The logs of the constants cancel between the two sides, leaving us with

$$kT \ln N(z) + mgz = kT \ln N(0).$$

Dividing through by kT and exponentiating both sides now yields the desired result,

$$N(z) = N(0)e^{-mgz/kT}.$$

Problem 3.38. For a mixture of ideal gases, we can write the partial pressure of any component as $P_i = x_i P = x_i NkT/V = N_i kT/V$. In other words, the partial pressure is the same as what the total pressure would be, if only that component were present. Thus, holding the partial pressure fixed as we add the other components is the same as holding the number of molecules fixed, that is, doing absolutely nothing to the component that is already present.

Now consider a mixture of just two ideal gases, A and B . (The generalization to mixtures of more than two gases is completely straightforward.) For this mixture, we can write the entropy as a simple sum,

$$S_{\text{total}} = S_A(U_A, V, N_A) + S_B(U_B, V, N_B),$$

where S_A and S_B are each the same as if only that gas were present. (Although the energies of the two components are not separately fixed, we may as well assume that they are, since in equilibrium, any fluctuations away from the most likely values of U_A and U_B will be negligible.) The chemical potential of gas A is then

$$\mu_A = T \left(\frac{\partial S}{\partial N_A} \right)_{U,V,N_B} = T \left(\frac{\partial S_A}{\partial N_A} \right)_{U,V},$$

which is the same as if gas B were not present. Similarly, μ_B involves only the derivative of S_B with respect to N_B , as if gas A were not present. So the chemical potential of any component of a mixture of ideal gases is unaffected by the presence of the other components.

Problem 3.39. The entropy of the flatland gas, as computed in Problem 2.32, is

$$S = Nk \left[\ln \left(\frac{A}{N} \frac{2\pi m U}{Nh^2} \right) + 2 \right].$$

To obtain the temperature, we differentiate with respect to U :

$$\frac{1}{T} = \frac{\partial S}{\partial U} = Nk \frac{1}{U}.$$

In other words, $U = NkT$, as expected for a system with two degrees of freedom per particle. To obtain the pressure, we differentiate with respect to the area A :

$$P = T \frac{\partial S}{\partial A} = T \left(\frac{Nk}{A} \right) = \frac{NkT}{A}.$$

This is the flatland version of the ideal gas law. Finally, to obtain the chemical potential, we differentiate with respect to N :

$$\begin{aligned} &= T \frac{\partial S}{\partial N} = kT \left[\ln \left(\frac{A}{N} \frac{2\pi m U}{Nh^2} \right) + 2 \right] - NkT \left(\frac{2}{N} \right) \\ &= kT \ln \left(\frac{A}{N} \frac{2\pi m U}{Nh^2} \right) = kT \ln \left(\frac{A}{N} \frac{2\pi m kT}{h^2} \right). \end{aligned}$$

This is very similar to the three-dimensional result. The chemical potential is negative, as expected (since the argument of the logarithm is normally quite large), and becomes less negative as the density of particles (N/A) increases.

4 Engines and Refrigerators

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Problem 4.1. (Ideal gas engine with rectangular PV cycle.)

- a) The net work done by the gas during one cycle is

$$|W| = (P_2 - P_1)(V_2 - V_1) = (P_1)(2V_1) = 2P_1V_1,$$

while the heat absorbed (during steps A and B) is

$$Q_h = \frac{5}{2}V_1(P_2 - P_1) + \frac{7}{2}P_2(V_2 - V_1) = \frac{5}{2}V_1P_1 + 14P_1V_1 = \frac{33}{2}P_1V_1.$$

Therefore the efficiency is

$$e = \frac{|W|}{Q_h} = \frac{2P_1V_1}{\frac{33}{2}P_1V_1} = \frac{4}{33} = 12\%.$$

- b) The relative temperatures at various points around the cycle can be determined from the ideal gas law, $PV = NkT$. The lowest temperature occurs at the bottom-left corner when P and V are both smallest. As the pressure doubles during step A the temperature also doubles; then as the volume is tripled during step B so is the temperature. Thus the highest temperature, at the upper-right corner, is six times as great as the lowest temperature. For these extreme temperatures the maximum possible efficiency would be

$$e_{\max} = 1 - \frac{T_c}{T_h} = 1 - \frac{T_c}{6T_c} = \frac{5}{6} = 83\%.$$

The rectangular cycle is extremely inefficient compared to a Carnot cycle.

Problem 4.2. (A steam power plant.)

- a) For these extreme temperatures the maximum efficiency would be

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{293 \text{ K}}{773 \text{ K}} = 62.1\%.$$

- b) With the higher steam temperature the maximum efficiency would be

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{293 \text{ K}}{873 \text{ K}} = 66.4\%.$$

If this efficiency is actually attained, then for a given Q_h we would get more work output than before by a factor of

$$\frac{.664}{.621} = 1.069,$$

that is, we get an additional .069 GW of power. To compute the additional profit, multiply the extra energy by the price charged:

$$\Delta \$ = (.069 \times 10^9 \text{ J/s})(3.16 \times 10^7 \text{ s/yr}) \left(\frac{1 \text{ kw-hr}}{3.6 \times 10^6 \text{ J}} \right) \left(\frac{.05 \text{ \$}}{1 \text{ kw-hr}} \right) = 3 \times 10^7 \text{ \$}.$$

Not bad: we make 30 megabucks!

Problem 4.3. (Waste heat from a power plant.)

- a) An efficiency of 40% means that the other 60% of the energy consumed ends up as waste heat. That's 1.5 times as much as the amount that ends up as work. More generally, by the definition of efficiency and the first law,

$$e = \frac{W}{Q_h} = \frac{W}{Q_c + W},$$

so the waste heat is

$$Q_c = W \left(\frac{1}{e} - 1 \right) = 1.5 W = 1.5 \text{ GW}.$$

- b) In one second, the waste heat dumped to the river is $1.5 \times 10^9 \text{ J}$, and this heat is spread among 10^5 kg of water, so each kilogram gets 15 kJ. With a heat capacity of $4186 \text{ J/}^\circ\text{C}$, the water's temperature increases by $\Delta T = Q/C = 15000 \text{ J}/4186 \text{ J/}^\circ\text{C} = 3.6^\circ\text{C}$.
 c) The latent heat to evaporate water is 2260 J/g (at 100°C). At room temperature it's about 8% more, as mentioned in Problem 1.54 and Figure 5.11; so I'll take $L = 2400 \text{ J/g}$. The total amount of water that must evaporate each second is then

$$\frac{1.5 \times 10^9 \text{ J}}{2400 \text{ J/g}} = 6 \times 10^5 \text{ g} = 600 \text{ kg}.$$

That's only 0.6 m^3 , or only 0.6% of the water in the river.

Problem 4.4. (Engine driven by the ocean's thermal gradient.)

- a) Converting the temperatures to the kelvin scale, we get a maximum possible efficiency of

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{277 \text{ K}}{295 \text{ K}} = 0.061,$$

or about 6%.

- b) A rigorous calculation of the absolute minimum amount of water that we must process is not easy. As the engine extracts heat from the warm water, the water's temperature

decreases and therefore so does the efficiency of the engine. To make a rough estimate, however, let's suppose that we extract heat from the warm water until its temperature drops by 9°C (half the temperature difference between the warm and cool water), and similarly that we expel heat into the cool water until its temperature increases by 9°C . Then the average temperatures of the reservoirs are 290.5 K and 281.5 K, so the efficiency is only

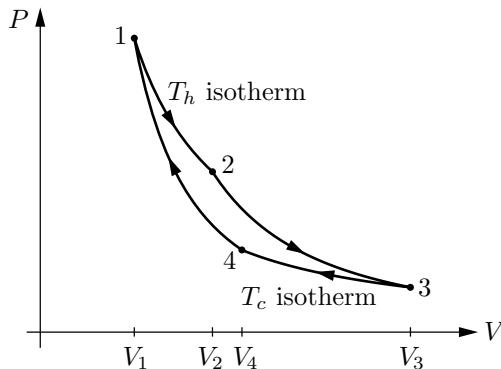
$$e = 1 - \frac{281.5}{290.5} = 0.031.$$

The heat extracted from each kilogram of the warm water is $9 \times 4186 \text{ J} = 38 \text{ kJ}$, but at 3.1% efficiency, this heat produces only 1.2 kJ of work. We need 10^9 J of work each second, so the amount of water required is

$$\frac{10^9 \text{ J}}{1200 \text{ J/kg}} = 8.6 \times 10^5 \text{ kg},$$

or about 900 cubic meters.

Problem 4.5. (Efficiency of an ideal gas Carnot engine.)



To compute Q_h and Q_c we need consider only the isothermal processes 1–2 and 3–4, since the other two steps are adiabatic. Furthermore, the heat input during an isothermal process is equal in magnitude to the work performed, since for an ideal gas $\Delta U \propto \Delta T = 0$. Therefore the heat input is

$$Q_h = |W_{12}| = \int_{V_1}^{V_2} P dV = NkT_h \ln \frac{V_2}{V_1},$$

and similarly,

$$Q_c = |W_{34}| = \int_{V_4}^{V_3} P dV = NkT_c \ln \frac{V_3}{V_4}.$$

The efficiency of the engine is

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c \ln(V_3/V_4)}{T_h \ln(V_2/V_1)},$$

which is equal to the Carnot efficiency provided that $V_3/V_4 = V_2/V_1$. To show that this is the case, note from equation 1.39 that for each of the adiabatic processes, $VT^{f/2}$ is constant

(where f is the number of degrees of freedom per molecule). For the adiabatic expansion 2–3, this implies

$$V_3 T_c^{f/2} = V_2 T_h^{f/2},$$

while for the adiabatic compression 4–1 we have

$$V_4 T_c^{f/2} = V_1 T_h^{f/2}.$$

Dividing these two equations, we obtain $V_3/V_4 = V_2/V_1$, as needed to cancel the logarithms in the preceding formula for the efficiency.

Problem 4.6. (Carnot cycle optimized for power.)

- a) The entropy gained by the engine as heat flows in is Q_h/T_{hw} , while the entropy lost by the engine as heat flows out is Q_c/T_{cw} . Assuming that no other entropy is created inside the engine, these two quantities must be equal:

$$\frac{Q_h}{T_{hw}} = \frac{Q_c}{T_{cw}} \quad \text{or} \quad \frac{Q_h}{Q_c} = \frac{T_{hw}}{T_{cw}}.$$

But the ratio Q_h/Q_c can also be expressed in terms of the four temperatures using the rate equations on the bottom of page 126. In this ratio, K and Δt cancel out, leaving us with

$$\frac{T_h}{T_{cw}} \frac{T_{hw}}{T_c} = \frac{T_{hw}}{T_{cw}}.$$

- b) The power output is the work done per unit time. The time required for the heat Q_h to flow in is

$$\Delta t = \frac{Q_h}{K(T_h - T_{hw})},$$

and the total time for the cycle is just twice this, so

$$\text{Power} = \frac{W}{2\Delta t} = \frac{Q_h - Q_c}{2} \frac{K(T_h - T_{hw})}{Q_h} = \frac{K}{2} \left(1 - \frac{T_{cw}}{T_{hw}}\right) (T_h - T_{hw}),$$

where in the second step I've used energy conservation ($W = Q_h - Q_c$) and in the final step I've again used $Q_h/Q_c = T_{hw}/T_{cw}$. Now solving the result of part (a) for T_{cw} gives

$$\frac{T_{cw}}{T_{hw}} = \frac{T_c}{2T_{hw} - T_h}, \tag{1}$$

so

$$\text{Power} = \frac{K}{2} \left(1 - \frac{T_c}{2T_{hw} - T_h}\right) (T_h - T_{hw}).$$

- c) To find the value of T_{hw} that maximizes the power, set the derivative equal to zero:

$$\begin{aligned} 0 &= \frac{d\text{Power}}{dT_{hw}} = \frac{K}{2} \left[\frac{2T_c}{(2T_{hw} - T_h)^2} (T_h - T_{hw}) - \left(1 - \frac{T_c}{2T_{hw} - T_h}\right) \right] \\ &= \frac{K}{2} \frac{2T_c(T_h - T_{hw}) - (2T_{hw} - T_h)^2 + T_c(2T_{hw} - T_h)}{(2T_{hw} - T_h)^2}. \end{aligned}$$

At this point the constant $K/2$ and the denominator are irrelevant, so the condition is

$$\begin{aligned} 0 &= 2T_c T_h - 2T_c T_{hw} - 4T_{hw}^2 + 4T_h T_{hw} - T_h^2 + 2T_c T_{hw} - T_c T_h \\ &= 4T_{hw}^2 + 4T_h T_{hw} + T_c T_h - T_h^2. \end{aligned}$$

Applying the quadratic formula now gives

$$T_{hw} = \frac{4T_h \pm \sqrt{(4T_h)^2 - 16(T_h^2 - T_c T_h)}}{8} = \frac{T_h}{2} \pm \frac{1}{2}\sqrt{T_c T_h} = \frac{1}{2}(T_h \pm \sqrt{T_c T_h}).$$

The $-$ sign in the \pm gives an unphysical solution, as you can see by considering the case where T_c is only slightly lower than T_h ; in this case the $-$ sign would give T_{hw} close to zero, whereas T_{hw} can't be lower than T_c . To find the corresponding formula for T_{cw} , just plug into equation (1):

$$T_{cw} = \frac{T_c T_{hw}}{2T_{hw} - T_h} = \frac{T_c - \frac{1}{2}(T_h + \sqrt{T_c T_h})}{T_h + \sqrt{T_c T_h} - T_h} = \frac{1}{2} \left(\frac{T_c T_h}{\sqrt{T_c T_h}} + T_c \right) = \frac{1}{2}(T_c + \sqrt{T_c T_h}).$$

d) The efficiency in the case of maximum power is

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_{cw}}{T_{hw}} = 1 - \frac{\frac{1}{2}(T_c + \sqrt{T_c T_h})}{\frac{1}{2}(T_h + \sqrt{T_c T_h})} = 1 - \frac{\sqrt{T_c}(\sqrt{T_c} + \sqrt{T_h})}{\sqrt{T_h}(\sqrt{T_c} + \sqrt{T_h})} = 1 - \sqrt{\frac{T_c}{T_h}}.$$

For the typical numbers given, this is

$$e = 1 - \sqrt{\frac{298 \text{ K}}{873 \text{ K}}} = 42\%,$$

much closer to reality than the “ideal” efficiency of $1 - (298/873) = 66\%$. Of course, if the cost of fuel ever increases to the point where it outweighs the cost of power plant construction, it will become advantageous to design plants to be less powerful and more efficient.

Problem 4.7. If you put an air conditioner in the middle of a building, then the only place it can dump the waste heat is into the building (rather than outside). Since the waste heat is always *greater* than the heat removed from the cold “reservoir,” the net effect would be to raise the temperature inside the building rather than to lower it.

Problem 4.8. If you open the door of your refrigerator, the kitchen will initially cool down somewhat as the cool air from inside the fridge mixes with the warm air in the room. But then, as the refrigerator tries to suck heat out of its interior, it will dump *more* waste heat into your kitchen. So the long-term effect will actually be to increase the temperature of the kitchen, as the refrigerator tries in vain to cool the same space where it is dumping its waste heat.

Problem 4.9. Suppose that the air conditioner must maintain a temperature of 20°C inside the building, while the outside temperature is 35°C. Then the maximum possible COP would be

$$\text{COP} = \frac{T_c}{T_h - T_c} = \frac{293 \text{ K}}{15 \text{ K}} = 19.5.$$

However, this theoretical maximum is unrealistically high, because real air conditioners are designed to work under more extreme temperatures, and to cool the air quickly rather than efficiently.

Problem 4.10. As computed in the text, an ideal kitchen refrigerator could have a COP of about

$$\text{COP} = \frac{T_c}{T_h - T_c} = \frac{255 \text{ K}}{298 \text{ K} - 255 \text{ K}} = 5.9.$$

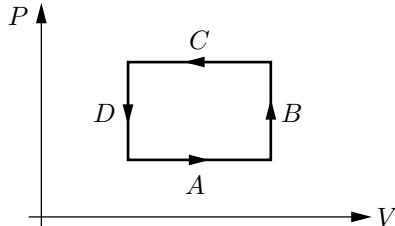
Therefore, by the definition of COP, $Q_c = 5.9W$ or $W = Q_c/5.9$. In each second, this refrigerator must remove 300 J of heat from the inside, so the work required is $W = 300 \text{ J}/5.9 = 50 \text{ J}$. In other words, the power drawn from the wall could be as little as 50 W. (In practice the operation won't be ideal, of course.)

Problem 4.11. For the temperatures given, the maximum COP would be

$$\text{COP} = \frac{T_c}{T_h - T_c} = \frac{0.01 \text{ K}}{1 \text{ K} - 0.01 \text{ K}} = 0.01.$$

In other words, for each joule of heat extracted from the very cold reservoir, we must supply at least 100 J (or 99, to be precise) of work.

Problem 4.12.



For an ideal gas to execute the rectangular PV cycle shown above, it must absorb heat throughout steps A and B and expel heat throughout steps C and D . The temperature of the gas is proportional to the product PV , so it varies continuously throughout the cycle, increasing during steps A and B and decreasing during steps C and D . But this means that the gas must absorb heat over the full range of temperatures in the cycle, then expel heat over the same full range of temperatures. If all of the absorbed heat comes from inside the fridge, then the inside must be hotter than the gas ever gets during the cycle. Similarly, if all of the expelled heat goes to kitchen, then the kitchen must be colder than the gas ever gets—and therefore much colder than the inside! So this device doesn't operate as a refrigerator at all. In a practical refrigerator, the working substance must absorb heat when it is *cold* and expel heat when it is *hot*. (There could, I suppose, be minor exceptions when heat flows "backwards" during parts of the cycle, but these would work against the intended operation of the refrigerator. A more sophisticated loophole in this argument could come from "regeneration," as in the Stirling cycle of Problem 4.21. But such complications are beyond the intended scope of this problem.)

Problem 4.13. The cost of operating an air conditioner is proportional to the energy put into it as work. Using the definition of the COP, this is

$$W = \frac{Q_c}{\text{COP}}.$$

But to maintain a constant temperature in the air conditioned space, Q_c must be equal to the amount of heat that leaks in from outside. Assuming that this amount is proportional to the temperature difference $T_h - T_c$, we have

$$W \propto \frac{T_h - T_c}{\text{COP}}.$$

Now let us assume that the COP is given roughly by the Carnot formula $T_c/(T_h - T_c)$, or at least, that it is roughly proportional to this function of the temperatures. Then

$$W \propto \frac{T_h - T_c}{T_c/(T_h - T_c)} = \frac{1}{T_c} (T_h - T_c)^2.$$

To maintain a given indoor temperature T_c , the work required to operate the air conditioner is proportional to the square of the difference in temperatures between inside and outside. Suppose, for example, that you wish to keep the temperature inside your house at 25°C. If the air conditioning costs you \$1 per hour when the outdoor temperature is 30°C, then it should cost roughly \$4 per hour when the outdoor temperature is 35°C.

Problem 4.14. The heat pump is physically the same as an ordinary refrigerator, so please refer to the energy-flow diagram in Figure 4.4.

- a) The COP should be defined as the benefit divided by the cost. In this case the benefit is the heat that enters the building, Q_h , while the cost is the electrical energy consumed, W . So benefit/cost = Q_h/W .
- b) The energy in is $Q_c + W$ and the energy out is Q_h , so

$$Q_h = Q_c + W$$

under cyclic operation. The COP is therefore

$$\text{COP} = \frac{Q_h}{Q_h - Q_c} = \frac{1}{1 - Q_c/Q_h},$$

which is *always* greater than 1.

- c) The entropy expelled during the cycle must be at least as great as the entropy absorbed, so

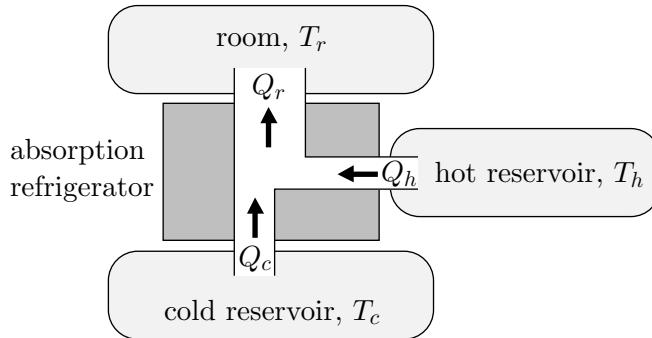
$$\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c} \quad \text{or} \quad \frac{T_c}{T_h} \geq \frac{Q_c}{Q_h}.$$

Because Q_c/Q_h must be *less* than or equal to T_c/T_h , the quantity $1 - Q_c/Q_h$ must be *greater* than or equal to $1 - T_c/T_h$, and therefore, by the result of part (b),

$$\text{COP} \leq \frac{1}{1 - T_c/T_h} = \frac{T_h}{T_h - T_c}.$$

- d) For an electric heater, all the electrical energy (W) is converted to heat (Q_h), so the COP is 1. An ideal heat pump, though, always has a COP greater than 1. For instance, if $T_h = 25^\circ\text{C}$ and $T_c = 0^\circ\text{C}$, then the COP can (in principle) be as high as $298/25 \approx 12$. In practice the COP is never this high, but as long as T_h and T_c aren't too different, a heat pump offers a big advantage in efficiency over an electric heater. On the other hand, a heat pump is more expensive to manufacture and maintain, since it is a complicated device with many moving parts. Fortunately, a central air conditioning system can double as a heat pump in the winter. So if you're already planning to install central air, and your winters aren't *too* cold, get a heat pump.

Problem 4.15. First let me draw an energy-flow diagram for the absorption refrigerator:



- a) The COP should be defined as the benefit/cost ratio, the quantity that we want to be as large as possible. Here the benefit is Q_c and the cost is Q_f , so $\text{COP} = Q_c/Q_f$.
- b) Cyclic operation requires that ΔU for the working substance be zero. Therefore the total energy entering during a cycle must equal the total energy leaving:

$$Q_f + Q_c = Q_r.$$

This relation says nothing about the ratio Q_c/Q_f (either Q_c or Q_f could be bigger than the other), so energy conservation *does* permit the COP to be greater than 1.

- c) For cyclic operation the working substance can't gain or lose any entropy over the long run, so the second law tells us that the total entropy expelled must be at least as much as the total entropy absorbed:

$$\frac{Q_r}{T_r} \geq \frac{Q_c}{T_c} + \frac{Q_f}{T_f}.$$

Since the COP involves Q_c and Q_f but not Q_r , let's use energy conservation to eliminate Q_r :

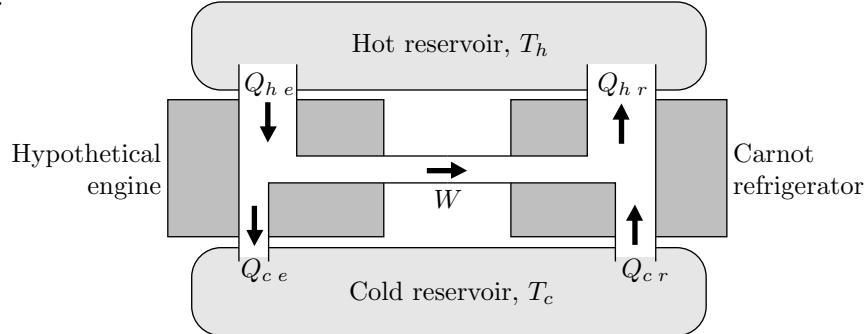
$$\frac{Q_f}{T_r} + \frac{Q_c}{T_r} \geq \frac{Q_c}{T_c} + \frac{Q_f}{T_f}, \quad \text{or} \quad \frac{Q_f}{T_r} - \frac{Q_f}{T_f} \geq \frac{Q_c}{T_c} - \frac{Q_c}{T_r}.$$

Solving for Q_c/Q_f and being careful with the direction of the inequality, we find

$$\frac{Q_c}{Q_f} \leq \frac{\frac{1}{T_r} - \frac{1}{T_f}}{\frac{1}{T_c} - \frac{1}{T_r}} = \frac{T_c(T_f - T_r)}{T_f(T_r - T_c)}.$$

This is the desired limit on the COP, in terms of the three temperatures. As expected, high T_f is good, as is a small difference between T_r and T_c .

Problem 4.16. Hook up the hypothetical engine to the Carnot refrigerator as shown below, so each uses the same reservoirs and the refrigerator uses all the work produced by the engine:

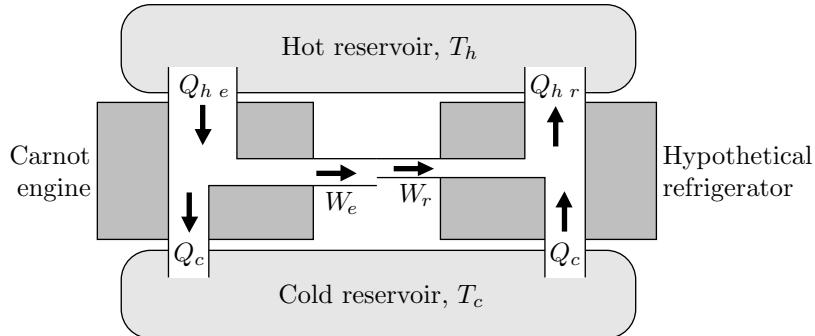


For the ideal Carnot refrigerator, the heat input and output are in the same ratio as the reservoir temperatures:

$$\frac{Q_{h,r}}{Q_{c,r}} = \frac{T_h}{T_c}.$$

For a given W , this equality and energy conservation ($Q_{h,r} - Q_{c,r} = W$) determine the values of $Q_{h,r}$ and $Q_{c,r}$. If the hypothetical engine were ideal, the same equalities would apply to it, so we would have $Q_{h,e} = Q_{h,r}$ and $Q_{c,e} = Q_{c,r}$. However, if the hypothetical engine is better than ideal, then it requires a smaller amount of heat input to produce the same amount of work, so $Q_{h,e} < Q_{h,r}$. Furthermore, energy conservation dictates that its waste heat output must be smaller by the same amount, so $Q_{c,e} < Q_{c,r}$. Thus, the net effect of the engine-refrigerator combination is to transfer heat (in an amount equal to $Q_{h,r} - Q_{h,e}$) from the cold reservoir to the hot reservoir, with no work input. It is a “perfect” refrigerator, too good to be true. We are therefore forced to conclude that no such hypothetical engine could possibly exist.

Problem 4.17. Hook up the hypothetical refrigerator to an ideal Carnot engine as shown below, so that they use the same two reservoirs and their Q_c values are adjusted to be equal:



For the ideal engine, energy and entropy conservation determine the values of W and $Q_{h,e}$, once we have fixed Q_c . If the refrigerator were also ideal, energy and entropy conservation would require that its W and Q_h values be the same as for the engine. However, if the refrigerator is better than ideal, then it requires less work input (and produces less waste heat output), so $W_r < W_e$ (and $Q_{h,r} < Q_{h,e}$). Thus, the net effect of the engine-refrigerator

combination is to produce work (in the amount $W_e - W_r$) with no net heat flow into the cold reservoir. It is a “perfect” engine, converting 100% of its net heat input from the hot reservoir into work. Such an engine is too good to be true, so we are forced to conclude that no such better-than-ideal refrigerator could possibly exist.

Problem 4.18. The efficiency of an engine can be written $e = 1 - (Q_c/Q_h)$, so we need to compute the ratio Q_c/Q_h . Note that Q_h is the heat added in step 2–3 (as labeled in Figure 4.5), while Q_c is the heat expelled during step 4–1. There is no work performed during either of these steps, so by the first law, equipartition, and the ideal gas law,

$$\begin{aligned} Q_h &= U_3 - U_2 = \frac{f}{2}Nk(T_3 - T_2) = \frac{f}{2}V_2(P_3 - P_2); \\ Q_c &= U_4 - U_1 = \frac{f}{2}Nk(T_4 - T_1) = \frac{f}{2}V_1(P_4 - P_1). \end{aligned}$$

The ratio Q_c/Q_h is therefore

$$\frac{Q_c}{Q_h} = \frac{V_1(P_4 - P_1)}{V_2(P_3 - P_2)}.$$

To eliminate the pressures from this equation, use the fact that PV^γ is constant during the adiabatic processes 3–4 and 1–2:

$$P_4V_1^\gamma = P_3V_2^\gamma; \quad P_1V_1^\gamma = P_2V_2^\gamma.$$

Solving these equations for P_4 and P_1 gives

$$P_4 - P_1 = P_3\left(\frac{V_2}{V_1}\right)^\gamma - P_2\left(\frac{V_2}{V_1}\right)^\gamma = (P_3 - P_2)\left(\frac{V_2}{V_1}\right)^\gamma,$$

so the ratio of heats is simply

$$\frac{Q_c}{Q_h} = \frac{V_1(P_3 - P_2)}{V_2(P_3 - P_2)}\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_2}{V_1}\right)^{\gamma-1},$$

and therefore the efficiency is 1 minus this ratio, as given in equation 4.10.

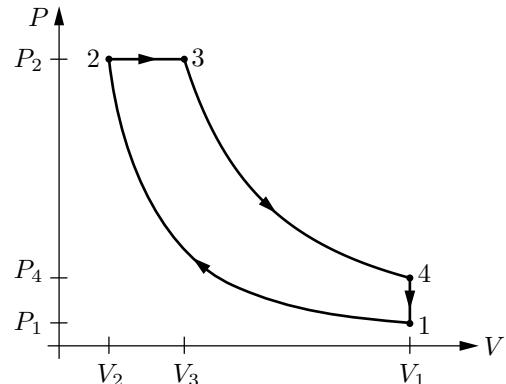
Problem 4.19. Other factors that would affect the efficiency of an automobile engine include friction, conductive heat loss, and incomplete combustion of the fuel. The energy loss due to friction of the pistons with the cylinder walls should be roughly the same per stroke regardless of the power and the amount of fuel consumed. As a fraction of the total energy produced, therefore, I would expect this loss to be smallest when the engine is operating at high power, producing as much work per stroke as possible. Conductive heat loss would be greater when the engine is hot, but this is probably offset by the lower viscosity of the motor oil, which lessens the friction. Incomplete combustion, however, would be worse when there is proportionally less oxygen present in the cylinders, that is, when more fuel is injected per stroke. So I would expect the greatest efficiency to be achieved at relatively high power levels, but not so high that incomplete combustion becomes a serious problem. Because most present-day auto engines are operated over a very wide range of power levels (lowest when idling at a stop light and highest when accelerating uphill), they come close to maximum efficiency only a small fraction of the time they are running. Much of the advantage of hybrid-electric engines is that the internal combustion engine always runs at near its peak efficiency, shutting off completely at other times.

Problem 4.20. Following the same method as in Problem 4.18, the heat input (during step 2–3) is

$$\begin{aligned} Q_h &= (U_3 - U_2) + P_2(V_3 - V_2) \\ &= \frac{f}{2} Nk(T_3 - T_2) + P_2(V_3 - V_2) \\ &= \frac{f+2}{2} P_2(V_3 - V_2), \end{aligned}$$

while the waste heat output is

$$Q_c = U_4 - U_1 = \frac{f}{2} V_1(P_4 - P_1).$$



Therefore the ratio of heats (which is 1 minus the efficiency) is

$$\frac{Q_c}{Q_h} = \frac{\frac{f}{2} V_1(P_4 - P_1)}{\frac{f+2}{2} P_2(V_3 - V_2)} = \frac{1}{\gamma} \frac{V_1(P_4 - P_1)}{P_2(V_3 - V_2)}.$$

Since steps 3–4 and 1–2 are adiabatic, we can relate the initial and final pressures:

$$P_4 V_1^\gamma = P_2 V_3^\gamma; \quad P_1 V_1^\gamma = P_2 V_2^\gamma.$$

Solving these equations for P_4 and P_1 , respectively, and plugging into the previous equation gives

$$\frac{Q_c}{Q_h} = \frac{1}{\gamma} \frac{V_1}{V_3 - V_2} \left[\left(\frac{V_3}{V_1} \right)^\gamma - \left(\frac{V_2}{V_1} \right)^\gamma \right].$$

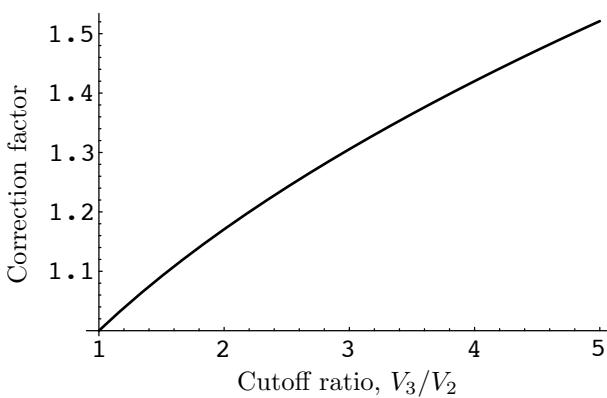
To better understand this result, divide the numerator and denominator of each volume ratio by V_2 , then factor out the compression ratio to obtain

$$\frac{Q_c}{Q_h} = \frac{1}{\gamma} \frac{V_1/V_2}{(V_3/V_2) - 1} \left[\left(\frac{V_3}{V_2} \right)^\gamma \left(\frac{V_2}{V_1} \right)^\gamma - \left(\frac{V_2}{V_1} \right)^\gamma \right] = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \frac{1}{\gamma} \frac{(V_3/V_2)^\gamma - 1}{(V_3/V_2) - 1}.$$

The efficiency is just 1 minus this quantity,

$$e = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1} \frac{1}{\gamma} \frac{(V_3/V_2)^\gamma - 1}{(V_3/V_2) - 1}.$$

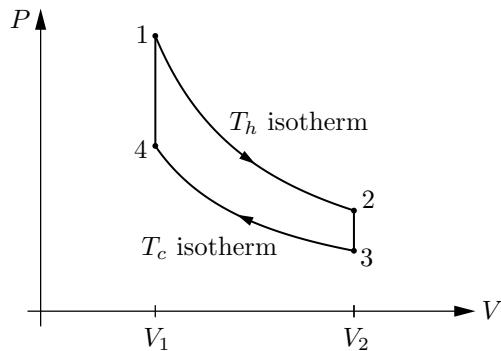
If we ignore the factor after the γ , this expression is the same as for the Otto cycle. The correction factor (after the γ) depends only on γ and the cutoff ratio V_3/V_2 . To prove rigorously that it is always greater than 1 (given that $\gamma > 1$ and $V_3 > V_2$) is not easy, but this fact is clear from the plot at right, drawn for $\gamma = 7/5$. The efficiency of the Diesel cycle is therefore always less than that of the Otto cycle, for a given compression ratio. Note



that as the cutoff ratio approaches 1, the correction factor goes to 1, so the efficiency becomes the same as for the Otto cycle. For $\gamma = 7/5$ and a compression ratio of 18, the ratio $(V_2/V_1)^{\gamma-1}$ is 0.31, so the efficiency of an ideal Otto cycle would be 69%. However, for an ideal Diesel cycle with a cutoff ratio of 2, the correction factor is 1.17, so the efficiency is reduced to $1 - (0.31)(1.17) = 0.63$.

Problem 4.21. (Stirling engine.)

- a) The cycle consists of two isothermal processes (at T_h and T_c) connected by constant-volume processes:



- b) To calculate the efficiency we need to know the net work done and the total heat input for one cycle. The work done by the gas during the power stroke is

$$W_{12} = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{NkT_h}{V} dV = NkT_h \ln \frac{V_2}{V_1},$$

and the work done by the gas during the compression stroke is similarly

$$W_{34} = \int_{V_2}^{V_1} \frac{NkT_c}{V} dV = -NkT_c \ln \frac{V_2}{V_1},$$

so the net work done per cycle is

$$W = W_{12} + W_{34} = Nk(T_h - T_c) \ln \frac{V_2}{V_1}.$$

Meanwhile the heat input occurs during the power stroke *and* during the transfer to the hot cylinder. Because the power stroke is isothermal, the energy of the gas doesn't change during this step and therefore, by the first law,

$$Q_{12} = W_{12} = NkT_h \ln \frac{V_2}{V_1}.$$

During the transfer to the hot cylinder there is no work done, so by the first law and the equipartition theorem, the heat input is

$$Q_{41} = U_1 - U_4 = \frac{f}{2} Nk(T_h - T_c),$$

where f is the number of degrees of freedom per molecule. Thus the total heat input is

$$Q_h = Q_{12} + Q_{41} = NkT_h \ln \frac{V_2}{V_1} + \frac{f}{2} Nk(T_h - T_c).$$

Now the efficiency is defined as $e = W/Q_h$. It's algebraically simpler to compute the reciprocal,

$$\frac{1}{e} = \frac{Q_h}{W} = \frac{NkT_h \ln(V_2/V_1) + \frac{f}{2} Nk(T_h - T_c)}{Nk(T_h - T_c) \ln(V_2/V_1)} = \frac{T_h}{T_h - T_c} + \frac{f}{2 \ln(V_2/V_1)}.$$

The first term is just the reciprocal of the Carnot efficiency, $e_C = 1/(T_c/T_h)$, so we can write

$$\frac{1}{e} = \frac{1}{e_C} + \frac{f}{2 \ln(V_2/V_1)}.$$

The second term is always positive, but is smaller for large compression ratios. Therefore $1/e$ is always *greater* than $1/e_C$, that is, e is *less* than e_C , by an amount that is smaller when the compression ratio is large. For instance, if T_h is twice as large as T_c (say 600 K compared to 300 K), so $e_C = 1/2$, and if the compression ratio is 10 and the gas has five degrees of freedom per molecule, then

$$\frac{1}{e} = \frac{1}{1/2} + \frac{5}{2 \ln 10} = 2 + \frac{5}{2 \cdot 2.3} = 2 + 1.1 = 3.1,$$

that is, the efficiency is about 32%.

- c) With an ideal regenerator, the heat input during step 41 comes for free, because it's exactly the same ($\frac{f}{2} Nk(T_h - T_c)$) as the heat output during step 23. Therefore only Q_{12} should be counted as part of Q_h when computing the efficiency. Following the steps of the preceding calculation, this means that the second term in the expression for $1/e$ is no longer present, and therefore, $e = e_C$.
- d) To really obtain $e = e_C$, the temperature difference between the gas and whichever reservoir it is exchanging heat with would always have to be infinitesimal; therefore the engine would have to operate infinitesimally slowly, just like an ideal Carnot engine. To get any power out of a Stirling engine you have to run it with nonzero temperature differences, just like the Carnot engine considered in Problem 4.6. You might think, then, that there is no advantage to a Stirling engine over a Carnot engine, but in fact the Stirling engine turns out to be easier (mechanically) to build and operate, since the walls of the cylinders can always be at the same temperature, and are always in approximate thermal equilibrium with the gas that is near them. Both the Stirling and Carnot engines should be contrasted with internal combustion engines, which are generally more compact (no external combustion chamber) but are limited to certain types of fuel and are more polluting because the fuel never burns completely. Compared to a steam engine, a Stirling engine has the advantage of greater simplicity and possibly higher efficiency, but the disadvantage of (probably) lower power. Announcements promising new, commercially viable Stirling-engine devices have been appearing regularly for several decades, yet so far, at least, Stirling engines seem to be limited to rather obscure niche uses.

Problem 4.22. To compute the efficiency we need to know H_1 , H_3 , and H_4 . At point 1 we have “saturated” (i.e., on the verge of boiling) liquid water at 20°C, so from Table 4.1 we see that the pressure must be 0.023 bar and the enthalpy (per kilogram) is 84 kJ. At point 3 we have “superheated” steam at 300°C and 10 bars, so from Table 4.2 we see that the enthalpy is 3051 kJ (per kilogram) and the entropy is 7.123 kJ/K. The expansion in the turbine is approximately adiabatic, so the entropy at point 4 should be the same as at point 3. At point 4, however, we have a mixture of saturated water ($S = 0.297 \text{ kJ/K}$) and saturated steam ($S = 8.667 \text{ kJ/K}$) at 20°C. If x is the fraction of water, then we require

$$7.123 = x(0.297) + (1 - x)(8.667), \quad \text{or} \quad x = \frac{8.667 - 7.123}{8.667 - 0.297} = 0.184.$$

This same mixture has an enthalpy of

$$H_4 = (0.184)(84 \text{ kJ}) + (0.816)(2538 \text{ kJ}) = 2085 \text{ kJ}.$$

So, finally, the efficiency of our engine is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{2085 - 84}{3051 - 84} = 0.33,$$

significantly less than that of the higher-temperature engine considered in the text.

Problem 4.23. Enthalpy is defined as $H = U + PV$. Therefore, under infinitesimal changes in conditions, the change in H is

$$dH = dU + P dV + V dP = T dS + V dP,$$

where in the second step I've used the thermodynamic identity (and set $dN = 0$ since we're interested in a fixed amount of fluid). Assuming that the compression of the water in step 1 → 2 is approximately adiabatic and quasistatic, the entropy doesn't change so $dH = V dP$. For our process the change in pressure isn't exactly infinitesimal, but the volume is still almost constant so we can write $\Delta H_{12} = V \Delta P_{12}$. For one kilogram of water taken from very low pressure up to 300 bars, this is

$$\Delta H_{12} = (10^{-3} \text{ m}^3)(300 \times 10^5 \text{ N/m}^2) = 30 \text{ kJ},$$

so the enthalpy at point 2 is approximately 114 kJ, rather than 84 kJ as approximated in equation 4.13. With this improved estimate of H_2 , the efficiency would be

$$e = 1 - \frac{1824 - 84}{3444 - 114} = 0.477,$$

rather than 0.482 as you would get if you set $H_2 = H_1 = 84 \text{ kJ}$. But this difference is only half a percent, and two significant figures is probably all that would be justified in any case.

Problem 4.24. (Effect of temperatures and pressures on Rankine cycle efficiencies.)

- a) Lowering the maximum temperature to 500°C reduces the enthalpy at point 3 to 3081 kJ (per kilogram) and the entropy to 5.791 kJ/K. To find the fraction x of liquid water at point 4, set this entropy equal to the sum of the liquid and gas components:

$$5.791 = x(0.297) + (1 - x)(8.667) \quad \Rightarrow \quad x = 0.344.$$

The enthalpy at point 4 is therefore

$$H_4 = (0.344)(84 \text{ kJ}) + (0.656)(2538 \text{ kJ}) = 1695 \text{ kJ}.$$

Thus the efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{1695 - 84}{3081 - 84} = 0.46.$$

As expected, a lower maximum temperature gives a lower efficiency. However, the reduction from when $T_h = 600^\circ\text{C}$ is quite small, only 2% out of 48%.

- b) Lowering the maximum pressure to 100 bar increases the enthalpy at point 3 to 3625 kJ (per kilogram) and the entropy to 6.903 kJ/K. To find the fraction x of liquid water at point 4, set this entropy equal to the sum of the liquid and gas components:

$$6.903 = x(0.297) + (1 - x)(8.667) \quad \Rightarrow \quad x = 0.211.$$

The enthalpy at point 4 is therefore

$$H_4 = (0.211)(84 \text{ kJ}) + (0.789)(2538 \text{ kJ}) = 2021 \text{ kJ}.$$

Thus the efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{2021 - 84}{3625 - 84} = 0.45.$$

Again, the efficiency is slightly less. This time, however, the reason is less clear, because the extreme temperatures are the same as before. Apparently, less of the heat transfer occurs at temperatures near the extremes, since the boiling occurs at a lower temperature and there is more steam exiting the turbine.

- c) Lowering the minimum temperature to 10°C reduces H_1 to 42 kJ (per kilogram). Point 3 is the same as in the example in the text, but we must redo the calculation of the fraction of liquid at point :

$$6.233 = x(0.151) + (1 - x)(8.901) \quad \Rightarrow \quad x = 0.305.$$

The enthalpy at point 4 is therefore

$$H_4 = (0.305)(42 \text{ kJ}) + (0.695)(2520 \text{ kJ}) = 1764 \text{ kJ},$$

and so the efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{1764 - 42}{3444 - 42} = 0.49.$$

Since we've widened the range of temperatures, the efficiency increases, as expected.

Problem 4.25. If the entropy increases in the turbine rather than remaining constant, then the composition upon leaving the turbine will include more steam and less water (since steam has more entropy than water at a given final pressure). The enthalpy at point 4 will therefore be greater than we've been assuming. And since H_4 appears with a minus sign in the formula

$$e = 1 - \frac{H_4 - H_1}{H_3 - H_2},$$

the efficiency will be less. Of course, we could have predicted this on general principles: Producing more entropy during the cycle means we must expel more waste heat to get rid of the entropy, and therefore there is less energy left to produce work.

Problem 4.26. The net work done by the Rankine cycle is

$$W = Q_h - Q_c = (H_3 - H_2) - (H_4 - H_1) \approx H_3 - H_4,$$

where in the last step I've approximated $H_2 \approx H_1$ as in the text. For a kilogram of steam under the conditions assumed in the text, this is

$$W = 3444 \text{ kJ} - 1824 \text{ kJ} = 1620 \text{ kJ}.$$

To generate 10^9 joules (in one second), the number of kilograms of steam required would therefore be

$$\frac{10^9 \text{ J}}{1,620,000 \text{ J/kg}} = 617 \text{ kg}.$$

If we take into account the 30-kJ difference between H_2 and H_1 (as calculated in Problem 4.23), the work done per kilogram is reduced by 30 kJ and so the number of kilograms required is increased to $10^9 / 1,590,000 = 630$.

Problem 4.27. Temperature isn't the only variable that's changing in Table 4.1; pressure varies as well. At a given *volume*, increasing the temperature of a system normally increases its entropy. For the liquid water, the volume doesn't vary much with pressure so that's the whole story. But for the steam, the increasing pressure reduces the volume significantly. Squeezing a gas into a smaller space reduces the number of microstates available to the gas molecules, and thus reduces the entropy. Apparently, this effect is enough to outweigh the increase in entropy caused by the increase in temperature.

Problem 4.28. Taking $S = 0$ for liquid water at the triple point, we can calculate the entropy of steam at the same temperature and pressure using

$$\Delta S = \frac{Q}{T} = \frac{\Delta H}{T} = \frac{2501 \text{ kJ}}{273 \text{ K}} = 9.156 \text{ kJ/K},$$

precisely in agreement with the number that my dog ate. To fill in the next row of the table, imagine starting with liquid water at the triple point and heating it to 10°C while the pressure increases to 0.012 bar. This is not a constant-pressure process, so strictly speaking, $Q \neq \Delta H$. Instead, we can write approximately

$$\Delta H = \Delta U + P \Delta V + V \Delta P = (Q - P \Delta V) + P \Delta V + V \Delta P = Q + V \Delta P.$$

For a kilogram of water, the quantity $V \Delta P$ is less than 1 J, quite negligible compared to $\Delta H = 42 \text{ kJ}$. Therefore,

$$\Delta S \approx \frac{Q}{T} \approx \frac{\Delta H}{T} = \frac{42 \text{ kJ}}{278 \text{ K}} = 0.151 \text{ kJ/K},$$

again in perfect agreement with the tabulated value. Getting S_{steam} at this temperature and pressure is no harder than before. Even for the much larger increase in T and P between the last two lines of the table, the same set of approximations gives for liquid water

$$\Delta S \approx \frac{210 \text{ kJ}}{348 \text{ K}} = 0.603 \text{ kJ/K},$$

right on the money.

To obtain the first entropy value listed in Table 4.2, start with the last one listed in Table 4.1 (which is at essentially the same pressure) and again compute

$$\Delta S = \frac{\Delta H}{T} \approx \frac{199 \text{ kJ}}{423 \text{ K}} = 0.470 \text{ kJ/K}.$$

This is too low by 0.009 kJ/K, presumably because the arithmetic mean temperature is the wrong weighted average; to do it right we would have to break up the calculation into smaller pieces covering smaller temperature ranges, which would require enthalpy data at intermediate temperatures. Moving across Table 4.2 involves similar inaccuracies; for instance, the change at 1 bar from 200°C to 300°C should be approximately

$$\Delta S \approx \frac{199 \text{ kJ}}{523 \text{ K}} = 0.380 \text{ kJ/K},$$

which is less than what the table says by 0.002 kJ/K. To move vertically in the table we would have to compute $V \Delta P$, or rather, the integral of $V dP$ over the pressure difference. At low pressures we could do this using the ideal gas law, but at high pressures the ideal gas law no longer applies and we'd be stuck. So I would hope that my dog would leave at least one entropy value in each row of Table 4.2, from which I could compute the rest (to good approximation) using the enthalpy data.

Problem 4.29. For each kilogram of the HFC-134a, the initial enthalpy (from Table 4.3) is 116 kJ. At the final pressure of 1 bar, the enthalpy of the liquid phase at the boiling point would be 16 kJ, while that of the gas phase would be 231 kJ. Since enthalpy is conserved in the throttling process, and 116 lies between 16 and 231, the final state will be a combination of liquid and gas at the boiling point, 26.4°C. To find out what combination, let x be the fraction that ends up as liquid. Setting the initial and final enthalpies equal to each other then gives

$$116 = x(16) + (1 - x)(231) \quad \text{or} \quad x = \frac{231 - 116}{231 - 16} = 0.53.$$

So by mass, 53% of the fluid remains a liquid and 47% vaporizes.

Problem 4.30. (Household refrigerator.)

- a) The entropy at point 1, for a kilogram of fluid, is 940 J/K (from Table 4.3). Looking at the 10-bar row of Table 4.4, note that at 50°C the entropy would be 943 J/K, only slightly higher. Assuming that S is a linear function of temperature between 40° and 50°, it would increase by 3.6 J/K per degree, or 3 J/K in 0.83 degrees. Therefore the temperature at point 2 must be 0.83 degrees less than 50°, or just over 49°C.
- b) From Table 4.3, $H_1 = 231$ kJ. To find H_2 , repeat the same interpolation in Table 4.4: Between 40 and 50 degrees the enthalpy increases by 2.1 kJ per degree, so 0.83 degrees below 50 the enthalpy should be less than 280 kJ by $(0.83)(2.1 \text{ kJ}) = 1.75 \text{ kJ}$, that is, $H_2 = 278.25 \text{ kJ} \approx 280 \text{ kJ}$. At point 3 the fluid is saturated liquid at 10 bars, so $H_3 = 105$ kJ from Table 4.3. And since the throttling process leaves the enthalpy unchanged, $H_4 = 105$ kJ as well. Plugging these results into equation 4.20, we obtain for the coefficient of performance

$$\text{COP} = \frac{H_1 - H_3}{H_2 - H_1} = \frac{231 - 105}{280 - 231} = 2.67.$$

To compare to a Carnot refrigerator operating between the same reservoir temperatures, note that the high-temperature reservoir can be no hotter than $T_3 = 39.4^\circ\text{C} = 312.6 \text{ K}$, while the low-temperature reservoir can be no colder than $T_4 = T_1 = -26.4^\circ\text{C} = 246.8 \text{ K}$. For this temperature range the Carnot COP would be

$$\frac{T_c}{T_h - T_c} = \frac{246.8}{312.6 - 246.8} = 3.75,$$

only moderately better than the actual efficiency of the cycle. To increase the efficiency we could reduce T_h to a value only slightly higher than the temperature of the kitchen ($32^\circ\text{C}?$), and/or increase T_c to a value only slightly lower than the temperature of the freezer ($-15^\circ\text{C}?$). However, for reasonably rapid heat transfer between the refrigerant and either reservoir, we should probably have a temperature difference of at least 10°C; therefore the temperatures assumed in this example are probably about right.

- c) Setting the initial enthalpy equal the enthalpy of the unknown final mixture, we have (with all numbers in kJ)

$$105 = 16x + 231(1 - x) \quad \text{or} \quad x = \frac{231 - 105}{231 - 16} = 0.59,$$

where x is the fraction that remains liquid. So 41% of the fluid (by mass) vaporizes during the throttling.

Problem 4.31. If the fluid expands by pushing a turbine, the step 3–4 will approximately conserve entropy (since it is adiabatic) rather than enthalpy. The entropy (per kilogram of fluid) at point 3 is 0.384 kJ/K. To find the fraction x that remains liquid at point 4, set the initial and final entropies equal:

$$0.384 = x(0.068) + (1 - x)(0.940) \quad \text{or} \quad x = \frac{0.940 - 0.384}{0.940 - 0.068} = 0.638.$$

The enthalpy at point 4 is then

$$H_4 = (0.638)(16 \text{ kJ}) + (0.362)(231 \text{ kJ}) = 94 \text{ kJ},$$

compared to 105 kJ for expansion at constant enthalpy. The COP is still given by equation 4.14 (but not by 4.20):

$$\text{COP} = \frac{H_1 - H_4}{H_2 - H_3} = \frac{231 - 94}{280 - 105} = 3.6.$$

This is larger than the COP computed in the previous problem (2.7), because the coolant, starting with a greater fraction of liquid, can absorb more heat in step 4–1. Note also that this efficiency is only slightly less than the Carnot efficiency computed in the previous problem for the temperature range T_1 to T_3 . However, the price of this higher efficiency is the mechanical complexity of more moving parts. Most people seem to prefer a refrigerator that is inexpensive to buy and reliable to operate, rather than efficient in its energy use.

Problem 4.32. For a household air conditioner, we want T_1 to be significantly colder than the temperature inside the house, so the coolant can remove heat at an appreciable rate. At 4 bar, the boiling temperature of HFC-134a is 8.9°C, which should be cool enough. We also want T_3 to be significantly higher than the highest expected outdoor temperature, for rapid transfer of the waste heat. If the outdoor temperature can be as high as 40°C, then we'd better use a pressure of 12 bar, where the boiling temperature is 46.3°C. (Even higher pressure might be desirable, but for this problem I'll stick to the options listed in the table.) For these pressures, we have $H_1 = 252 \text{ kJ}$ (per kilogram of refrigerant) and $H_3 = 116 \text{ kJ}$. To find H_2 , we need to know the temperature at point 2. Assuming isentropic compression, the entropy at point 2 should be the same as at point 1, 0.915 kJ/K. This is almost exactly equal to the entropy of the superheated gas at 12 bar and 50°C, so to the nearest degree, $T_2 = 50^\circ\text{C}$ and therefore $H_2 = 276 \text{ kJ}$. Therefore the COP is

$$\text{COP} = \frac{H_1 - H_3}{H_2 - H_1} = \frac{252 - 116}{276 - 252} = 5.7.$$

For comparison, an ideal Carnot air conditioner operating between reservoirs at 40°C and 20°C would have a COP of

$$\text{COP}_{\text{Carnot}} = \frac{T_c}{T_h - T_c} = \frac{293 \text{ K}}{20 \text{ K}} \approx 15.$$

Of course, this high efficiency is outweighed by the infinitesimal rate of heat transfer. A Carnot air conditioner operating with the same minimum temperature differences as our real air conditioner would have a COP of

$$\frac{T_c}{T_h - T_c} = \frac{282 \text{ K}}{37 \text{ K}} \approx 7.6,$$

still somewhat better than our real air conditioner.

Problem 4.33. (Throttling nitrogen.)

- a) The initial (molar) enthalpy is 8174 J; in order for the enthalpy to stay fixed at this value, the temperature must decrease to some value between 200 K (where $H = 5800$ J) and 300 K (where $H = 8717$ J). Interpolating linearly between these values, I find that each degree increase in temperature increases the enthalpy by 29.2 J. Our H is less than that at 300 K by 543 J, so the temperature must drop by $543/29.2 = 19$ K. The final temperature is therefore 281 K.
- b) Again the temperature must drop. Between 100 K and 200 K (at 1 bar) the enthalpy changes by 29.4 J/K. Our initial enthalpy, 4442 J, is less than 5800 J (the value at 1 bar and 200 K) by 1358 J, so the temperature must drop by $1358/29.4 = 46$ K. The final temperature is therefore 154 K.
- c) Starting at 100 K, the enthalpy is 1946 J. This value lies between the enthalpies of the saturated liquid and saturated gas at 1 bar, so we end up with a mixture of liquid and gas at 77 K. To find the fraction x that ends up as liquid, just do another interpolation:

$$3407x + 2161(1 - x) = 1946 \quad \Rightarrow \quad x = \frac{2161 + 1946}{2161 + 3407} = 0.74.$$

- d) The highest temperature at which some (in nitesimal) liquefaction takes place would be the temperature at which the initial enthalpy is 2161 J. Now at 100 bars, between 100 K and 200 K, the enthalpy rises by 63.9 J/K. But 2161 is greater than 1946 by 4107, so the initial temperature is greater than 100 K by $4107/63.9 = 64.3$ K, that is, it's 164 K.
- e) At 600 K, the enthalpy at 1 bar is slightly less than at 100 bar, so the constant-enthalpy throttling process would have to result in an *increase* in temperature.

Problem 4.34. (Liquefaction by the Hampson-Linde cycle.)

- a) We already know (from the argument on page 139) that the throttling process itself conserves enthalpy. What about the heat exchanger? The heat lost from the high-pressure gas as it flows toward the throttle is equal to the decrease in its enthalpy, since this is a constant-pressure process. Similarly, the heat absorbed by the low-pressure gas coming back from the throttle is equal to the increase in its enthalpy. Assuming that no heat is lost in the heat exchanger, so the heat lost by the high-pressure gas equals the heat absorbed by the low-pressure gas, the enthalpy lost by the former is equal to the enthalpy gained by the latter and so there is no net change in the enthalpy of the fluid throughout the heat exchanger and throttle. (The output, though, consists of both the condensed liquid and the gas returned to the compressor.)
- b) Consider one mole of high-pressure gas entering the heat exchanger, with enthalpy H_{in} . This fluid converts to x moles of liquid with enthalpy xH_{liq} , plus $(1 - x)$ moles of low-pressure gas returning from the heat exchanger, with enthalpy $(1 - x)H_{\text{out}}$. Conservation of enthalpy therefore implies

$$H_{\text{in}} = xH_{\text{liq}} + (1 - x)H_{\text{out}}, \quad \text{or} \quad x = \frac{H_{\text{out}} - H_{\text{in}}}{H_{\text{out}} - H_{\text{liq}}}.$$

- c) For nitrogen at 100 bars and 300 K, we have $H_{\text{in}} = 8174 \text{ J}$. The condensed liquid at 1 bar will be at the boiling temperature, 77 K, so $H_{\text{liq}} = 3407 \text{ J}$. And the returned gas, after passing through the heat exchanger, will again be at 300 K, so $H_{\text{out}} = 8717 \text{ J}$. Therefore the fraction liquefied will be

$$x = \frac{8717 - 8174}{8717 - 3407} = 0.045,$$

only four and a half percent. But for an initial temperature of 200 K, we instead have $H_{\text{in}} = 4442 \text{ J}$ and $H_{\text{out}} = 5800 \text{ J}$, so

$$x = \frac{5800 - 4442}{5800 - 3407} = 0.15,$$

considerably better. This example shows the advantage of precooling the gas as much as possible before putting it into the heat exchanger.

Problem 4.35. (Limits on magnetic cooling.)

- a) The field strength of one of these dipoles at a distance of 1 nm is

$$B = \frac{0}{4\pi r^3} = (10^{-7}) \frac{(9 \times 10^{-24})}{(10^{-9})^3} \text{ T} = 9 \times 10^{-4} \text{ T}.$$

If a dipole has several neighbors, each creating a field of this strength but not necessarily in the same direction, I suppose the total field might be roughly 2 or 3 times 10^{-3} T .

- b) Suppose that the effective field strength is reduced from 1 T to $2 \times 10^{-3} \text{ T}$, that is, by a factor of 500. Then, according to equation 4.21, the temperature must also drop by a factor of 500 in order to maintain constant magnetization (and hence constant entropy).
- c) The graph of S vs. T rises most steeply at around $kT = B$. Setting B equal to the effective minimum field of $2 \times 10^{-3} \text{ T}$ gives

$$T_{\text{steep}} \approx \frac{(9 \times 10^{-24} \text{ J/T})(2 \times 10^{-3} \text{ T})}{1.4 \times 10^{-23} \text{ J/K}} \approx 1 \text{ mK}.$$

- d) At temperatures significantly below 1 mK, where the graph of S vs. T is practically horizontal, the heat capacity must be very small: $C = Q/\Delta T = T \Delta S/\Delta T \approx 0$. Even the smallest leakage of heat into the system will therefore raise the temperature significantly. In practice you can't completely stop heat leakage, so there's no point in trying to cool this system much below 1 mK.

Problem 4.36. The momentum of a photon is $p = h/\lambda$. An atom emitting or absorbing the photon will recoil with a comparable momentum, and a corresponding kinetic energy of $K = p^2/2m$. Setting this “minimum” kinetic energy equal to $\frac{3}{2}kT$ and solving for T , we obtain

$$kT \approx \frac{2}{3}K = \frac{2}{3} \frac{p^2}{2m} = \frac{h^2}{3m\lambda^2}.$$

The mass of a rubidium atom is about 85 u, and the wavelength is given as 780 nm, so

$$kT \approx \frac{(6.63 \times 10^{-34} \text{ J s})^2}{3(85)(1.66 \times 10^{-27} \text{ kg})(780 \times 10^{-9} \text{ m})^2} = 1.7 \times 10^{-30} \text{ J} = 1.1 \times 10^{-11} \text{ eV.}$$

Dividing by k gives $T \approx 1.2 \times 10^{-7} \text{ K}$, or about 0.1 K. To attain lower temperatures than this, we would apparently have to make the atoms absorb and emit fractions of a photon. And yet, according to the references given in the text, this limit has been surpassed by ingenious techniques.

Problem 4.37. The third law of thermodynamics states that the entropy of a system approaches zero (or perhaps some other finite constant) at absolute zero temperature. As discussed in Section 3.2, this implies that the heat capacity of a system must approach zero as $T \rightarrow 0$. But this means that at very low temperature, even the tiniest heat leak into a system will increase its temperature significantly. Any cooling mechanism therefore reaches a point of diminishing returns when the temperature drops to the point where the system's heat capacity becomes negligibly small. For example, evaporative cooling of liquid helium is ineffective below about 1 K because the heat capacity of the helium is so small at subkelvin temperatures. Similarly, magnetic cooling of a paramagnet is ineffective at temperatures where most of the dipoles line up spontaneously, reducing the entropy and the heat capacity to negligible levels (see Problem 4.35). Nuclear paramagnets can be cooled to very low temperatures precisely because the temperatures where they magnetize spontaneously are so low. And as discussed in Chapter 7, even a laser-cooled gas will eventually "condense" into a state where its entropy and heat capacity become negligible. Fortunately, whenever a system has "interesting" behavior in a very low temperature range, there seems to be a way to exploit that behavior to cool the system to that temperature range. The unattainably low temperatures are precisely those for which the entropy is already negligible, so that no further interesting behavior occurs.

5

Free Energy and Chemical Thermodynamics

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Problem 5.1. The energy of a mole of argon is given by the equipartition theorem:

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT = \frac{3}{2}(1)(8.31 \text{ J/K})(300 \text{ K}) = 3.74 \text{ kJ.}$$

The entropy is given by the Sackur-Tetrode equation:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] = Nk \left[\ln \left(\frac{kT}{P} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right],$$

where I've used the ideal gas law and equipartition in the last expression. Since an argon atom has a mass of about 40 times the proton mass, the argument of the logarithm is

$$\frac{[(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})]^{5/2}}{1.01 \times 10^5 \text{ N/m}^2} \left(\frac{(2\pi)(40)(1.67 \times 10^{-27} \text{ kg})}{(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 1.02 \times 10^7.$$

Therefore

$$S = Nk \left[\ln(1.02 \times 10^7) + \frac{5}{2} \right] = Nk(18.6) = (18.6)R = 155 \text{ J/K.}$$

The enthalpy is

$$H = U + PV = U + nRT = \frac{5}{2}nRT = \frac{5}{2}(8.31 \text{ J/K})(300 \text{ K}) = 6.23 \text{ kJ.}$$

The Helmholtz free energy is

$$F = U - TS = (3.74 \text{ kJ}) - (300 \text{ K})(155 \text{ J/K}) = -42.6 \text{ kJ,}$$

while the Gibbs free energy is

$$G = F + PV = F + RT = (-42.6 \text{ kJ}) + (8.31 \text{ J/K})(300 \text{ K}) = -40.1 \text{ kJ.}$$

Since the term TS is much larger in magnitude than U or PV , both of the free energies turn out to be negative. But the sign of F or G isn't any more significant than the sign of U : it's *differences* that matter, not actual values. (If we planned on tapping the rest energies, mc^2 , of the argon atoms, then we would want to include this energy in U , and then U , H , F , and G would all be increased by an enormous amount.)

Problem 5.2. Because the reactants N₂ and H₂ are elements in their most stable states, the ΔH and ΔG values for this reaction are just the values for the “formation” of ammonia listed on page 405, times 2 because we’re forming two moles of ammonia. To check the relation $\Delta G = \Delta H - T \Delta S$, we also need to know ΔS , the entropy of two moles of ammonia minus the entropies of a mole of N₂ and three moles of H₂:

$$\Delta S = 2(192.45 \text{ J/K}) - 191.61 \text{ J/K} - 3(130.68 \text{ J/K}) = -198.75 \text{ J/K}.$$

Therefore we should have

$$\begin{aligned}\Delta G &= \Delta H - T \Delta S = 2(-46.11 \text{ kJ})(298 \text{ K}) - (-198.75 \text{ J/K}) \\ &= -92.22 \text{ kJ} + 59.23 \text{ kJ} = -32.99 \text{ kJ}.\end{aligned}$$

And indeed, the tabulated ΔG value is -16.45 kJ per mole of ammonia, or -32.90 kJ for two moles, in very good agreement.

Problem 5.3. To compute ΔH or ΔG for the reaction



from the tabulated values for formation of each compound from its elements, the trick is to imagine first decomposing the reactants into elements in their most stable states, then assembling these elements into the products. For the first step, the ΔH value (for instance) is minus the sum of all the ΔH ’s of formation, while for the second step, the ΔH value is plus the sum of the ΔH ’s of formation. Therefore, to obtain the net ΔH , we subtract the formation values for the reactants from the formation values for the products:

$$\Delta H = 2(-920.0 \text{ kJ}) + 2(-285.8 \text{ kJ}) - 0 - (-277.4 \text{ kJ}) - 4(0) - 2(-909.3 \text{ kJ}) = 315.6 \text{ kJ}.$$

Similarly,

$$\Delta G = 2(-813.0 \text{ kJ}) + 2(-237.1 \text{ kJ}) - 0 - (-217.3 \text{ kJ}) - 4(0) - 2(-744.5 \text{ kJ}) = 393.9 \text{ kJ}.$$

Problem 5.4. From the half-reactions given in the problem, we see that two electrons are pushed around the circuit for each water molecule produced. When an entire mole of water is produced, the available electrical work is $\Delta G = 237 \text{ kJ}$, so the work per electron is

$$\frac{237 \text{ kJ}}{2 \cdot 6.02 \times 10^{23}} = 1.97 \times 10^{-19} \text{ J} = 1.23 \text{ eV}.$$

The voltage of the cell is therefore 1.23 V. To operate the cell in reverse as an electrolysis cell, we must provide an amount of electrical work equal to $\Delta G = 237 \text{ kJ}$ per mole, or 1.23 eV per electron. Therefore we must provide a voltage of at least 1.23 V (more if we want the reaction to proceed at a non-instantaneous rate).

Problem 5.5. (Methane fuel cell.)

- a) Subtracting Δ_f of the reactants from Δ_f of the products, we have

$$\Delta H = 2(-285.83 \text{ kJ}) + (-393.51 \text{ kJ}) - (-74.81 \text{ kJ}) = -890.36 \text{ kJ};$$

$$\Delta G = 2(-237.13 \text{ kJ}) + (-394.36 \text{ kJ}) - (-50.72 \text{ kJ}) = -817.90 \text{ kJ}.$$

- b) Under ideal conditions, all of the decrease in G comes out as electrical work, so the electrical work output is 818 kJ.
- c) The decrease in enthalpy of 890 kJ is the sum of the electrical work output plus the heat given off. Under ideal conditions the work output is 818 kJ, so the heat is the difference, 72 kJ.
- d) For each methane molecule that reacts, eight electrons are pushed around the circuit. Therefore the voltage is

$$\text{voltage} = \frac{\text{electrical work done}}{\text{total charge}} = \frac{818 \text{ kJ}}{(8)(6.02 \times 10^{23})(1.6 \times 10^{-19} \text{ C})} = 1.06 \text{ V}.$$

Problem 5.6. (Muscle as a fuel cell.)

- a) The data as tabulated on pages 404 and 405 are (for one mole of each substance under standard conditions):

	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)
Glucose	1273	910	212
O ₂ (g)	0	0	205
CO ₂ (g)	393.5	394.4	214
H ₂ O (l)	285.8	237.1	70

To obtain ΔH or ΔG for the reaction glucose + 6O₂ → 6CO₂ + 6H₂O, we subtract Δ_f of the reactants from Δ_f of the products. Therefore, in kilojoules,

$$\Delta H = 6(-393.5) + 6(-285.8) - (1273) = -2803$$

(as computed in Problem 1.51), and

$$\Delta G = 6(-394.4) + 6(-237.1) - (910) = -2879.$$

- b) The maximum “other” work performed is just the amount by which G decreases for the system: 2879 kJ for each mole of glucose consumed.
- c) Under ideal conditions, the amount of work output, 2879 kJ, is *more* than the amount by which the system’s enthalpy decreases (2803 kJ). To make up for the net loss of enthalpy, 76 kJ of heat must flow *into* the system.
- d) The total entropy of the reactants is (in J/K)

$$212 + 6(205) = 1442,$$

while the total entropy of the products is (in J/K)

$$6 \cdot 214 + 6 \cdot 70 = 1704.$$

Therefore the system *gains* 262 J/K of entropy during this reaction. Because the entropy increases, heat can flow into the system. In the ideal case, the amount of heat entering is the maximum allowed for this entropy increase, namely $(262 \text{ J/K})(298 \text{ K}) = 78 \text{ kJ}$. (This number agrees reasonably well with the result of part (c), 76 kJ; the small difference gives some indication of the uncertainties in the data.)

- e) Under nonideal operation, new entropy would be created in the system during the reaction, allowing less heat to enter (or even requiring that heat be expelled, if the entropy created exceeds 262 J/K). Therefore less energy would leave the system as “other” work. The values of ΔH and ΔG , however, are the same whether the operation is “ideal” or not.

Problem 5.7. As computed in the previous problem, the metabolism of a mole of glucose can, in principle, release up to 2879 kJ of energy in the form of “other” work (in this case contracting the muscle). Dividing this number by Avogadro’s number should give the maximum work per glucose molecule, and dividing by 38 should give the maximum work per ATP molecule:

$$\text{maximum work per ATP} = \frac{2879 \text{ kJ}}{(6 \times 10^{23})(38)} = 1.26 \times 10^{-19} \text{ J}.$$

The actual work performed, though, is

$$\text{actual work} = (\text{force})(\text{displacement}) = (4 \times 10^{-12} \text{ N})(11 \times 10^{-9} \text{ m}) = 4.4 \times 10^{-20} \text{ J},$$

about 35% of the maximum allowed by the laws of thermodynamics. (As a fraction of ΔH , the work performed is very slightly higher, about 36%; this number is the efficiency as defined for an engine in Chapter 4.)

Problem 5.8. Under any infinitesimal change,

$$dG = d(U - TS + PV) = dU - T dS - S dT + P dV + V dP.$$

But $dU = T dS - P dV + dN$, so the $T dS$ and $P dV$ terms cancel, leaving

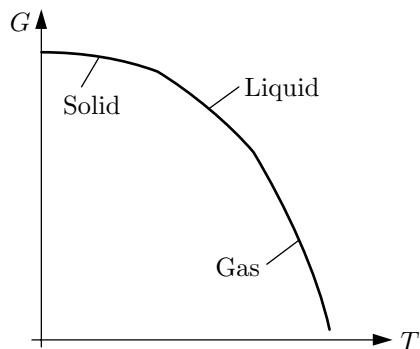
$$dG = -S dT + V dP + dN.$$

If dN and dP are zero, then $dG = -S dT$, i.e., $\left(\frac{\partial G}{\partial T}\right)_{N,P} = -S$.

If dN and dT are zero, then $dG = V dP$, i.e., $\left(\frac{\partial G}{\partial P}\right)_{N,T} = V$.

If dT and dP are zero, then $dG = dN$, i.e., $\left(\frac{\partial G}{\partial N}\right)_{T,P} = 1$.

Problem 5.9. According to equation 5.24, the slope of a graph of G vs. T at fixed P should be minus the entropy. Therefore the slope is always negative, and becomes steeper as T and S increase. When the substance undergoes a phase transformation, its entropy increases abruptly, so the slope of the graph of G should be discontinuous. The graph at right shows all these features qualitatively.



Problem 5.10. From the relation $(\partial G/\partial T)_P = -S$, we can write the change in G as $dG = -SdT$. The table on page 405 lists the entropy of a mole of water under standard conditions as 69.91 J/K, so the change in G from 25°C to 30°C is

$$dG = -(69.91 \text{ J/K})(5 \text{ K}) = -349.6 \text{ J}.$$

In other words, the Gibbs free energy is about 350 J lower at 30°C than at 25°C. If we now imagine increasing the pressure at fixed temperature, the relation $(\partial G/\partial P)_T = V$ tells us that $dG = VdP$, where V is the volume of a mole of water, $18.07 \times 10^{-6} \text{ m}^3$. Raising the pressure therefore increases G . To produce an increase of 349.6 J, we would need to increase the pressure by

$$dP = \frac{dG}{V} = \frac{349.6 \text{ J}}{18.07 \times 10^{-6} \text{ m}^3} = 1.93 \times 10^7 \text{ Pa} = 193 \text{ bars.}$$

The moral of the story is that temperature changes tend to have much larger effects on G than pressure changes, at least within the realm of conditions familiar to us in everyday life.

Problem 5.11. (Hydrogen fuel cell at 75°C.)

- a) Under an “infinitesimal” temperature change dT , the Gibbs free energy changes by $dG = -SdT$. Taking $dT = 50 \text{ K}$ and looking up the room-temperature entropies, we obtain (for a mole of each substance)

$$\text{H}_2: G = 0 \quad (131 \text{ J/K})(50 \text{ K}) = 6550 \text{ J};$$

$$\text{O}_2: G = 0 \quad (205 \text{ J/K})(50 \text{ K}) = 10250 \text{ J};$$

$$\text{H}_2\text{O}: G = 237000 \text{ J} \quad (70 \text{ J/K})(50 \text{ K}) = 240500 \text{ J}.$$

(Of course, the entropies are not constant over this temperature interval, so it would be better to first estimate the entropy of each substance in the middle of the interval, at 323 K, and use that value instead of the room-temperature value. For H_2 , the increase in entropy between 298 K and 323 K is approximately $C_P \ln(T_f/T_i) = (29 \text{ J/K}) \ln(323/298) = 2.3 \text{ J/K}$. The entropies of the O_2 and H_2O are likewise only slightly greater at 323 K.)

b) At 75°C, ΔG for the reaction is

$$G_{\text{H}_2\text{O}} - G_{\text{H}_2} - \frac{1}{2}G_{\text{O}_2} = 240500 \text{ J} + 6550 \text{ J} + 5125 \text{ J} = 229 \text{ kJ.}$$

Thus, the maximum electrical work done by the cell is only 229 kJ (per mole of hydrogen consumed), about 3.5% less than the room-temperature value of 237 kJ. Why the difference? The reacting gases have a lot of entropy, which must be gotten rid of by dumping waste heat into the environment. At the higher temperature, we need to dump *more* waste heat to get rid of this entropy, so less of the energy is left to perform electrical work.

Problem 5.12. (Maxwell relations.) Starting with the function $U(S, V)$, we assume that this function is well enough behaved that the mixed second derivatives are equal:

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right).$$

But the thermodynamic identity for U , $dU = T dS - P dV$, tells us that $(\partial U / \partial S)_V = T$ and $(\partial U / \partial V)_S = -P$. Plugging in these quantities gives us our first Maxwell relation,

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V.$$

Next, consider the enthalpy H , which due to the thermodynamic identity $dH = T dS + V dP$ is best considered a function of S and P . Equality of the mixed second derivatives tells us that

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right).$$

But by the thermodynamic identity for H , $(\partial H / \partial S)_P = T$ and $(\partial H / \partial P)_S = V$. Plugging in these quantities gives us a Maxwell relation for H ,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.$$

The Helmholtz free energy, due to its thermodynamic identity $dF = -S dT - P dV$, is most naturally considered a function of T and V . The equality of mixed second derivatives is therefore

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right).$$

But the thermodynamic identity for F tells us that $(\partial F / \partial T)_V = -S$ and $(\partial F / \partial V)_T = -P$. Plugging in these values gives a third Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Finally, consider the Gibbs free energy, $G(T, P)$. The relevant equality of mixed second derivatives is

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right).$$

The thermodynamic identity for G is $dG = S dT + V dP$, which implies $(\partial G / \partial T)_P = S$ and $(\partial G / \partial P)_T = V$. Plugging in these quantities gives us our fourth Maxwell relation,

$$\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P.$$

Problem 5.13. The thermal expansion coefficient is defined as the fractional change in volume per unit temperature change:

$$\beta = \frac{\Delta V/V}{\Delta T} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

(The assumption that P is held fixed is the natural one to make, though it was unstated in Problem 1.7.) According to the last Maxwell relation derived in the previous problem, this partial derivative is equal to $(\partial S / \partial P)_T$; therefore,

$$\beta = \frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T.$$

But the third law of thermodynamics says that as $T \rightarrow 0$, the entropy approaches zero (or perhaps some other constant), independent of pressure. Therefore, $(\partial S / \partial P)_T$ goes to zero as $T \rightarrow 0$. Since V remains nonzero, we conclude that $\beta \rightarrow 0$ as $T \rightarrow 0$.

Problem 5.14. (Difference between C_P and C_V .)

- a) Expanding dS in terms of the desired partial derivatives, we have

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV.$$

According to the result of Problem 3.33, the partial derivative in the first term is equal to C_V/T .

- b) Similarly, expanding dV in terms of the desired partial derivatives gives us

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP.$$

Plugging this expression into the result of part (a) and setting $dP = 0$ gives

$$(dS)_P = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P dT,$$

that is,

$$\left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P.$$

Multiplying through by T and using the results of Problem 3.33, we obtain

$$C_P = C_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P.$$

- c) We need a Maxwell relation that will eliminate the entropy (which is hard to measure) from the right-hand side. The relation that we need is the one that comes from the Helmholtz free energy,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Plugging this into the result of part (b) gives

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P.$$

Using the result of Problem 1.46(c), this becomes

$$C_P - C_V = T \left(\frac{\partial V}{\partial T} \right)_P^2 / \left(\frac{\partial V}{\partial P} \right)_T.$$

Now recall the definitions of the coefficient of (volume) expansion and isothermal compressibility:

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P; \quad \kappa_T \equiv \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

Plugging these relations into our expression for $C_P - C_V$ yields the final result,

$$C_P - C_V = T(\beta V)^2 / (-\kappa_T V) = +\frac{TV\beta^2}{\kappa_T}.$$

- d) For an ideal gas,

$$\beta = \frac{1}{V} \left(\frac{Nk}{P} \right) = \frac{1}{T},$$

while

$$\kappa_T = \frac{1}{V} \left(-\frac{NkT}{P^2} \right) = \frac{1}{P}.$$

Therefore the result of part (c) predicts

$$C_P - C_V = \frac{TV/T^2}{1/P} = \frac{PV}{T} = Nk,$$

in agreement with equation 1.48.

- e) Although β can be negative (as it is for water between 0°C and 4°C), it is squared in the formula. Meanwhile κ_T can never be negative, since that would imply that adding pressure to a system *increases* the volume. For the type of system we're talking about the temperature is always positive (since there is no upper limit on the energy). Therefore the formula derived in part (c) for $C_P - C_V$ is always positive (or zero, if $\beta = 0$).
- f) For one gram of water at room temperature (using the data in Problem 1.46(e)),

$$C_P - C_V = \frac{(298 \text{ K})(10^{-6} \text{ m}^3)(2.57 \times 10^{-4} \text{ K}^{-1})^2}{4.52 \times 10^{-10} \text{ Pa}^{-1}} = 0.0435 \text{ J/K},$$

which is just over 1% of the heat capacity (4.186 J/K). For one mole of mercury (using the data on page 405 for V),

$$C_P - C_V = \frac{(298 \text{ K})(14.8 \times 10^{-6} \text{ m}^3)(1.81 \times 10^{-4} \text{ K}^{-1})^2}{4.04 \times 10^{-11} \text{ Pa}^{-1}} = 3.58 \text{ J/K},$$

which is just under 13% of C_P (28.0 J/K). This percentage seems unusually large to me, but is of the same order as the percentages for lead and aluminum indicated by Figure 1.14.

- g) The volume of a solid is not strongly dependent on temperature; nor is the compressibility. Therefore, the temperature dependence of $C_P - C_V$ is approximately proportional to $T\beta^2$. As shown in Problem 5.13, $\beta(T)$ goes to zero as $T \rightarrow 0$; therefore the difference of the heat capacities should also go to zero as $T \rightarrow 0$, as verified by Figure 1.14. At high temperatures, assuming that $\beta(T)$ is relatively constant, the difference $C_P - C_V$ should be approximately linear in T . And indeed, the C_P data in Figure 1.14 seem to diverge linearly from the predicted curves for C_V .

Problem 5.15. First consider U to be a function of T and V , and expand dU in terms of partial derivatives:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

The partial derivative in the first term is C_V , so we're making progress. To deal with the second term, consider V to be a function of T and P , and expand dV similarly:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP.$$

Plugging this into the previous equation and setting $dP = 0$, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P.$$

The left-hand side is related to C_P , but not equal; rather, C_P is defined as $(\partial H/\partial T)_P$, where $H = U + PV$. In other words,

$$C_P = \left(\frac{\partial(U + PV)}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P.$$

Combining this relation with the previous equation gives

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right].$$

Now comes the trick: Rewrite P as $(\partial F/\partial V)_T$, then combine the two terms in square brackets into a single derivative of $U - F = TS$:

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T - \left(\frac{\partial F}{\partial V}\right)_T \right] = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial V}\right)_T.$$

This is identical to the result of Problem 5.14(b). From here on the derivation proceeds as in Problem 5.14(c), using a Maxwell relation to eliminate the entropy and then rewriting the partial derivatives in terms of β and κ_T .

Problem 5.16. The isothermal and adiabatic compressibilities are defined as

$$\kappa_T = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{and} \quad \kappa_S = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S.$$

So, following the technique used in Problem 5.14, consider V to be a function of P and T , and expand dV in terms of partial derivatives:

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT.$$

The first term is simply related to κ_T . To deal with the second term, consider T to be a function of P and S , and expand dT similarly:

$$dT = \left(\frac{\partial T}{\partial P} \right)_S dP + \left(\frac{\partial T}{\partial S} \right)_P dS.$$

Plugging this expression into the previous equation and setting $dS = 0$ gives

$$\left(\frac{\partial V}{\partial P} \right)_S = \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_S,$$

or, in terms of the compressibilities and $\beta = (1/V)(\partial V / \partial T)_P$,

$$V\kappa_S = V\kappa_T + V\beta \left(\frac{\partial T}{\partial P} \right)_S, \quad \text{that is,} \quad \kappa_T - \kappa_S = \beta \left(\frac{\partial T}{\partial P} \right)_S.$$

The remaining partial derivative is one that is not easy to measure. However, the Maxwell relation derived from H in Problem 5.12 says that this derivative is equal to $(\partial V / \partial S)_P$. Multiplying and dividing this derivative by dT gives

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial S} \right)_P.$$

In the last expression, the first partial derivative is just βV , while the second is T/C_P . Finally, therefore,

$$\kappa_T - \kappa_S = \frac{TV\beta^2}{C_P}. \quad (1)$$

This result shows that κ_T is always greater than (or equal to) κ_S , since any system for which these quantities are defined has positive T and C_P .

To check this result for an ideal gas, first recall from Problem 1.39 that

$$\kappa_T = \frac{1}{P} \quad \text{and} \quad \kappa_S = \frac{1}{\gamma P}.$$

Therefore the difference is

$$\kappa_T - \kappa_S = \frac{1}{P} \left(1 - \frac{1}{\gamma} \right) = \frac{1}{P} \left(1 - \frac{f}{f+2} \right) = \frac{1}{P} \left(\frac{2}{f+2} \right),$$

where f is the number of degrees of freedom per molecule. But the thermal expansion coefficient is

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{\partial}{\partial T} \left(\frac{NkT}{P} \right) = \frac{Nk}{PV} = \frac{1}{T},$$

while the constant-pressure heat capacity is

$$C_P = \frac{f}{2} Nk + Nk = \left(\frac{f+2}{2} \right) Nk,$$

from equations 1.46 and 1.48. Therefore the right-hand side of equation 1 is

$$\frac{TV\beta^2}{C_P} = \frac{TV/T^2}{Nk} \left(\frac{2}{f+2} \right) = \frac{1}{P} \left(\frac{2}{f+2} \right),$$

which is indeed equal to the left-hand side.

Problem 5.17. (Magnetic systems.)

- a) Faraday's law relates the back-emf in the coil (against which we must do work) to the time rate of change of the magnetic flux. At any moment the magnetic flux is $\Phi_B = NAB$, where A is the cross-sectional area of the coil. According to Faraday's law, therefore, the magnitude of the back-emf is

$$\text{emf} = \mathcal{E} = \frac{d\Phi_B}{dt} = NA \frac{dB}{dt},$$

and so the power that we must supply is

$$\text{power} = \mathcal{E}I = NIA \frac{dB}{dt} = \mathcal{H}LA \frac{dB}{dt} = \mathcal{H}V \frac{dB}{dt},$$

since $\mathcal{H} = NI/L$. To obtain the total energy (work) required for an infinitesimal change in the current, we integrate the power over time to obtain

$$\text{work} = \mathcal{H}V \int \frac{dB}{dt} dt = \mathcal{H}V dB.$$

- b) From the definition of \mathcal{H} , we can write

$$B = \mu_0(\mathcal{H} + M/V),$$

and hence

$$dB = \mu_0(d\mathcal{H} + dM/V).$$

The result of part (a) is therefore

$$\text{work} = V\mathcal{H} \mu_0(d\mathcal{H} + dM/V) = \mu_0 V \mathcal{H} d\mathcal{H} + \mu_0 \mathcal{H} dM.$$

In the first term we can write $\mathcal{H} d\mathcal{H} = d(\frac{1}{2}\mathcal{H}^2)$, so this term is the change in the quantity $\frac{\mu_0}{2} V \mathcal{H}^2$. If there were no specimen inside the solenoid, this term would give

the change in the vacuum field energy; *with* the specimen, \mathcal{H} is the same as without, so this term represents the work we would have to do to increase the field if there were no specimen. If we define the work done on the “system” to exclude this term but include everything else, then

$$W = \text{work done on system} = {}_0\mathcal{H} dM.$$

- c) The work done on a mechanical system is $P dV$. Apparently, the analogous term for a magnetic system is $+ {}_0\mathcal{H} dM$. The thermodynamic identity for a magnetic system should therefore be

$$dU = T dS + {}_0\mathcal{H} dM.$$

- d) The magnetic analogue of the enthalpy would be

$$H_m = U - {}_0\mathcal{H} M,$$

in analogy with the ordinary enthalpy $H = U + PV$. An infinitesimal change in H_m can then be written

$$dH_m = dU - {}_0\mathcal{H} dM - {}_0M d\mathcal{H} = T dS - {}_0M d\mathcal{H},$$

where I’ve used the thermodynamic identity for U in the last step. Interpretation? Apparently the quantity H_m is less than the “system” energy (at least for our situation), and is the more natural “energy” function to use when a process takes place at constant \mathcal{H} . To obtain the magnetic analogue of the Gibbs free energy, we can subtract TS just as for a mechanical system:

$$G_m = H_m - TS.$$

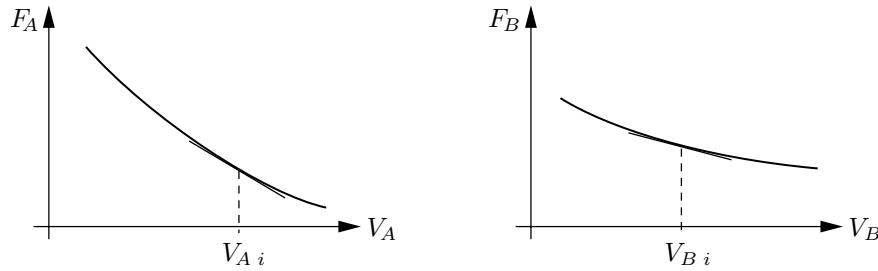
Under an infinitesimal change in conditions,

$$dG_m = dH_m - T dS - S dT = -S dT - {}_0M d\mathcal{H}.$$

Presumably, G_m is the energy that can be extracted as work when the system is held at constant T and constant \mathcal{H} (whereas the Helmholtz free energy, $F = U - TS$, would give the available work in a process at constant T and M). [The references given in the text provide further interpretations of the various energy functions for a magnetic system.]

Problem 5.18. When you drop a brick, its total energy (kinetic plus gravitational) is conserved as it falls, at least if we neglect air resistance. This downward motion is not a consequence of the decrease of free energy or of any other law of thermodynamics—think of it as merely a result of the initial condition of zero velocity and nonzero height. However, when the brick lands, its energy suddenly decreases. The thud removes macroscopic kinetic energy from the brick and converts this energy into various forms, primarily thermal energy of random molecular motions. Some of this thermal energy might initially remain in the brick, but with time it dissipates into the environment as the brick’s temperature returns to that of its surroundings. So in the end, the free energy of the brick has spontaneously decreased, just as it’s supposed to do. This decrease is entirely a result of a decrease in the brick’s energy, since the entropy of the brick ends up unchanged. And the reason why the brick’s energy decreased spontaneously is because the entropy of its *environment* increased as a result of the transfer of energy. The total entropy of the universe therefore increased.

Problem 5.19. Consider two systems *A* and *B*, held at a common, fixed temperature by interaction with a reservoir. Assume that the two systems are free to exchange volume with each other (for instance, they could be separated by a movable partition), with their total volume held fixed. The graphs of F vs. V for these two systems might look something like this:



(The slopes of the graphs are negative because adding volume to a system at fixed temperature generally increases S and thus decreases F .) Under these conditions, the analysis on page 161 tells us that the total Helmholtz free energy of the combined system tends to decrease. Notice, that, for the case shown, the slope of the F vs. V graph of system *A* is steeper (more negative) than that of system *B*. This means that volume will tend to be transferred from system *B* to system *A*, since the decrease in F for system *A* will more than outweigh the increase in F for system *B*. More generally, the steeper the slope of the graph of F vs. V , the more a system “wants” to gain volume, in order to lower its free energy. But this is just the property that we normally associate with pressure. Therefore, after checking that the units work out right (they do), we might guess that the pressure is equal to minus the slope of the graph of F vs. V . In other words, $(\partial F / \partial V)_T = -P$.

Problem 5.20. The Helmholtz free energy of the first excited level is

$$F = U - TS = (10.2 \text{ eV}) - T(k \ln 4).$$

At low temperatures this is positive, so the atom would rather be in the ground state (which has $F = 0$); at high temperatures, however, F for the excited level becomes negative, so this level becomes preferred over the ground state. The transition temperature is where $F = 0$, i.e., when $kT \ln 4 = 10.2 \text{ eV}$ or $kT = 7.36 \text{ eV}$ or

$$T = \frac{7.36 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 8.5 \times 10^4 \text{ K}.$$

This is more than ten times hotter than the surface of the sun.

Problem 5.21. Heat capacity (C) is extensive, since the heat required to raise the temperature of an object by a given amount is directly proportional to the size of the object. For $C_V = (\partial U / \partial T)_V$, we can also see this from the fact that U is extensive and T is intensive: Dividing an extensive quantity by an intensive quantity results in an extensive quantity. Specific heat capacity, $c = C/m$, is intensive, because it is the ratio of two extensive quantities. It doesn't depend on how much of the stuff you have.

Problem 5.22. In Section 3.5 I showed that the chemical potential of a monatomic ideal gas is

$$= kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] = kT \ln \left[\frac{kT}{P} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right].$$

In the last expression I've substituted $V/N = kT/P$, since equation 5.40 is written in terms of pressure rather than volume. To bring in the reference pressure P° , multiply and divide by it inside the logarithm:

$$= kT \ln \left[\frac{P^\circ}{P} \frac{kT}{P^\circ} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] = kT \ln \left[\frac{kT}{P^\circ} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + kT \ln(P/P^\circ).$$

This expression is now in the form of equation 5.40, with the first term equal to $\phi^\circ(T)$, a function of temperature but not pressure. (The reference pressure, P° , is just a constant, conventionally taken to be 1 bar.)

Problem 5.23. (Grand free energy.)

- a) Using the product rule for derivatives, an infinitesimal change in Φ can be written

$$d\Phi = dU - T dS - S dT - dN - N d .$$

Plugging in the ordinary thermodynamic identity for dU and canceling terms, this becomes

$$d\Phi = -S dT - P dV - N d .$$

Thus the natural variables for the function Φ are temperature, volume, and chemical potential. Holding any two of these fixed yields a partial-derivative formula:

$$\left(\frac{\partial \Phi}{\partial T} \right)_V = -S; \quad \left(\frac{\partial \Phi}{\partial V} \right)_T = -P; \quad \left(\frac{\partial \Phi}{\partial \mu} \right)_{T,V} = -N.$$

- b) As in the text (page 161), consider an infinitesimal change in the total entropy of the system plus its environment (the “reservoir”):

$$dS_{\text{total}} = dS + dS_R.$$

Applying the thermodynamic identity to dS_R and assuming that V is fixed, we can substitute

$$dS_R = \frac{1}{T} dU_R - \frac{1}{T} dN_R = -\frac{1}{T} dU + \frac{1}{T} dN,$$

where I've used the fact that the changes in the system's U and N are minus the changes for the reservoir. Therefore,

$$dS_{\text{total}} = dS - \frac{1}{T} dU + \frac{1}{T} dN = -\frac{1}{T} (dU - T dS - dN) = \frac{1}{T} d\Phi,$$

provided that T and μ are constant. Spontaneous changes are those for which dS_{total} is positive, or equivalently, for which $d\Phi$ is negative.

- c) To prove that $\Phi = PV$, you could make an argument analogous to that used to prove $G = N$ on page 164. Given that result, however, we can simply write

$$\Phi = U - TS \quad N = U - TS + PV - PV \quad N = G - PV \quad N = PV.$$

- d) For the unoccupied state, $U = S = N = 0$ so $\Phi = 0$. For the occupied state, S is still zero but $N = 1$ so

$$\Phi_{\text{occupied}} = U_0 = U_0 + kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right],$$

where $U_0 = 13.6$ eV and I've used equation 3.63 for the chemical potential. For electrons at $T = 5800$ K, the complicated factor inside the logarithm is

$$\begin{aligned} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} &= \left(\frac{(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(9.11 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(5800 \text{ K})} \right)^{3/2} \\ &= 9.4 \times 10^{-28} \text{ m}^3. \end{aligned}$$

The volume per electron, V/N , is much larger than this: $0.5 \times 10^{-19} \text{ m}^3$; so the argument of the logarithm is 5.3×10^7 and the logarithm itself is 17.8. Therefore the grand free energy is

$$\Phi_{\text{occupied}} = 13.6 \text{ eV} + (17.8)(8.62 \times 10^{-5} \text{ eV/K})(5800 \text{ K}) = 4.7 \text{ eV}.$$

Because this is less than Φ for the unoccupied state, the occupied state must be more stable. To get a rough estimate of the temperature at which the two states would be equally stable, we can neglect the gradual T -dependence of the logarithm to obtain the simple equation

$$U_0 = (17.8)kT \quad \text{or} \quad T = \frac{U_0}{(17.8)k} = \frac{13.6 \text{ eV}}{(17.8)(8.62 \times 10^{-5} \text{ eV/K})} = 8800 \text{ K}.$$

This is not that much hotter than the sun and is cooler than the surfaces of many stars. (To check the approximation, note that this is a 50% increase over the sun's temperature, so the logarithm should increase by $\ln[(1.5)^{3/2}] = 0.6$, fairly insignificant compared to 17.8.)

Problem 5.24. We're free to choose an arbitrary reference point for measuring G values, so for convenience let's take $G = 0$ for graphite at 1 bar. Then for diamond, $G = 2.9 \text{ kJ}$ at 1 bar. The equations of the lines drawn in Figure 5.15 are

$$G_g = V_g P \quad \text{and} \quad G_d = V_d P + (2.9 \text{ kJ}),$$

where the subscripts are g for graphite and d for diamond, and technically, P is measured relative to 1 bar, though we'll soon see that the difference between 0 bar and 1 bar is negligible. To find the intersection of the lines, set these expressions equal and solve for P :

$$V_g P = V_d P + (2.9 \text{ kJ}) \quad \Rightarrow \quad P = \frac{(2.9 \text{ kJ})}{V_d - V_g} = \frac{2900 \text{ J}}{1.89 \times 10^{-6} \text{ m}^3} = 1.53 \times 10^9 \text{ Pa}.$$

So the intersection is at 1.53 GPa, which is 15.3 kbar.

Problem 5.25.

$$1 \frac{\text{kJ}}{\text{kbar}} = \left(1 \frac{\text{J}}{\text{bar}}\right) \left(\frac{1 \text{ bar}}{10^5 \text{ N/m}^2}\right) = 10^{-5} \frac{\text{N m}}{\text{N/m}^2} = 10^{-5} \text{ m}^3 = 10 \text{ cm}^3.$$

The volumes in the table on pages 404–405 are given in cm^3 , so to convert them to kJ/kbar , just divide by 10.

Problem 5.26. While it is true that a given quantity of graphite always has more entropy than the same quantity of diamond (at the same temperature and pressure), diamond can still be more stable than graphite under high pressure because it is the *total* entropy of the system plus the environment that tends to increase. When graphite converts to diamond under high pressure, it takes up less space so there is more space for whatever material surrounds it. With more space available to the environment, the entropy of the environment increases. This effect is more pronounced at high pressure, since pressure is proportional to $(\partial S/\partial V)_U$. However, to be precise about this effect, we are better off working with G instead of S , since we want to know what happens at fixed T , not fixed U .

Problem 5.27. (Diamonds and graphite, taking compressibility into account.)

- a) The compressibility of graphite means that at high pressures its volume will be smaller, closer to that of diamond. This effect will decrease the tendency of graphite to convert to diamond at high pressure. It will reduce the slope of the G vs. P graph for graphite, moving the intersection in Figure 5.15 to the right, to higher pressure.
- b) The definition of the isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T,$$

so at constant temperature, $\partial V/\partial P = -\kappa_T V$. Since we don't know how κ_T varies with pressure, we'll just have to hope that it's fairly constant. Alternatively, and for ease of calculation, we can assume that the product $\kappa_T V$ is constant. Then we can express the volume as

$$V(P) = V(0) + \frac{\partial V}{\partial P} P = V(0) - \kappa_T VP,$$

where $V(0)$ is the volume at zero pressure, or, to a good approximation, the volume at 1 bar. Integrating this expression with respect to P then gives the Gibbs free energy,

$$G(P) = G(0) + V(0)P - \frac{1}{2}\kappa_T VP^2.$$

As in Problem 5.24, let's take $G(0) = 0$ for graphite. Then for diamond, $G(0) = 2900 \text{ J}$, but κ_T is negligible. To find the pressure at which the two phases are equally stable, set the G values of graphite and diamond equal to each other:

$$V_g P - \frac{1}{2}\kappa_T V_g P^2 = (2.9 \text{ kJ}) + V_d P.$$

We could solve this equation using the quadratic formula, but that's a bit cumbersome. Instead, recall from Problem 5.24 that without the quadratic term, the solution would be $P = 15.3$ kbar. Plugging in this value of P , we can estimate the size of the quadratic term as

$$\frac{1}{2}\kappa_T V_g P^2 \approx \frac{1}{2}(3 \times 10^{-3} \text{ kbar}^{-1})(0.531 \text{ kJ/kbar})(15.3 \text{ kbar})^2 = 0.186 \text{ kJ.}$$

(I've expressed V_g in kJ/kbar, as discussed in Problem 5.25.) With this estimate of the correction term due to compression, we have for the transition pressure

$$P = \frac{1}{V_g - V_d}(2.9 \text{ kJ} + 0.186 \text{ kJ}) = \frac{3.086 \text{ kJ}}{.189 \text{ kJ/kbar}} = 16.3 \text{ kbar,}$$

only about 7% higher than what we got neglecting compression. The small effect of the correction, moreover, justifies the various approximations made in this solution.

Problem 5.28. (Calcite and aragonite.)

- a) The table on page 404 gives the molar Gibbs free energies of formation of both calcite and aragonite, with the value for calcite being lower by 1.0 kJ. This means that the Gibbs free energy of a mole of calcite is less than that of a mole of aragonite by this amount, under standard conditions. Calcite is therefore the more stable phase, at room temperature and atmospheric pressure.
- b) In analogy with the diamond-graphite system, we can imagine plotting G vs. P (at fixed T) for both calcite and aragonite. The slopes of the two graphs are $V_c = 3.693 \text{ kJ/kbar}$ and $V_a = 3.415 \text{ kJ/kbar}$, according to the data in the table and the conversion factor derived in Problem 5.25. Since the volume of aragonite is less, it should become stable at high pressure, that is, the two lines should intersect at some $P > 0$. For convenience, I'll set $G_c = 0$ at $P = 0$; then $G_a = 1.0 \text{ kJ}$ at $P = 0$. The equations of the two lines are then

$$G_c = V_c P \quad \text{and} \quad G_a = V_a P + (1.0 \text{ kJ}).$$

Equating these two expressions and solving for P gives the transition pressure,

$$P = \frac{1.0 \text{ kJ}}{V_c - V_a} = \frac{1.0 \text{ kJ}}{0.278 \text{ kJ/kbar}} = 3.6 \text{ kbar.}$$

Problem 5.29. (The aluminosilicate system.)

- a) The $\Delta_f G$ values on page 404 indicate that at room temperature and atmospheric pressure, kyanite has the lowest Gibbs free energy of the three phases. Furthermore, it also has the lowest molar volume of the three; this means that increasing the pressure causes its G value to increase more slowly than those of the other two phases. Since it starts out lowest and increases slowest, it will never intersect the G values of the other phases (in contrast to the graphite-diamond case illustrated in Figure 5.15).

- b) For either phase, $(\partial G / \partial T)_P = S$. Integrating this relation from T_1 to T_2 gives

$$G(T_2) - G(T_1) = \int_{T_1}^{T_2} S(T) dT.$$

If we write this equation separately for two different phases and then subtract one equation from the other, the G 's become ΔG 's and the S becomes ΔS , so we obtain the desired result,

$$\Delta G(T_2) = \Delta G(T_1) + \int_{T_1}^{T_2} \Delta S(T) dT.$$

- c) Taking ΔS to be independent of T , we can pull it outside the integral to obtain

$$\Delta G(T_2) = \Delta G(T_1) + (T_2 - T_1) \Delta S.$$

If we take T_2 to be the temperature at which the phase transition occurs (the two phases are in equilibrium), then $\Delta G(T_2) = 0$. Solving for T_2 then gives simply

$$T_2 = T_1 + \frac{\Delta G(T_1)}{\Delta S}.$$

Our thermodynamic data is at 298 K, so we'll use this value for T_1 . For the kyanite-andalusite transition, $\Delta G(T_1) = 1.22$ kJ (for one mole of material), while $\Delta S = 9.41$ J/K. Therefore, the temperature at which andalusite becomes more stable than kyanite should be approximately

$$T_2 = 298 \text{ K} + \frac{1.22 \text{ kJ}}{9.41 \text{ J/K}} = 428 \text{ K}.$$

Similarly, for the kyanite-sillimanite transition,

$$T_2 = 298 \text{ K} + \frac{2.89 \text{ kJ}}{12.30 \text{ J/K}} = 533 \text{ K}.$$

And for the andalusite-sillimanite transition,

$$T_2 = 298 \text{ K} + \frac{1.67 \text{ kJ}}{2.89 \text{ J/K}} = 876 \text{ K}.$$

So at atmospheric pressure, kyanite should be stable up to (approximately) 428 K, andalusite should be stable from 428 K up to 876 K, and sillimanite should be stable above 876 K.

- d) The change in entropy as the temperature is increased is given by equation 3.50,

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_P}{T} dT.$$

If we write this equation for two different phases and then subtract, we obtain

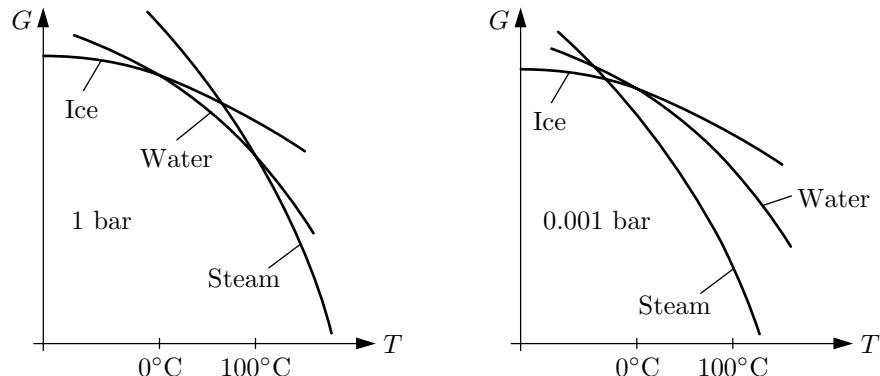
$$\Delta S(T_2) = \Delta S(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_P}{T} dT.$$

Suppose, for the sake of a rough estimate, that ΔC_P is independent of temperature. Then

$$\Delta S(T_2) = \Delta S(T_1) + \Delta C_P \ln(T_2/T_1).$$

For kyanite \rightarrow andalusite, $\Delta C_P = 1.01 \text{ J/K}$ (at room temperature). Taking $T_1 = 298 \text{ K}$ and $T_2 = 428 \text{ K}$, I find that the final term in this equation is 0.37 J/K , compared to $\Delta S(T_1) = 9.41 \text{ J/K}$. So over this range, ΔS is reasonably independent of temperature. However, for andalusite \rightarrow sillimanite, $\Delta C_P = 1.80 \text{ J/K}$ and we should take $T_2 = 876 \text{ K}$; with these numbers I get a correction term of 1.94 J/K , compared to $\Delta S(T_1) = 2.89 \text{ J/K}$. With ΔS varying by nearly 70% over the temperature range of interest, I conclude that the calculated temperature of the transition could be off by as much as 100–200 K. To make a significantly improved calculation, however, we would really need heat capacity data over the whole temperature range.

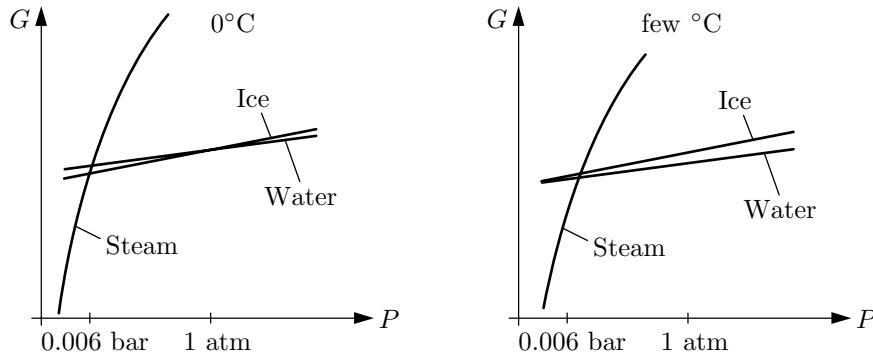
Problem 5.30. The slope of a graph of G vs. T is $-S$, so the slope of each graph should be negative, and become more negative with increasing temperature. Furthermore, at any given temperature, the stable phase should have the lowest value of G . For H_2O at atmospheric pressure, the stable phase is ice below 0°C , water between 0°C and 100°C , and steam above 100°C . The plot at left below shows these features qualitatively.



As the pressure is reduced, the relation $(\partial G/\partial P)_T = V$ tells us that the Gibbs free energy of each phase will decrease. However, that of the gas phase will decrease the fastest by far, since its volume is so much greater. At pressures below the triple point (0.006 bar), there is no temperature at which liquid water is stable. So at 0.001 bar, the graphs of G vs. T would look something like the plot above right.

Problem 5.31. The slope of a graph of G vs. P is V , so the slope of each graph should be positive, with the ice graph slightly steeper than the water graph and the steam graph much steeper than either. The steam graph, furthermore, should have a significant downward curvature due to its compressibility. At any given temperature, the curve for the stable phase should be the lowest of the three. At 0°C , the stable phase is steam up to 0.006 bar,

ice from there up to 1 bar, and water above 1 bar. The graph at left below shows these features qualitatively.



As the temperature is raised, the relation $(\partial G / \partial T) = -S$ tells us that the Gibbs free energy of each phase will decrease. That of the gas phase will decrease the most, since it has the most entropy, while that of the solid will decrease the least. Above 0.01°C , the intersection of the solid and liquid G curves moves to the left of the gas curve, indicating that the solid is no longer stable at any temperature. At a few degrees Celsius, the graphs would look something like the plot above right.

Problem 5.32. (The water-ice phase boundary.)

- As ice melts into water the change in entropy (or the latent heat) is positive, while the change in volume is negative (since ice is less dense), so the slope of the phase boundary, $\Delta S / \Delta V$, must be negative. In more fundamental terms, converting ice to water lets the entropy of the environment increase (by making more volume available), and this effect is more important at high pressure since $P = T(\partial S / \partial V)$. So high pressures tend to push the equilibrium in the direction of the phase that takes up less volume.
- Instead of considering a mole of ice/water, let's just consider one gram. Then the latent heat is 333 J, the volume of the ice is $(917,000)^{-1} \text{ m}^3 = 1.091 \times 10^{-6} \text{ m}^3$, and the volume of the water is $1.000 \times 10^{-6} \text{ m}^3$. Therefore the slope of the phase boundary is

$$\frac{dP}{dT} = \frac{L}{T \Delta V} = \frac{333 \text{ J}}{(273 \text{ K})(.091 \times 10^{-6} \text{ m}^3)} = 1.35 \times 10^7 \text{ Pa/K} = 135 \text{ bar/K.}$$

So if the temperature decreases by one degree (from 0 to 1°C), the pressure must increase by 135 bars to remain on the phase boundary. In other words, ice will melt at 1°C if the pressure is above 135 bars (or 133 atmospheres).

- Treating the glacier ice as a fluid, the increase in pressure at depth z is simply $\rho g z$, where ρ is the density. (To derive this formula, consider a column of ice extending down to depth z . The weight of the column per unit area is $\rho g z$, and this must be balanced by the pressure from below.) In our case, to reach a pressure of 135 bars,

$$z = \frac{P}{\rho g} = \frac{135 \times 10^5 \text{ N/m}^2}{(917 \text{ kg/m}^3)(9.8 \text{ N/kg})} = 1500 \text{ m.}$$

That's pretty deep, just to lower the melting temperature by one degree. Apparently the flow of glaciers is not caused primarily by lowering of the melting point under pressure.

- d) The blade of an ice skate measures a few millimeters across by perhaps 25 cm long, so the total area is perhaps 10 cm^2 . Even if you're leaning on the "corner" of the blade, the total area in contact with the ice is probably more than $1 \text{ cm}^2 = 10^{-4} \text{ m}^2$. If your mass is 50 kg, then your weight is about 500 N so the pressure on the blade is roughly $(500 \text{ N})/(10^{-4} \text{ m}^2) = 5 \times 10^6 \text{ Pa} = 50 \text{ bars}$. Under this pressure the melting temperature drops by only $50/135 \approx .4^\circ\text{C}$. This mechanism of friction reduction would work *only* if the ice temperature is already within less than half a degree of melting, and even then, only when you're minimizing the area of the blade in contact with the ice. In practice, the ability to glide doesn't depend so critically on the ice temperature or on how the blade touches the ice, so I don't think this mechanism can be very important.

Problem 5.33. The flaw in the inventor's reasoning is that the weight that can be lifted by the water as it freezes into ice is limited, because too much weight would apply enough pressure to lower the freezing point of the water below 1°C , and then the water wouldn't freeze at all. Let the water in the cylinder have height h_w and cross-sectional area A . When it freezes into ice, its height increases to h_i . If the mass it lifts is m , then the work performed upon freezing is $mg(h_i - h_w)$. If L is the heat needed to remelt the ice, then the efficiency of the engine is

$$\epsilon = \frac{W}{Q_h} = \frac{mg(h_i - h_w)}{L}.$$

If the pressure on the system with the weight absent is atmospheric pressure, then there's really no need for the high-temperature reservoir to be hotter than $T_h = 0^\circ\text{C}$; higher T_h would just lead to wasted heat as the system is cooled back to 0°C . If T_c is the temperature of the cold reservoir, then according to the Clausius-Clapeyron relation, the maximum pressure we can add to the system without shifting the freezing point below T_c is

$$dP = \frac{L}{T_h(V_i - V_w)}(T_h - T_c),$$

where $V_i = h_i A$ and $V_w = h_w A$ are the volumes of the two phases, and I've used T_h in the denominator because L refers to the heat input from the hot reservoir. Setting this quantity equal to the pressure exerted by the lifted mass gives

$$\frac{mg}{A} = \frac{L(T_h - T_c)}{T_h A(h_i - h_w)}, \quad \text{or} \quad \frac{mg(h_i - h_w)}{L} = \frac{T_h - T_c}{T_h}.$$

In other words, the maximum efficiency of the engine is $1 - (T_c/T_h)$.

Problem 5.34. (Liquid-solid phase boundary of ${}^3\text{He}$.)

- a) The denser phase is always the one that is stable at higher pressure, according to $(\partial G/\partial P)_T = V$: Smaller volume implies a shallower slope to the G vs. P curve and hence a lower value of G than the other phase at sufficiently high pressures. In our case,

the solid phase is stable at higher pressures, so it must be more dense. Meanwhile, the negative slope of the phase boundary, together with the Clausius-Clapeyron relation $dP/dT = \Delta S/\Delta V$, tells us that ΔS and ΔV have opposite signs: Whichever phase has the smaller volume has the larger entropy. So near the phase boundary below 0.3 K, the solid phase of ${}^3\text{He}$ must actually have more entropy than the liquid. The reason for this strange behavior is explained in Problem 7.26.

- b) The third law of thermodynamics says that the entropy of either phase must go to zero as $T \rightarrow 0$. Therefore the difference in entropy between the two phases goes to zero, and therefore, by the Clausius-Clapeyron relation, the slope of the phase boundary must go to zero.
- c) If you compress liquid ${}^3\text{He}$ adiabatically (and quasistatically), its entropy should remain unchanged. Mere conversion to a solid at $T = 0.1$ K, however, would increase the entropy, as explained in part (a). The only way for the entropy to remain constant is therefore for the temperature to drop, which it does. This method of cooling ${}^3\text{He}$ was first suggested by I. Y. Pomeranchuk in 1950, and has been used with great success as a method of reaching temperatures as low as 1 mK.

Problem 5.35. (Vapor pressure equation.) Neglecting the volume of the condensed phase and using the ideal gas law for the volume of the gas, the difference in volume between the two phases is approximately

$$\Delta V \approx V_g \approx \frac{RT}{P},$$

assuming one mole. Therefore the Clausius-Clapeyron equation becomes

$$\frac{dP}{dT} = \frac{LP}{RT^2}, \quad \text{or} \quad \frac{dP}{P} = \frac{L}{R} \frac{dT}{T^2}.$$

Integrating both sides then gives

$$\ln P = \frac{L}{RT} + (\text{const}), \quad \text{or} \quad P = (\text{const})e^{L/RT}.$$

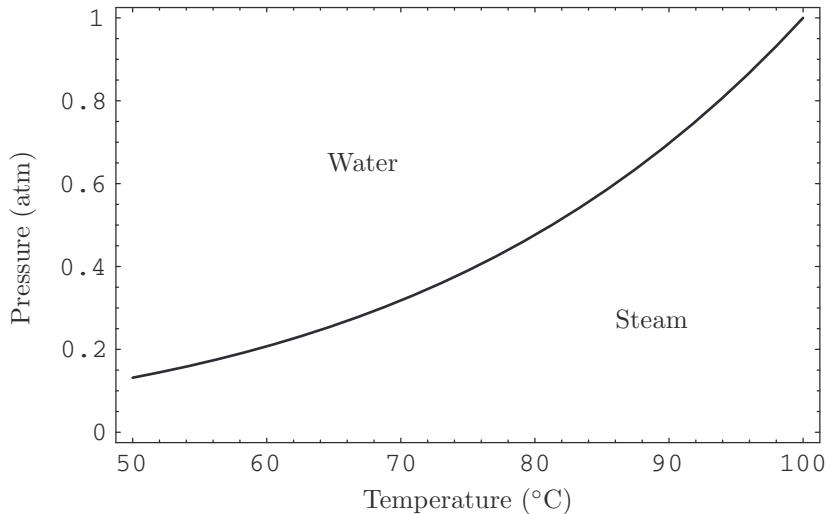
Problem 5.36. (Effect of altitude on boiling water.)

- a) I'll use the data given at 100°C, or 373 K. Then the vapor pressure is just 1.013 bar, or 1 atm. Plugging in $L = 4.066 \times 10^4$ J/mol and $R = 8.315$ J/mol-K, I find $L/R = 4890$ K, so I can solve for the constant (which I'll call P_0) in the vapor pressure equation:

$$1 \text{ atm} = P_0 e^{-4890/373} \quad \rightarrow \quad P_0 = 4.91 \times 10^5 \text{ atm.}$$

(There's not much point in trying to interpret this constant physically. According to the equation, it's the pressure at which the boiling temperature would go to infinity. But the critical point is reached long before, and the value of L changes significantly)

even before that.) Here's a plot of part of the phase boundary:



At $T = 50^\circ\text{C}$ the predicted pressure is .132 atm, about 7% higher than the actual value.

- b) To find the boiling temperature at a given pressure one can either read the value off the graph or solve the vapor pressure equation for T :

$$T = \frac{L}{R \ln(P_0/P)} = \frac{4890 \text{ K}}{\ln(491,000 \text{ atm}/P)}.$$

For the elevations of Problem 1.13, I find:

Ogden (4700 ft)	.84 atm	95°C
Leadville (10,500 ft)	.69 atm	90°C
Mt. Whitney (14,500 ft)	.59 atm	86°C
Mt. Everest (29,000 ft)	.35 atm	73°C

If you're camping in the mountains at 10,000 ft above sea level, the boiling point is about 90°C. At this temperature, noodles cook much slower than at 100°C. (I've heard a rough rule of thumb that cooking time doubles for every drop of 5°C in the boiling temperature. If this is correct, then noodles that are supposed to cook in 5 minutes will actually take 10 minutes in Ogden, 20 minutes in Leadville, and nearly 40 minutes on the summit of Mt. Whitney. I suspect that the actual cooking times don't increase quite this dramatically.)

- c) From the values computed above, you can see that the boiling temperature decreases by roughly 1°C for every 1000 ft of elevation gain. Alternatively, recall the general result of Problem 1.16:

$$P(z) = (1 \text{ atm})e^{-mgz/kT} = (1 \text{ atm})e^{-z/28,000 \text{ ft}}.$$

Plugging this into the vapor pressure equation yields the boiling temperature as a function of z :

$$T_b = \frac{L/R}{\ln(P_0/P)} = \frac{L/R}{\ln\left(\frac{P_0}{1 \text{ atm}}\right) + \frac{z}{28,000 \text{ ft}}}.$$

The logarithm in the denominator now evaluates to 13.1; dividing through by this constant and plugging in the value of L/R computed previously yields

$$T_b = \frac{373 \text{ K}}{1 + \frac{z}{367,000 \text{ ft}}}.$$

For any reasonable value of z we can expand this using the binomial theorem to obtain

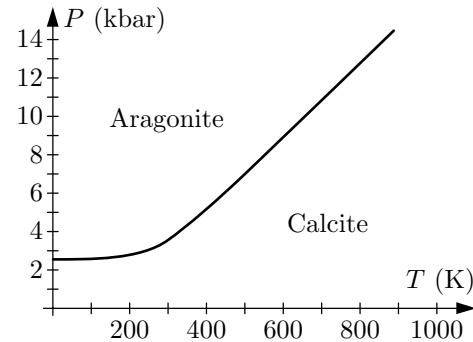
$$T_b \approx (373 \text{ K}) \left(1 - \frac{z}{367,000 \text{ ft}} \right) = 373 \text{ K} - (.00102 \text{ K/ft})z.$$

Thus the boiling temperature drops by about 1.02 degrees Celsius per thousand feet of elevation gain, or about 3.35 degrees Celsius per kilometer (assuming as in Problem 1.16 that the atmospheric temperature is constant).

Problem 5.37. Neglecting any variation in ΔS and ΔV with temperature and pressure, the slope of the calcite-aragonite phase boundary should be

$$\frac{dP}{dT} = \frac{S_c - S_a}{V_c - V_a} = \frac{92.9 \text{ J/K}}{36.93 \text{ cm}^3} - \frac{88.7 \text{ J/K}}{34.15 \text{ cm}^3} = \frac{4.2 \text{ J/K}}{2.78 \times 10^{-6} \text{ m}^3} = 1.52 \times 10^6 \frac{\text{Pa}}{\text{K}} = 15.2 \frac{\text{bar}}{\text{K}}.$$

So the transition pressure should increase by about 1.5 kbar when the temperature increases by 100 K. However, the slope must go to zero at $T = 0$, since the third law of thermodynamics requires $S_c = S_a = 0$ at $T = 0$. At room temperature we know from Problem 5.28 that the transition pressure is roughly 3.6 kbar. Above room temperature the slope may also vary, but I won't try to guess how much. The phase diagram should look something like the figure at right, with reasonably large uncertainties.



Problem 5.38. Using the entropies calculated in Problems 3.30 and 3.31, we have

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{12.33 \text{ J/K}}{(5.30 - 3.42) \times 10^{-6} \text{ m}^3} - \frac{7.59 \text{ J/K}}{3.42 \times 10^{-6} \text{ m}^3} = 2.52 \times 10^6 \frac{\text{Pa}}{\text{K}} = 25.2 \frac{\text{bar}}{\text{K}}$$

at $T = 500$ K. For comparison, I estimate the slope of the phase boundary in Figure 5.17 to be between 26 and 27 bar/K at temperatures of about 500 K and higher. We should expect the slope to be fairly constant at sufficiently high temperatures because the molar heat capacities should both plateau at the value $3R$ (neglecting the difference between C_P and C_V), and when the heat capacities are equal, there can be no further changes in the difference in entropies. For diamond, however, this plateau is not reached until around 700 K, so I'm a bit surprised that the slope of the phase boundary in Figure 5.17 is so constant between 500 K and 700 K. As $T \rightarrow 0$, on the other hand, the entropies of both phases must go to zero, so ΔS goes to zero, so the phase boundary becomes horizontal.

Problem 5.39. As in Problem 5.29, I'll assume that the differences in entropies between the various phases are independent of temperature, even though the individual entropies increase significantly with temperature. Then we can just use the room temperature data on page 404. Also recall from Problem 5.25 that a volume in cm^3 can be converted to J/bar by dividing by 10. For the kyanite-andalusite boundary the slope should therefore be

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{93.22 \text{ J/K}}{5.153 \text{ J/bar}} - \frac{83.81 \text{ J/K}}{4.409 \text{ J/bar}} = 12.65 \text{ bar/K.}$$

Similarly, for the kyanite-sillimanite boundary,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{96.11 \text{ J/K}}{4.990 \text{ J/bar}} - \frac{83.81 \text{ J/K}}{4.409 \text{ J/bar}} = 21.17 \text{ bar/K.}$$

And for the andalusite-sillimanite boundary,

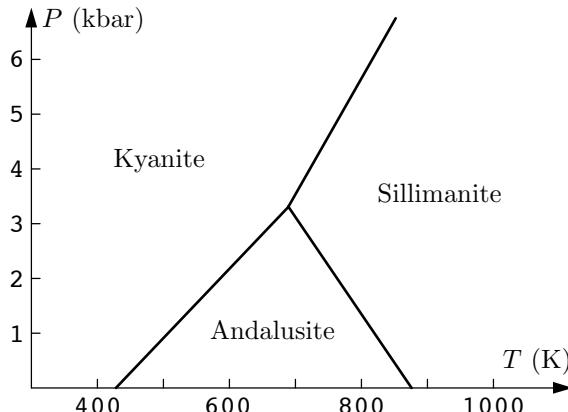
$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{96.11 \text{ J/K}}{4.990 \text{ J/bar}} - \frac{93.22 \text{ J/K}}{5.153 \text{ J/bar}} = 17.73 \text{ bar/K.}$$

Meanwhile, from Problem 5.29, we know that the phase boundary lines intersect the temperature axis at 428 K, 533 K, and 876 K, respectively. From this information you can easily sketch the phase diagram. I plotted it with *Mathematica*, using the instruction

```
Plot[{.01265*(t-428), .02117*(t-533), -.01773*(t-876)},
{t,300,1100}, PlotRange->{{300,1100},{0,6.75}}]
```

This instruction produced the plot at right, in which I've erased the unphysical portions of the phase boundaries. Notice that the three lines intersect at a common point (a good check), at 690 K and 3.3 kbar. You can also locate the triple point algebraically, by solving for the intersection of any two of the lines; for instance, set

$$.01265(T - 428) = .02117(T - 533)$$



and solve for T . As in Problem 5.29, the uncertainties in the diagram are significant. Experimental measurements of the aluminosilicate phase boundaries generally place the triple point at somewhat higher temperature and pressure. For instance, M. J. Holdaway, in *American Journal of Science* **271**, 97–131 (1971), places the triple point at 774 ± 20 K and 3.76 ± 0.30 kbar.

Problem 5.40. For the reaction albite \rightarrow jadeite + quartz, the standard ΔG value, at room temperature and atmospheric pressure, is

$$\Delta G = 2852.1 \text{ kJ} - 856.6 \text{ kJ} + 3711.5 \text{ kJ} = 2.8 \text{ kJ},$$

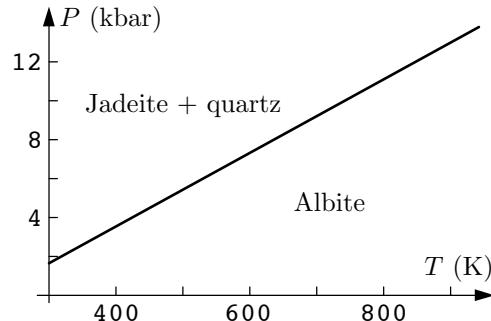
according to the data on page 405. Because this number is positive, albite is more stable than jadeite + quartz under these conditions. However, the jadeite-quartz combination takes up considerably less volume than albite, so it should become stable at high pressure. Solving for the transition pressure as in Problems 5.24 and 5.28, we obtain

$$P = \frac{2.8 \text{ kJ}}{\Delta V} = \frac{2.8 \text{ kJ}}{\frac{10.007 \text{ kJ/kbar}}{6.040 \text{ kJ/kbar}} - \frac{2.269 \text{ kJ/kbar}}{}} = 1.65 \text{ kbar.}$$

The slope of the phase boundary, meanwhile, is given by the Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{207.4 \text{ J/K}}{1.70 \text{ J/bar}} - \frac{133.5 \text{ J/K}}{} - \frac{41.8 \text{ J/K}}{} = 18.9 \text{ bar/K.}$$

The diagram at right shows the regions of stability of the two phases, assuming that ΔS and ΔV are independent of temperature and pressure, hence that the phase boundary is a straight line. As $T \rightarrow 0$, however, the slope of the phase boundary would have to be horizontal, as in Figure 5.17, according to the third law of thermodynamics.



Problem 5.41. (Effect of total pressure on vapor pressure.)

- a) We want to consider the change in the chemical potentials of the two phases under an infinitesimal change in total pressure. For the gas, according to equation 5.40,

$$g_g = \text{constant} + kT \ln P_v,$$

where P_v is the partial pressure of the gas, assumed to be equal to the vapor pressure. Differentiating with respect to the total pressure P , we obtain

$$\frac{d g_g}{dP} = \frac{kT}{P_v} \frac{dP_v}{dP}.$$

(I'll write the derivatives as total derivatives, even though they're really partial derivatives, with temperature understood to be held fixed.) Meanwhile, for the liquid, $\mu_l = G/N$ (since it remains pure), so

$$\frac{d \mu_l}{dP} = \frac{1}{N_l} \frac{dG}{dP} = \frac{V_l}{N_l}.$$

For the two phases to remain in equilibrium as we change the total pressure, the changes in their chemical potentials must be equal, so

$$\frac{kT}{P_v} \frac{dP_v}{dP} = \frac{V_l}{N_l} \quad \text{or} \quad \frac{dP_v}{dP} = \frac{V_l}{N_l kT} P_v.$$

This is the desired differential equation for the function $P_v(P)$.

- b) The solution to this equation is a simple exponential function,

$$P_v(P) = (\text{constant}) e^{PV/NkT},$$

where I've dropped the l subscripts on the V and N in the exponent. Plugging in $P = P_v$ (for the initial situation with no inert gas), this equation becomes

$$P_v(P_v) = (\text{constant}) e^{P_v V/NkT}.$$

Dividing the previous equation by this one cancels out the constant, leaving us with

$$\frac{P_v(P)}{P_v(P_v)} = e^{(P - P_v)V/NkT},$$

where again the quantity V/N in the exponent is for the liquid.

- c) For water at 25°C, the vapor pressure is only 0.03 bar, so the P_v in the exponent is negligible compared to $P = 1$ bar. It's simplest to take N to be one mole, so $Nk = R$ and $V = 18 \text{ cm}^3$; the exponential factor is thus

$$\exp\left(\frac{(10^5 \text{ N/m}^2)(18 \times 10^{-6} \text{ m}^3)}{(8.31 \text{ J/K})(298 \text{ K})}\right) = \exp(0.00073) = 1.00073,$$

implying that the vapor pressure is greater by 0.07% than its value in the absence of the air. More generally, the quantity PV/NkT , where V/N refers to the *liquid*, will always be much less than 1 as long as the molar volume of the liquid is much less than that of the gas (for which $PV/NkT \approx 1$). Only near the critical point (which is at fairly high pressures for most fluids) would this ratio be comparable to 1.

Problem 5.42. (Relative humidity and dew point.)

- a) The result of Problem 5.35 for the shape of the vapor pressure curve was

$$P = P_0 e^{-L/RT}.$$

Using the data for $T = 25^\circ\text{C}$ from Figure 5.11, we have

$$\frac{L}{R} = \frac{43,990 \text{ J/mol}}{8.315 \text{ J/mol K}} = 5290 \text{ K};$$

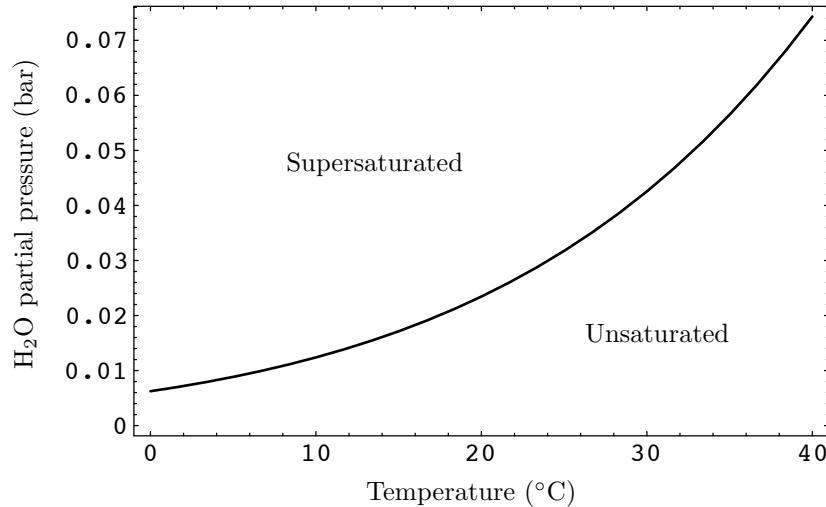
solving for the constant P_0 therefore gives

$$P_0 = (0.0317 \text{ bar}) \exp\left(5290 \text{ K}/298 \text{ K}\right) = 1.626 \times 10^6 \text{ bar}.$$

I then plotted the vapor pressure curve using the *Mathematica* instruction

```
Plot[1626000*Exp[-5290/(t+273)], {t, 0, 40}, Frame -> True]
```

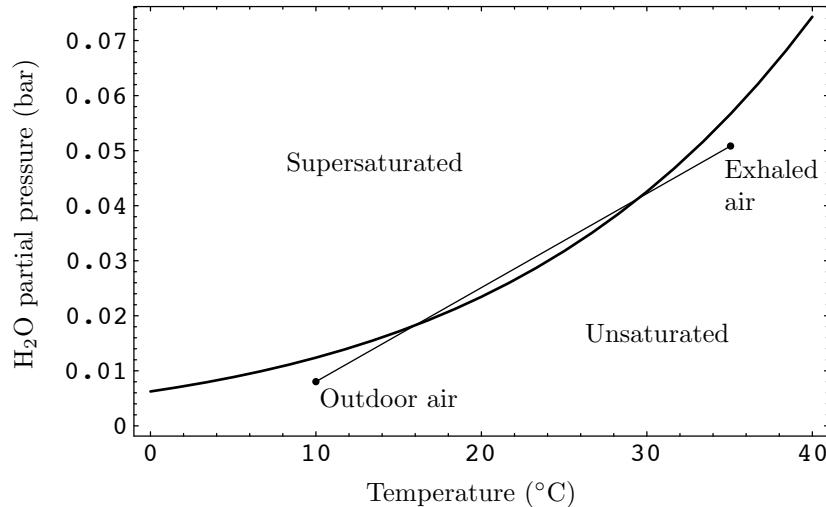
which produced the graph on the following page.



Indeed, the equilibrium vapor pressure of water approximately doubles for every 10°C increase in temperature: 0.006 bar at 0°C; 0.012 bar at 10°C; 0.023 bar at 20°C; 0.043 bar at 30°C; and 0.074 bar at 40°C.

- b) At 30°C, a relative humidity of 100% would imply a partial pressure of water vapor equal to 0.043 bar, so a relative humidity of 90% means 90% of this, or 0.038 bar. To find the dew point, just find the temperature at which the equilibrium vapor pressure of water is 0.038 bar; I estimate about 28°C from the graph, and calculate 28.2°C from the formula. A relative humidity of 40%, on the other hand, implies a partial pressure of water vapor equal to only 0.017 bar. The dew point at this humidity is 14.9°C.

Problem 5.43. On the diagram below (the same one plotted in the previous problem), I've plotted the composition of the exhaled air (35°C, 90% relative humidity) and also one possible composition of the outdoor air (10°C) as dots. Consider, now, the mixing of parcels of air with these two initial temperatures and initial H₂O partial pressures. If the



parcels have equal mass, then the mixture will end up at a temperature halfway between them (since the heat capacity of air is independent of its temperature), and also at an H₂O partial pressure that is halfway between the partial pressures of the initial parcels. More generally, for any value of the ratio of the initial masses, the mixture will have a temperature and H₂O partial pressure that lie somewhere on a straight line on the diagram, connecting the dots representing the two initial states. (As the exhaled air mixes with larger and larger amounts of environmental air, the state of the mixture will move downward along this straight line.) To get cloud droplets, the state of the mixture must lie above the curve representing the equilibrium vapor pressure; since this curve is concave-upward, this is possible even when both initial states lie below the curve. By moving the dot representing the outdoor air state vertically, we see that if it goes too low, the line will no longer cross the vapor pressure curve. The minimum H₂O partial pressure of the outdoor air in this case is about 0.0032 bar, corresponding to a relative humidity of about 25%. If we do get cloud droplets, therefore, we can conclude that the relative humidity is at least 25%.

Problem 5.44. At 25°C and 50% relative humidity, the partial pressure of water vapor is (from the graph in Problem 5.42 or directly from the data in Figure 5.11) 0.016 bar. To estimate roughly the elevation at which a cloud will begin to form, we can just read off from the graph in Problem 5.42 the temperature at which this partial pressure is the equilibrium vapor pressure—13.8°C—and then calculate the height at which the temperature would drop to this level: at 9.8°C/km (as calculated in Problem 1.40), a height of 1.14 km. However, in rising to this level, the air will expand and the the partial pressure of water vapor will drop, along with the total pressure. In Problem 1.16 we saw that the pressure of the atmosphere decreases with height approximately as an exponential function,

$$P(z) = P(0) e^{-z/(8.5 \text{ km})}.$$

At our estimated height, therefore, the pressure will have dropped by a factor of $e^{1.14/8.5} = 0.87$, and therefore the partial pressure of water vapor will be only $0.87 \cdot 0.016 \text{ bar} = 0.014 \text{ bar}$. This pressure is equal to the equilibrium vapor pressure at 11.8°C, and to cool to this temperature, the air must rise 1.35 km. Of course, by the time the air has risen to this height, its pressure will have dropped somewhat further, but not enough to affect the answer by much. I'll just round the answer upward and say that the cloud probably starts to form at about 1.4 km.

Problem 5.45. (Wet adiabatic lapse rate.)

- a) I'll do this part of the problem two ways, the first a bit sloppy and the second more careful. First, consider the “system” to be a rising (and expanding) mass of air, *not* including the water vapor or water droplets mixed with the air. The work done by this system is mainly due to its expansion, so $W = -P dV$. The “heat” that enters the system is mainly due to the condensation of water vapor, so $Q = -L dn_w$ (note that when n_w , the number of moles of water vapor, decreases, “heat” is given up by the water to the air). Therefore the first law tells us

$$dU = Q + W = -L dn_w - P dV.$$

The energy of the system is $U = \frac{f}{2}nRT$, where $f = 5$ for nearly all the molecules in the air, so

$$\frac{5}{2}nRdT = Ldn_w - PdV.$$

Now the only problem is to rewrite the last term in terms of dT and dP . From the ideal gas law and the product rule for derivatives, note that

$$PdV + VdP = nRdT.$$

Therefore our result is

$$\frac{5}{2}nRdT = Ldn_w + VdP - nRdT,$$

where the V in the second-to-last term can be expressed as nRT/P . Solving for dT then yields

$$dT = \frac{2T}{7P}dP - \frac{2L}{7nR}dn_w.$$

For a somewhat more rigorous derivation, let us now treat the entire rising air mass, including the water vapor and water droplets, as the “system.” For this system, $Q = 0$ so the first law tells us simply

$$dU = PdV.$$

Now rewrite this relation in terms of enthalpy. Since $H = U + PV$,

$$dH = dU + PdV + VdP \quad \text{or} \quad dH = VdP,$$

for our adiabatic process. The enthalpy of the system is the sum of the enthalpy of the H_2O (vapor plus liquid) and the enthalpy of the “dry” air (all the other gases). For the dry air,

$$H_{\text{dry air}} = U + PV = \frac{5}{2}nRT + PV = \frac{7}{2}nRT,$$

so $dH_{\text{d.a.}} = \frac{7}{2}nRdT$. (This n includes only the dry air, not the water vapor.) The enthalpy of the H_2O can also change because of its “heat capacity,” but the dominant contribution to its change in enthalpy comes from condensation; in fact, the precise definition of L is the enthalpy change per mole due to the phase transformation. Therefore

$$dH_{\text{H}_2\text{O}} \approx Ldn_w,$$

where the \approx symbol indicates that I’ve omitted the small terms that come from the change in temperature of the vapor and the liquid. Plugging in these two contributions to dH , we have

$$\frac{7}{2}nRdT + Ldn_w = VdP.$$

Again we can write $V = nRT/P$, where n technically includes the water vapor but is approximately equal to n for the dry air alone. Therefore, to a good approximation,

$$\frac{7}{2}nRdT = \frac{nRT}{P}dP - Ldn_w,$$

which can be solved to yield the same result for dT as before. This time, though, the approximations being made are more explicit: I'm assuming that the H_2O makes up only a small percentage of the entire air mass.

- b) Because the air and the water vapor are both approximately ideal gases, the ratio n_w/n should be the same as P_v/P , the ratio of the vapor pressure to the total pressure. (Again I'm assuming that the water vapor makes up only a small fraction of the air, so P is approximately the same as the partial pressure of the "dry" air.) In other words,

$$n_w = \frac{n P_v}{P}.$$

Notice that n_w depends on temperature, through P_v . To differentiate with respect to z , we can use the chain rule for partial derivatives:

$$\begin{aligned}\frac{dn_w}{dz} &= \frac{\partial n_w}{\partial T} \frac{dT}{dz} + \frac{\partial n_w}{\partial P} \frac{dP}{dz} \\ &= \frac{n}{P} \frac{dP_v}{dT} \frac{dT}{dz} + n P_v \left(\frac{1}{P^2} \right) \frac{dP}{dz} \\ &= \frac{n}{P} \frac{L}{TV} \frac{dT}{dz} - \frac{n P_v}{P^2} \frac{dP}{dz}.\end{aligned}$$

In the last step I've used the Clausius-Clapeyron relation, so the V in the first term represents the volume of one mole of water vapor, which is RT/P_v . Therefore we have

$$\frac{dn_w}{dz} = \frac{n P_v L}{P R T^2} \frac{dT}{dz} - \frac{n P_v}{P^2} \frac{dP}{dz}.$$

- c) Dividing the result of part (a) by dz and inserting the result of part (b), we have

$$\frac{dT}{dz} = \frac{2}{7} \frac{T}{P} \frac{dP}{dz} - \frac{2}{7} \frac{L}{nR} \left(\frac{n P_v L}{P R T^2} \frac{dT}{dz} - \frac{n P_v}{P^2} \frac{dP}{dz} \right),$$

or

$$\left(1 + \frac{2}{7} \frac{P_v L^2}{P R^2 T^2} \right) \frac{dT}{dz} = \frac{2}{7} \left(\frac{T}{P} + \frac{L P_v}{R P^2} \right) \frac{dP}{dz}.$$

But from Problem 1.16(b) we know that pressure decreases with altitude according to $dP/dz = -MgP/RT$, where M is the mass of a mole of air. Inserting this relation gives

$$\left(1 + \frac{2}{7} \frac{P_v L^2}{P R^2 T^2} \right) \frac{dT}{dz} = - \frac{2}{7} \left(\frac{M g P}{R T} \right) \left(\frac{T}{P} + \frac{L P_v}{R P^2} \right) = - \left(\frac{2}{7} \frac{M g}{R} \right) \left(1 + \frac{L P_v}{R T P} \right),$$

and solving for dT/dz gives our final result,

$$\frac{dT}{dz} = - \left(\frac{2}{7} \frac{M g}{R} \right) \frac{1 + \frac{P_v}{P} \frac{L}{R T}}{1 + \frac{2}{7} \frac{P_v}{P} \left(\frac{L}{R T} \right)^2}.$$

This formula should be quite accurate as long as the water vapor and water droplets make up only a small percentage of the mass of the system.

- d) As shown in Problem 1.40, the prefactor evaluates to 9.8 K/km. At 1 bar and 25°C, the ratio P_v/P is 0.032 (see page 167), while $L/RT = (43,990 \text{ J})/(8.31 \text{ J/K})(298 \text{ K}) = 17.8$. Therefore the correction factor is

$$\frac{1 + (0.032)(17.8)}{1 + (2/7)(0.032)(17.8)^2} = \frac{1 + 0.56}{1 + 2.85} = 0.41,$$

implying that the lapse rate is only 4.0 K/km for saturated air under these conditions. At 1 bar and 0°C, on the other hand, P_v/P is only 0.0061, while L/RT is slightly higher, 19.8. The correction factor is therefore

$$\frac{1 + (0.0061)(19.8)}{1 + (2/7)(0.0061)(19.8)^2} = \frac{1 + 0.12}{1 + 0.69} = 0.66,$$

implying that the lapse rate is 6.5 K/km. Whereas the dry adiabatic lapse rate is independent of temperature and pressure, the wet lapse rate decreases with increasing temperature; that is, saturated air tends to convect more readily when it is warmer. Why is this? Mostly because the amount of water vapor in saturated air is so much greater for warm air, and the rate at which droplets must form (and give up energy) is therefore much greater if the air is warm. At lower pressures (higher altitudes), the correction terms in both the numerator and the denominator increase by the same percentage, but term in the denominator is larger to begin with and therefore has a larger effect, yielding a lapse rate that is somewhat lower still. Regardless of the initial temperature and pressure, when a rising air mass reaches the dew point and a cloud begins to form, the air mass becomes even more unstable to convection and tends to rise more quickly. This tendency is greater if the temperature is still relatively high when the dew point is reached, as it would be on a humid summer day. The result is often towering cumulonimbus clouds and thunderstorms.

Problem 5.46. (Nucleation of cloud droplets.)

- a) For any pure system we can write the Gibbs free energy as $G = N$. For a liquid droplet surrounded by vapor, the total Gibbs free energy would be simply the sum of contributions from the two subsystems:

$$G = N_l \ l + N_v \ v = N_l \ l + (N - N_l) \ v = N \ v + N_l(l - v),$$

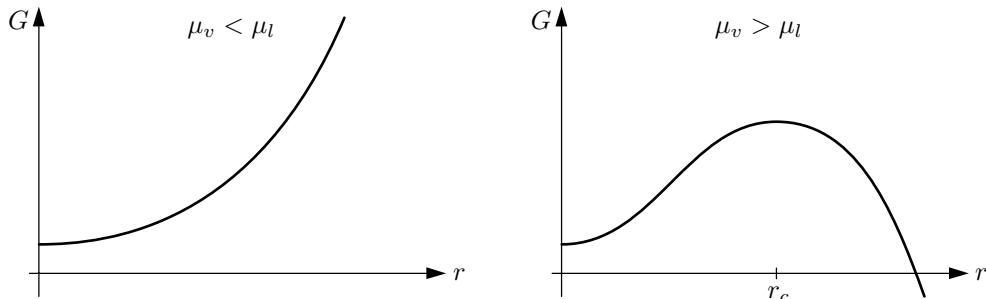
where the subscript l is for liquid and v is for vapor. If v_l is the volume per molecule in the liquid, then N_l is the ratio of the total volume of the liquid to v_l . Assuming a spherical droplet, we therefore have

$$G = N \ v + \frac{4\pi r^3}{3v_l}(l - v).$$

- b) The Gibbs free energy of the droplet's surface is simply the surface area times the surface tension, σ . So if we include this contribution, the total Gibbs free energy is

$$G = N \ v + \frac{4\pi r^3}{3v_l}(l - v) + 4\pi r^2\sigma.$$

- c) The r dependence of G comes from the second and third terms in the preceding expression. The third term is always positive and is quadratic in r , so its graph is an upward-opening parabola. The second term is cubic in r , but can be positive or negative depending on which is larger, μ_v or μ_l . If $\mu_v > \mu_l$, indicating that molecules would tend to diffuse from the liquid to the vapor (even neglecting surface tension), then this term is also positive so the graph of G looks like that shown below, left. The only equilibrium point is the minimum at $r = 0$, so the tendency of G to decrease will cause any water droplet to evaporate and disappear. On the other hand, if $\mu_v < \mu_l$, then the cubic term is negative so the graph of G vs. r looks like that shown below, right. Now there is a nontrivial equilibrium radius r_c , where G reaches a maximum. This equilibrium is unstable, however. Droplets smaller than r_c will evaporate, while droplets larger than r_c will grow until the vapor becomes depleted of water molecules and μ_v is no longer greater than μ_l .



- d) To find the critical radius, set the derivative of G equal to zero:

$$0 = \frac{dG}{dr} \Big|_{r_c} = -\frac{4\pi r_c^2}{v_l} (\mu_v - \mu_l) + 8\pi r_c \sigma.$$

Solving for r_c gives

$$r_c = \frac{2\sigma v_l}{\mu_v - \mu_l}.$$

Now the chemical potential of the vapor can be written in terms of its partial pressure P using equation 5.40:

$$\mu_v = \mu_v^\circ + kT \ln(P/P^\circ),$$

where \circ refers to any convenient reference pressure. If we take the reference pressure to be the nominal vapor pressure, that is, the pressure of vapor that would be in equilibrium with a flat surface of the liquid, then P/P° is just the relative humidity (which I'll call RH) and μ_v° is equal to μ_l . The difference $\mu_v - \mu_l$ can therefore be written as $kT \ln(\text{RH})$, and our expression for the critical radius becomes

$$r_c = \frac{2\sigma v_l}{kT \ln(\text{RH})} \quad \text{or} \quad \text{RH} = \exp\left(\frac{2\sigma v_l}{kT r_c}\right) = \exp\left(\frac{2\sigma V_l}{R T r_c}\right),$$

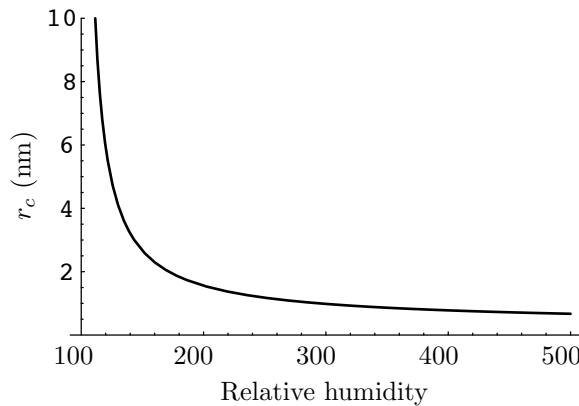
where V_l is the volume of one mole of the liquid. (This result is known as the Kelvin equation.) For water at 20°C,

$$\frac{2\sigma V_l}{R T} = \frac{2(0.073 \text{ J/m}^2)(18 \times 10^{-6} \text{ m}^3)}{(8.315 \text{ J/K})(293 \text{ K})} = 1.08 \times 10^{-9} \text{ m} = 1.08 \text{ nm},$$

so the Kelvin equation becomes

$$r_c = \frac{1.08 \text{ nm}}{\ln(\text{RH})} \quad \text{or} \quad \text{RH} = e^{(1.08 \text{ nm})/r_c}.$$

The critical radius goes to zero as the relative humidity goes to infinity, and goes to infinity as the relative humidity goes to 100% (from above). A plot of r_c vs. relative humidity is shown at right. We know from experience that the relative humidity in our atmosphere is never much greater than 100%; therefore, according to this analysis, droplets smaller than about 10 nm in radius should never be stable. But a 10-nm droplet contains more than 10^5 molecules, so it could never form spontaneously out of a random density fluctuation. We are forced to conclude that clouds droplets in our atmosphere must nucleate through some other process.



Problem 5.47. (Phase diagrams of magnetic systems.)

- a) In analogy with the derivation on pages 172–173, imagine a magnetic system that is just at the boundary between two phases. Under these conditions, let the (magnetic) Gibbs free energy be G_1 if the system is in phase 1, and G_2 if the system is in phase 2. Because neither phase is more stable than the other, $G_1 = G_2$. Now consider an infinitesimal change in conditions (T and \mathcal{H}) such that the system remains on the phase boundary. Because the two phases must remain equally stable, the changes in their Gibbs free energies must be equal: $dG_1 = dG_2$. But by the thermodynamic identity for G_m , this implies

$$S_1 dT - \partial M_1 d\mathcal{H} = S_2 dT - \partial M_2 d\mathcal{H}.$$

Rearranging the terms in this equation gives

$$\partial(M_2 - M_1)d\mathcal{H} = (S_2 - S_1)dT,$$

or

$$\frac{d\mathcal{H}}{dT} = \frac{S_2 - S_1}{\partial(M_2 - M_1)}.$$

This is the analogue of the Clausius-Clapeyron relation for a magnetic system.

- b) The phase boundary for the up- and down-magnetized phases in Figure 5.14 is horizontal, so according to the result of part (a), the difference in entropy between the two phases should be zero. This makes sense, because of the symmetry of the situation; there's no reason why one phase or the other should have more entropy.
- c) Let phase 1 be the normal phase and phase 2 be the superconducting phase. By the definition of \mathcal{H} , the condition that $B = 0$ inside a superconductor implies that

$\mathcal{H} = M_2/V$ or $M_2 = V\mathcal{H}$. Assuming that M_1 is negligible in comparison, the result of part (a) then becomes

$$\frac{d\mathcal{H}}{dT} = \frac{S_2 - S_1}{_0V\mathcal{H}},$$

or

$$S_2 - S_1 = {}_0V\mathcal{H} \frac{d\mathcal{H}}{dT}.$$

Looking at Figure 5.14, we see that the slope of the phase boundary ($d\mathcal{H}/dT$) is everywhere negative, except at $T = 0$ where the slope is zero. This indicates that the entropy of the superconducting phase (S_2) is *less* than the entropy of the normal phase (S_1) along the entire phase boundary except at the two ends. At the $T = 0$ end, both phases presumably have zero entropy, in accord with the third law of thermodynamics. At the $\mathcal{H} = 0$ end we must also have $S_2 = S_1$, but here it's because neither phase is magnetized at all.

Problem 5.48. From the van der Waals equation (5.52) we can differentiate to obtain

$$\frac{\partial P}{\partial V} = \frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3}; \quad \frac{\partial^2 P}{\partial V^2} = \frac{2NkT}{(V - Nb)^3} - \frac{6aN^2}{V^4}.$$

At the critical point, both of these expressions should equal zero, so

$$\frac{NkT_c}{(V_c - Nb)^2} = \frac{2aN^2}{V_c^3} \quad \text{and} \quad \frac{2NkT_c}{(V_c - Nb)^3} = \frac{6aN^2}{V_c^4}. \quad (1)$$

Dividing the first of these equations by the second gives

$$\frac{1}{2}(V_c - Nb) = \frac{1}{3}V_c, \quad \text{or} \quad V_c = 3Nb.$$

To obtain the critical temperature, plug this result into the first equation in (1):

$$\frac{NkT_c}{(3Nb - Nb)^2} = \frac{2aN^2}{(3Nb)^3} \quad \Rightarrow \quad \frac{NkT_c}{4N^2b^2} = \frac{2aN^2}{27N^3b^3} \quad \Rightarrow \quad kT_c = \frac{8}{27} \frac{a}{b}.$$

Finally, to obtain the critical pressure, plug both these results back into the van der Waals equation itself:

$$P_c = \frac{NkT_c}{V_c - Nb} \quad \frac{aN^2}{V_c^2} = \frac{8Na/27b}{2Nb} \quad \frac{aN^2}{9N^2b^2} = \left(\frac{4}{27} - \frac{1}{9}\right) \frac{a}{b^2} = \frac{1}{27} \frac{a}{b^2}.$$

Problem 5.49. Rather than punching all the formulas on my calculator, I set up a small spreadsheet to compute the critical constants:

Critical constants					
	a (J-m^3)	b (m^3)	T_c (K)	P_c (Pa)	V_c/n (m^3)
N ₂	4.00E-49	6.0E-29	143	4.1E+06	0.000108
H ₂ O	1.60E-48	6.0E-29	573	1.6E+07	0.000108
He	1.00E-50	1.0E-29	21.5	3.7E+06	0.000018

For the a and b values I used the numbers given on page 181, except that I guessed that the b value for He would be several times smaller than that of N₂ and H₂O. The final column shows V_c/n , the volume per mole; the volume per molecule would be simply $3b$. As it turns out, these a and b values predict critical constants for N₂ and H₂O that are all within a factor of 2 of the correct values (see page 168). My guessed b value for He, however, turned out to be much too low. To remedy this, and to improve the other numbers as well, I adjusted all the a and b values until the critical temperatures and pressures came out to the correct experimental values:

Critical constants					
	a (J-m^3)	b (m^3)	T_c (K)	P_c (Pa)	V_c/n (m^3)
N ₂	3.75E-49	6.4E-29	126	3.4E+06	0.0001152
H ₂ O	1.54E-48	5.1E-29	647	2.2E+07	0.0000918
He	9.40E-51	3.9E-29	5.2	2.3E+05	0.0000702

I was surprised that I needed to use a b value for He that was not much lower than that for the other molecules. Please note, though, that even these a and b values are in no sense “exact”; for instance, they predict V_c values that are significantly higher than measured, as indicated in the following problem.

Problem 5.50. Using the results of Problem 5.48, we have for a van der Waals fluid at the critical point

$$\frac{P_c V_c}{NkT_c} = \frac{1}{27} \frac{a}{b^2} - \frac{3Nb}{N} - \frac{27b}{8a} = \frac{3}{8} = 0.375.$$

This is indeed significantly higher than the experimental values quoted in the problem.

Problem 5.51. Substituting $T = tT_c$, $P = pP_c$, and $V = vV_c$ into the van der Waals equation gives

$$pP_c = \frac{NktT_c}{vV_c} - \frac{aN^2}{Nb} - \frac{aN^2}{v^2V_c^2}.$$

Plugging in the results of Problem 5.48, we then obtain

$$p \left(\frac{1}{27} \frac{a}{b^2} \right) = \frac{Nt}{3Nb} - \frac{8}{27} \frac{a}{b} - \frac{aN^2}{9N^2b^2v^2} = \frac{a}{27b^2} \left(\frac{8t}{3v} - \frac{3}{v^2} \right),$$

that is,

$$p = \frac{8t}{3v} - \frac{3}{v^2}.$$

The constants a and b have conveniently disappeared. This means that when we use reduced variables, our calculations apply to all van der Waals fluids, regardless of their a and b values.

Problem 5.52. To plot $p(v)$ (in reduced variables) for $t = 0.95$, I gave the following instructions to Mathematica:

```
p[v_] := (8*.95)/(3*v - 1) - 3/v^2
Plot[p[v], {v, .5, 3}, PlotRange -> {{0, 3}, {.6, 1}}]
```

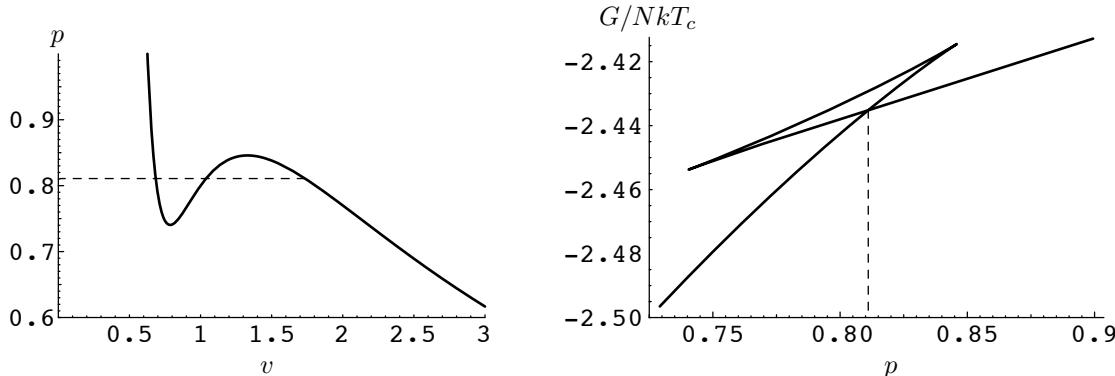
This produced the plot shown below, left. I added the horizontal line by hand, adjusting it vertically until the enclosed loops appeared to have equal areas. By this method, I estimate the pressure of the phase transition to be at $p = 0.81$. To plot the Gibbs free energy, let me first express it in terms of reduced variables. Starting from equation 5.56,

$$\begin{aligned}\frac{G}{NkT_c} &= t \ln(3Nb v - Nb) + \frac{Nbt}{3Nb v - Nb} - \frac{2aN^2}{NkT_c v V_c} + c(T) \\ &= t \ln(3v - 1) - t \ln(Nb) + \frac{t}{3v - 1} - \frac{2aN^2}{N \cdot 3Nb} - \frac{27b}{8a} + c(T) \\ &= t \ln(3v - 1) + \frac{t}{3v - 1} - \frac{9}{4v} + C(T),\end{aligned}$$

where in the last step I've absorbed the term $-t \ln(Nb)$ into the new constant $C(T)$. To plot G/NkT vs. p , I used the following instructions:

```
g[v_] := -(0.95)Log[3v-1] + .95/(3v-1) - 9/(4v)
ParametricPlot[{p[v], g[v]}, {v, .65, 2.25}]
```

This produced the plot shown below, right, on which we again see that the transition is at $p = 0.81$.



It's a bit more satisfying, though hardly necessary, to actually calculate the transition pressure. To do so, I first defined a Mathematica function for the antiderivative of $p(v)$:

```
pInt[v_] := (8/3)*.95*Log[3*v - 1] + 3/v
```

I then defined a function to compute the difference between the areas of the two enclosed loops, for any value of p_0 , the pressure at which the horizontal line is drawn:

```
AreaDiff[p0_, v1guess_, v2guess_] := (
  v1 = FindRoot[p[v] == p0, {v, v1guess}] [[1, 2]];
  v2 = FindRoot[p[v] == p0, {v, v2guess}] [[1, 2]];
  pInt[v2] - pInt[v1] - p0*(v2 - v1))
```

In order to find the volumes v_1 and v_2 where the pressure equals the given value p_0 , the `FindRoot` function requires approximate starting points, called `v1guess` and `v2guess`. The final line of the function computes the integral of $p(v)$ from v_1 to v_2 , then subtracts off the area of the rectangle under the horizontal line, to obtain the difference between the areas of the enclosed loops. To find the value of p_0 that makes this difference equal to zero now requires just a single instruction:

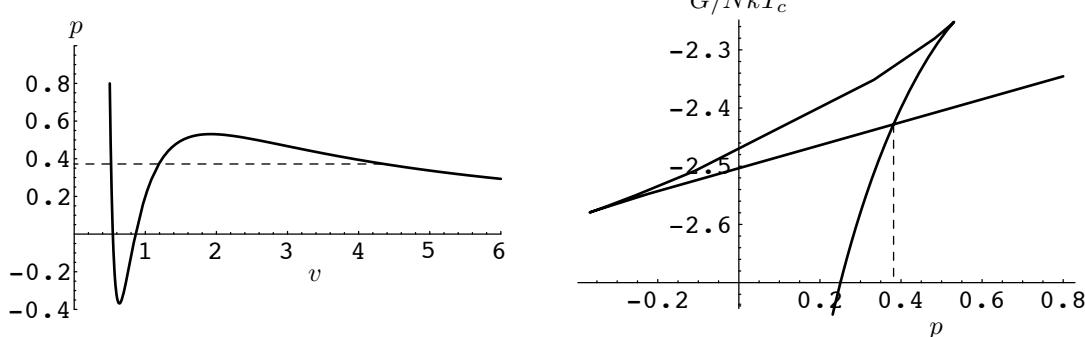
```
FindRoot [AreaDiff [p0, .7, 2]==0, {p0, .8, .82}]
```

The returned value of p_0 was 0.8119.

Problem 5.53. This problem is just like the previous one, but with the temperature (in units of T_c) changed to 0.8. It's also necessary to change the ranges of variables covered by the plots. Here is the *Mathematica* code that I used to plot $p(v)$ and G/NkT_c vs. p :

```
p[v_] := (8*.8)/(3*v - 1) - 3/v^2
Plot[p[v], {v, .5, 6}, PlotRange->{{0, 6}, {-4, 1}}]
g[v_] := -(0.8)Log[3v-1] + .8/(3v-1) - 9/(4v)
ParametricPlot[{p[v], g[v]}, {v, .5, 8}]
```

And here are the plots:



From either plot, we can see that the transition pressure is at approximately $p = 0.38$. To calculate the transition pressure more precisely, I used the same `AreaDiff` function as in the previous problem, but with a new temperature in the definition of `pInt` and different starting points for the `FindRoot` functions:

```
pInt[v_] := (8/3)*.8*Log[3*v - 1] + 3/v
FindRoot [AreaDiff [p0, .5, 5]==0, {p0, .35, .4}]
```

The p_0 value returned was 0.3834.

Problem 5.54. Since $F = G - PV$ for any system, we can start with equation 5.56 for the Gibbs free energy, then subtract off PV , using the van der Waals equation to express

P in terms of V :

$$\begin{aligned} F &= NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} \frac{2aN^2}{V} PV + c(T) \\ &= NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} \frac{2aN^2}{V} \frac{NkTV}{V - Nb} + \frac{aN^2}{V} + c(T) \\ &= NkT \ln(V - Nb) - NkT \frac{aN^2}{V} + c(T) \\ &= NkT \ln(V - Nb) - \frac{aN^2}{V} + C(T), \end{aligned}$$

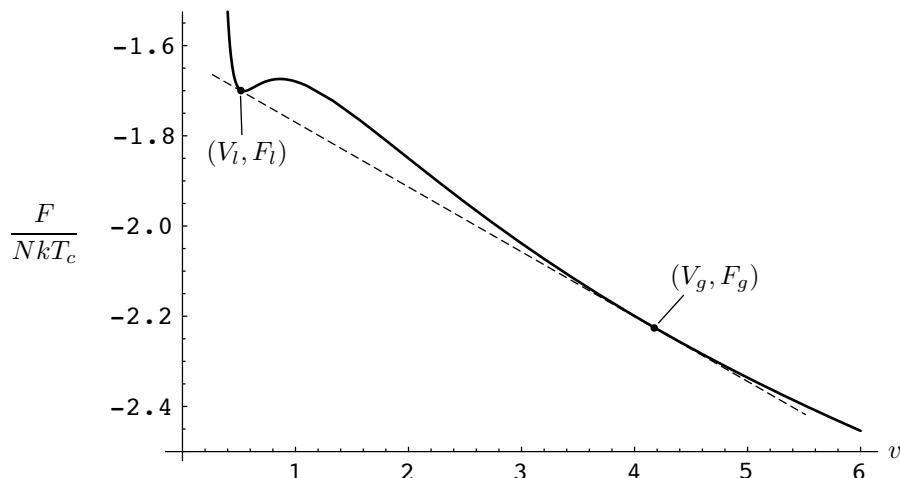
where in the last step I've absorbed the term NkT into the constant $C(T)$. Now divide by NkT_c and put the expression in terms of the dimensionless variables $v = V/V_c$ and $t = T/T_c$, where $V_c = 3Nb$ and $kT_c = 8a/27b$:

$$\begin{aligned} \frac{F}{NkT_c} &= t \ln(vV_c - Nb) - \frac{aN^2}{NkT_c v V_c} + C(T) \\ &= t \ln(3v - 1) - t \ln(Nb) - \frac{aN^2}{Nv} \frac{27b}{3Nb} \frac{27b}{8a} + C(T) \\ &= t \ln(3v - 1) - \frac{9}{8v} + f(t), \end{aligned}$$

where again I've absorbed terms that don't depend on v into the final constant term. To plot this function (without the constant term) I used the *Mathematica* instruction

```
Plot[-.8*Log[3v-1] - 9/(8v), {v, .4, 6}]
```

Here's the graph, on which I've added dots at points corresponding to the liquid and gas at the vapor pressure:



Now suppose the system consists of a combination of two different states represented by the dots: it is part liquid and part gas. Let x be the fraction (by mass) of liquid, so the fraction of gas is $1 - x$. The total volume of the system is then

$$V = xV_l + (1 - x)V_g = V_g - x(V_g - V_l)$$

and the total free energy is

$$F = xF_l + (1-x)F_g = F_g - x(F_g - F_l).$$

Combining these two equations to eliminate x , we obtain

$$F = F_g - \frac{(V_g - V)}{(V_g - V_l)}(F_g - F_l).$$

This equation for $F(V)$ describes a straight line going through the points (V_l, F_l) and (V_g, F_g) ; it is drawn as a dashed line in the preceding plot. Notice that this straight line lies *below* the original curve representing the free energy of a homogeneous state of uniform density. Since a system at constant T and V tends to minimize its free energy, the stable states at volumes between V_l and V_g are those represented by the dashed line, not the solid curve. Notice also that at the points where the line meets the curve at each end, it is tangent to the curve, indicating that this is the lowest possible straight line that can be drawn between any two points on the curve, lying entirely below it. In fact, had we not known the transition volumes V_l and V_g , we could have found them by drawing the lowest possible such straight line and then looking at where it meets the curve at a tangent. This process is just another way of doing the so-called Maxwell construction.

Problem 5.55. (Critical behavior of a van der Waals fluid.)

- a) In reduced variables, the van der Waals equation is

$$p = 8t(3v - 1)^{-1} - 3v^{-2}.$$

We want to expand this in a Taylor series about the point $v = 1$, keeping terms through third order. We therefore need the first, second, and third derivatives of p with respect to v :

$$\begin{aligned}\frac{\partial p}{\partial v} &= 24t(3v - 1)^{-2} + 6v^{-3}; \\ \frac{\partial^2 p}{\partial v^2} &= 144t(3v - 1)^{-3} - 18v^{-4}; \\ \frac{\partial^3 p}{\partial v^3} &= 1296t(3v - 1)^{-4} + 72v^{-5}.\end{aligned}$$

Our series expansion is therefore

$$\begin{aligned}p(v) &\approx p(1) + \left.\frac{\partial p}{\partial v}\right|_1(v - 1) + \frac{1}{2}\left.\frac{\partial^2 p}{\partial v^2}\right|_1(v - 1)^2 + \frac{1}{6}\left.\frac{\partial^3 p}{\partial v^3}\right|_1(v - 2)^3 \\ &= (4t - 3) - 6(t - 1)(v - 1) + 9(t - 1)(v - 1)^2 - \frac{3}{2}(9t - 8)(v - 1)^3.\end{aligned}$$

If you find this calculation tedious, you can instead do it all with a single instruction to *Mathematica*:

```
Series[8t/(3v-1) - 3/v^2, {v, 1, 3}]
```

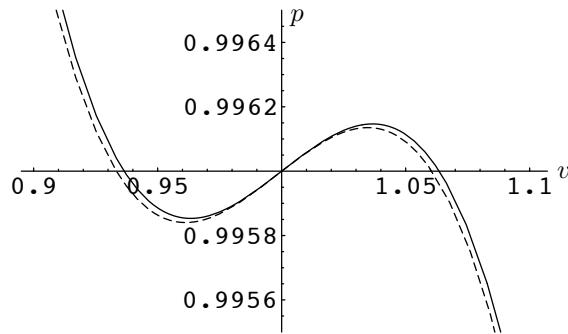
Now imagine plotting this formula for p as a function of v , with t held fixed at a value that is very close to 1. When $(v - 1)$ is as small as $(t - 1)$ or smaller, the term

linear in $(v - 1)$ will be much larger than the quadratic or the cubic term, so the graph will be approximately linear. When $(v - 1)^2$ becomes comparable to $(t - 1)$, the cubic term becomes comparable in size to the linear term, while the quadratic term remains smaller than either. Therefore, to plot the isotherm and perform the Maxwell construction, we need to keep the cubic term (which produces the “loops”) but we can neglect the quadratic term. We can, however, set $t = 1$ in the cubic term, to obtain the expression

$$p \approx (4t - 3) - 6(t - 1)(v - 1) - \frac{3}{2}(v - 1)^3.$$

- b) The plot at right shows the approximate van der Waals isotherm for $t = 0.999$, with the dashed curve including the entire Taylor expansion computed in part (a) and the solid curve omitting the term quadratic in $(v - 1)$. As t gets even closer to 1, the two curves become indistinguishable over the range of v values relevant to performing the Maxwell construction. Notice that the solid curve is antisymmetric about the point $v = 1$. This means that the horizontal, constant-pressure line that results in equal areas enclosed by the two “loops” should run directly through the point of symmetry, $v = 1$. In other words, the pressure of the phase transition is exactly the same as the pressure predicted by the van der Waals equation at the (unphysical) point $v = 1$. This pressure is simply $p = 4t - 3$. The slope of the phase boundary in the p - t plane is therefore $dp/dt = 4$, in the limit where $t \rightarrow 1$, that is, at the critical point.
- c) The volumes of the liquid and gas at the transition pressure are just the values of v at the transition pressure found in part (b). That pressure is $4t - 3$, so set

$$\begin{aligned} 4t - 3 &= 4t - 3 - 6(t - 1)(v - 1) - \frac{3}{2}(9t - 8)(v - 1)^3 \\ \Rightarrow 0 &= 6(t - 1) + \frac{3}{2}(9t - 8)(v - 1)^2 \end{aligned}$$



Since we’re interested in the limit $t \rightarrow 1$, we can set $t = 1$ in the last term and solve for $(v - 1)$ to obtain

$$v - 1 = \pm 2\sqrt{1 - t}.$$

The two solutions correspond to the volumes of the liquid (–) and the gas (+) at the transition pressure. The difference between the two volumes is

$$v_g - v_l = (1 + 2\sqrt{1 - t}) - (1 - 2\sqrt{1 - t}) = 4\sqrt{1 - t}.$$

This difference is proportional to $(T - T_c)^{1/2}$, so the van der Waals model predicts that the exponent β is equal to $1/2$.

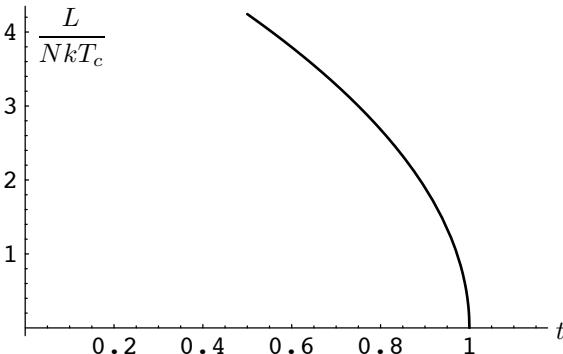
- d) By the Clausius-Clapeyron relation, the latent heat is

$$L = T(V_g - V_l) \frac{dP}{dT} = P_c V_c (v_g - v_l) \frac{dp}{dt} = \frac{3}{8} N k T_c (v_g - v_l) \frac{dp}{dt},$$

where in the last step I've used the result of Problem 5.50. Plugging in the results of parts (b) and (c), this expression becomes

$$\frac{L}{NkT_c} = \frac{3}{8} \cdot 4\sqrt{1-t} \cdot 4 = 6\sqrt{1-t},$$

in the limit $t \rightarrow 1$. This equation describes a parabola opening to the left, decreasing to zero as $t \rightarrow 1$ (as expected).



- e) Setting $t = 1$, our Taylor-expanded van der Waals equation becomes

$$p = 1 - \frac{3}{2}(v-1)^3.$$

In conventional notation, this says that at $T = T_c$, the quantity $P - P_c$ is proportional to $(V - V_c)^3$. Therefore the critical exponent δ is equal to 3 (in the van der Waals model).

- f) In terms of reduced variables, the isothermal compressibility is

$$\kappa = \frac{1}{P_c} \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_t \approx \frac{1}{P_c} \left(\frac{\partial v}{\partial p} \right)_t,$$

where the approximation is accurate near the critical point. So we need to compute the partial derivative $(\partial v / \partial p)_t$, or equivalently, its reciprocal, $(\partial p / \partial v)_t$, which is just the slope of the isotherm plotted in the p - v plane. From the result of part (a) we have, to a good approximation,

$$\left(\frac{\partial p}{\partial v} \right)_t = 6(t-1) - \frac{9}{2}(v-1)^2.$$

The tricky part is deciding where to evaluate this expression. When t approaches 1 from above, there is only one volume for a given pressure, so we can just set $v = 1$ to obtain $(\partial p / \partial v)_t = 6(t-1)$. The compressibility is therefore

$$\kappa = \frac{1}{P_c} \frac{1}{6(t-1)} = \frac{T_c}{6P_c(T-T_c)} \quad (T \rightarrow T_c \text{ from above}),$$

which diverges as $1/(T-T_c)$, indicating that $\gamma = 1$. When $t < 1$, however, there are three volumes for any given pressure and temperature, of which only two are physical, and for these, $v-1 \approx \pm 2\sqrt{1-t}$. In this case we have

$$\left(\frac{\partial p}{\partial v} \right)_t = 6(1-t) - \frac{9}{2} \cdot 4(1-t) = -12(1-t),$$

for either the liquid or the gas. The compressibility is therefore

$$\kappa = \frac{1}{P_c} \frac{1}{-12(1-t)} = \frac{T_c}{12P_c(T_c-T)} \quad (T \rightarrow T_c \text{ from below}),$$

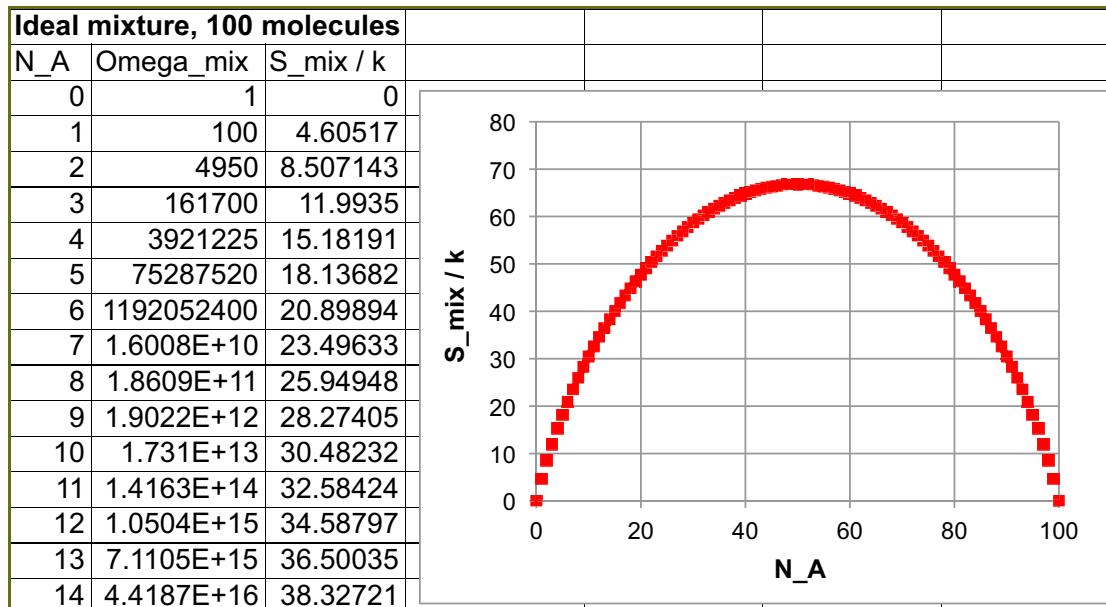
which again diverges as $1/(T-T_c)$ (though with a different coefficient), indicating that $\gamma' = 1$.

Problem 5.56. Starting from equation 5.60, we have

$$\begin{aligned}\frac{d}{dx} \Delta S_{\text{mixing}} &= R \left[\ln x + x \cdot \frac{1}{x} + (-1) \ln(1-x) - (1-x) \cdot \frac{1}{1-x} \right] \\ &= R [\ln x - \ln(1-x)].\end{aligned}$$

The first term in this expression goes to ∞ as $x \rightarrow 0$, while the second term goes to ∞ as $x \rightarrow 1$.

Problem 5.57. I created an Excel spreadsheet with a row for each possible value of N_A from 0 to 100. The “multiplicity” of mixing is then the number of ways of choosing N_A molecules out of 100, computed in Excel as `COMBIN(100,A3)`, for example, and the entropy of mixing, in units of k , is the natural logarithm of the multiplicity. Here are the first several rows of my spreadsheet, and a plot of the entropy:



Notice that if all the molecules are initially of the same type, converting one of them to the other type creates 4.6 units of entropy, but converting a second one creates only 3.9 units, and a converting a third creates only 3.5 units. These differences may not be huge, but they are quite significant: they indicate that the graph of S vs. N_A continues to steepen even when one is already very close to the endpoint. In the thermodynamic limit where the number of molecules is large, the slope of S vs. x becomes infinite as x goes to 0 or 1.

Problem 5.58. (A simple model of a nonideal mixture.)

- a) When the system is unmixed, the potential energy due to the interaction of each neighboring pair is u_0 . There are N molecules, each with n nearest neighbors, so you might think that the total potential energy is Nnu_0 . However, this formula counts every pair interacting pair twice, so we need to divide by 2 to obtain $U = \frac{1}{2}Nnu_0$.

- b) When the molecules are mixed randomly, each A molecule has, on average, xn neighbors that are B molecules and $(1-x)n$ neighbors that are A molecules. So the energy due to the interaction of this A molecule with all its neighbors is $xnu_{AB} + (1-x)nu_0$. Similarly, the energy due to the interaction of any given B molecule with all its neighbors is (on average) $xnu_0 + (1-x)nu_{AB}$. The total potential energy of the entire system is therefore

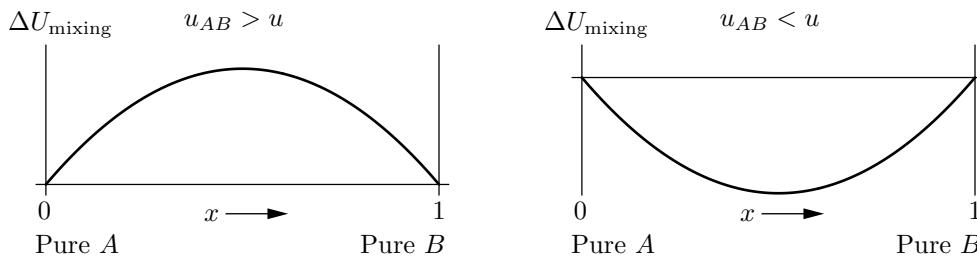
$$\begin{aligned} U &= \frac{1}{2} \left(N_A [xnu_{AB} + (1-x)nu_0] + N_B [xnu_0 + (1-x)nu_{AB}] \right) \\ &= \frac{1}{2} \left((1-x)N [xnu_{AB} + (1-x)nu_0] + xN [xnu_0 + (1-x)nu_{AB}] \right) \\ &= \frac{1}{2} Nn \left([x^2 + (1-x)^2]u_0 + 2x(1-x)u_{AB} \right), \end{aligned}$$

where again I've divided by 2 to avoid double-counting the pairs.

- c) Subtracting the result of part (a) from the result of part (b) gives for the energy change upon mixing

$$\begin{aligned} \Delta U &= \frac{1}{2} Nn \left([x^2 + (1-x)^2 - 1]u_0 + 2x(1-x)u_{AB} \right) \\ &= \frac{1}{2} Nn \left([2x^2 - 2x]u_0 + 2x(1-x)u_{AB} \right) \\ &= Nnx(1-x)(u_{AB} - u_0). \end{aligned}$$

This equation describes a parabola, symmetrical about $x = 1/2$, opening downward if $u_{AB} > u_0$ and opening upward if $u_{AB} < u_0$ (see illustration below).



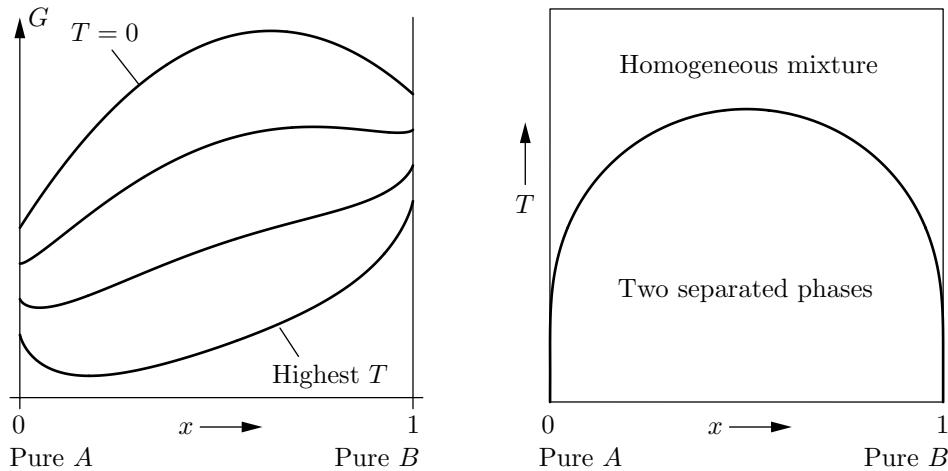
- d) The slope of the mixing energy function is just the derivative of the preceding expression with respect to x :

$$\text{slope} = \frac{d}{dx} \left[Nnx(1-x)(u_{AB} - u_0) \right] = Nn(u_{AB} - u_0) \frac{d}{dx}(x - x^2) = Nn(u_{AB} - u_0)(1 - 2x).$$

This quantity is finite for all x between 0 and 1. At the endpoints, the magnitude of the slope is $Nn|u_{AB} - u_0|$.

- e) Adding the mixing energy term to equation 5.61 results in a free energy function like that shown in Figure 5.26, reproduced on the next page. At $t = 0$ the mixing entropy does not contribute, while at high temperature, the concave-up contribution of the mixing entropy dominates over the concave-down mixing energy. At intermediate temperatures, the function $G(x)$ is concave-up near the endpoints and concave-down

near the middle. This implies that there is a solubility gap at relatively low temperatures.



- f) There is a solubility gap whenever the function $G(x)$ is concave-down at $x = 1/2$. So the critical temperature, T_c , at which the solubility gap disappears would be the temperature at which the second derivative of G , at $x = 1/2$, vanishes. Adding the mixing-energy term onto equation 5.61, we have

$$\begin{aligned} G &= (1-x)G_A^\circ + xG_B^\circ + NkT[x \ln x + (1-x) \ln(1-x)] + Nn(u_{AB} - u_0)(x - x^2); \\ \frac{dG}{dx} &= G_B^\circ - G_A^\circ + NkT[\ln x - \ln(1-x)] + Nn(u_{AB} - u_0)(1 - 2x); \\ \frac{d^2G}{dx^2} &= NkT\left[\frac{1}{x} + \frac{1}{1-x}\right] - 2Nn(u_{AB} - u_0). \end{aligned}$$

Setting $x = 1/2$ and setting this expression equal to zero gives

$$NkT_c[2+2] = 2Nn(u_{AB} - u_0), \quad \text{or} \quad T_c = \frac{n(u_{AB} - u_0)}{2k}.$$

- g) Solving the preceding expression for $u_{AB} - u_0$, we have

$$u_{AB} - u_0 = \frac{2kT_c}{n} \approx \frac{2(8.62 \times 10^{-5} \text{ eV/K})(373 \text{ K})}{10} = 0.006 \text{ eV},$$

typical of intermolecular interaction energies.

- h) To plot the phase diagram, we need to locate the points x_a and x_b where a straight connecting line can be drawn tangent to the curve $G(x)$ (see Figure 5.27). This straight connecting line has the same slope as the straight-line graph of G without mixing (Figure 5.25), so if we neglect the terms in G that gave that straight line, the derivative of the remaining terms should be zero at the tangent points:

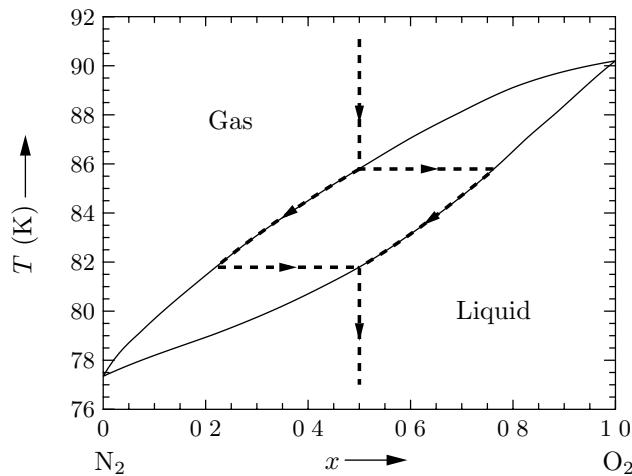
$$0 = NkT[\ln x - \ln(1-x)] + Nn(u_{AB} - u_0)(1 - 2x).$$

This equation is always satisfied at $x = 1/2$, but that's not the solution we want; at other x values we get the nontrivial solution. Solving for T gives simply

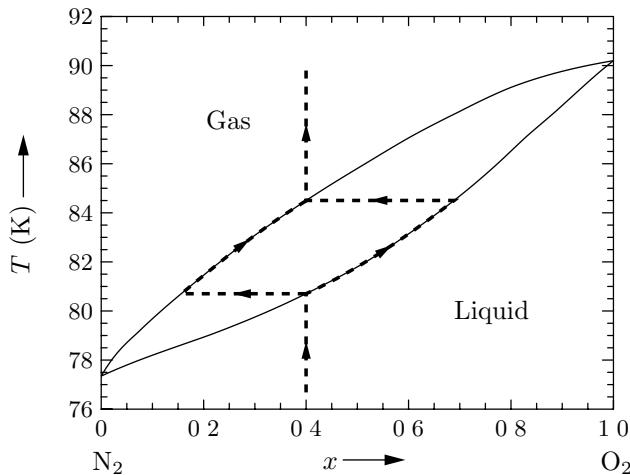
$$T = \frac{n(u_{AB} - u_0)}{k} \frac{2x - 1}{\ln x - \ln(1 - x)}$$

for the temperature of the phase boundary. To plot the quantity $kT/n(u_{AB} - u_0)$ is gave the instruction `Plot[(2x-1)/(Log[x]-Log[1-x]),{x,0,1}]` to *Mathematica*. This produced the theoretical phase diagram shown in Figure 5.28, reproduced above.

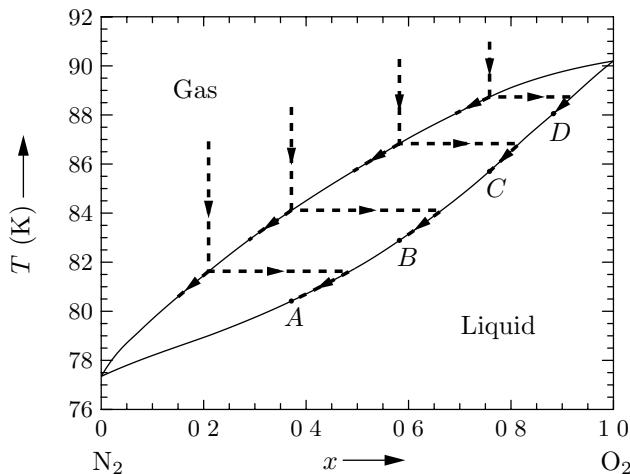
Problem 5.59. Refer to the reproduction of Figure 5.31, below. At a composition of 50% nitrogen and 50% oxygen, the mixture is stable as a gas until the temperature reaches about 85.8 K. At this point, the stable state is combination of the 50/50 gas with a liquid composed of 76% oxygen, so as the temperature is lowered further, a liquid begins to condense, initially composed of 76% oxygen. This condensation reduces the percentage of oxygen in the gas, so its composition moves downward and to the left, along the upper curve of the phase diagram, while that of the liquid also moves downward and to the left, to remain in equilibrium with the gas at each temperature. When the temperature reaches 81.8 K, the composition of the liquid is 50% oxygen, so there can't be any gas left; just before this, the last remaining gas has a composition of 22% oxygen.



Problem 5.60. Refer to the reproduction of Figure 5.31 on the following page. This mixture is stable as a liquid until the temperature reaches 80.7 K, at which point it begins to boil. The gas that boils off consists of 16% oxygen, the composition that can exist in equilibrium with a liquid of 40% oxygen. As this gas boils off, however, the liquid becomes more oxygen-rich, so its composition moves upward and to the right along the lower curve of the phase diagram. The composition of the gas also moves upward and to the right, to stay in equilibrium with the liquid at each temperature. (I'm assuming that the whole system is in a closed container—none of the gas is siphoned off.) Eventually the composition of the gas reaches 40% oxygen, so at this point there can't be any liquid left. The temperature is then 84.5 K, and the last bit of liquid to boil has a composition of about 69% oxygen.



Problem 5.61. One method of purifying oxygen from air is shown on the phase diagram below. Lower the temperature of air until a portion of it (perhaps about a third) condenses, resulting in a liquid with composition A . Then discard the remaining gas, let the liquid evaporate, and partially condense it a second time to obtain a liquid with composition B . Again discard the gas and repeat the process to obtain compositions C , D , etc., until the condensed liquid has the required purity. For the case shown in the diagram, the four steps indicated plus a n th step should suffice to produce at least a small amount of oxygen that is 95% pure. Of course, this liquid is only a tiny fraction, less than 1%, of the original air.



Alternatively, and a bit more simply, you could start by liquefying all the air, then raise its temperature until a nitrogen-rich gas boils off. Instead of keeping this gas in the same container, pump it away continuously and discard it. Then the composition of the remaining liquid will move upward and to the right along the lower phase boundary line, all the way to the end point of 100% oxygen, although again, only a tiny fraction of the original fluid will remain by the end.

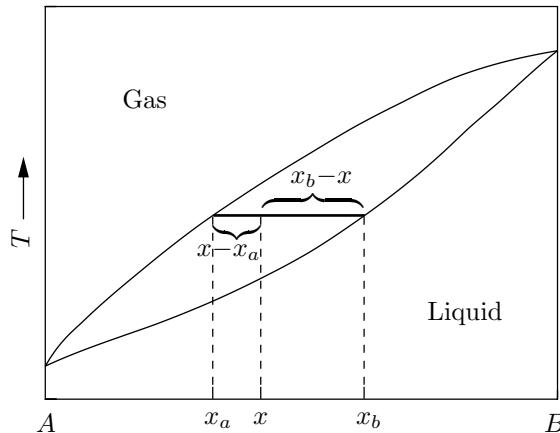
Problem 5.62. If the overall composition of the system is x , then the number of molecules of type B is xN , where N is the total number of molecules. Furthermore, the number of B molecules in the gas is $x_a N_g$, and the number of B molecules in the liquid is $x_b N_l$, where N_g and N_l are the numbers of molecules in the gas and liquid phases. But this means that the total number of B molecules must equal $x_a N_g + x_b N_l$, and therefore,

$$x_a N_g + x_b N_l = x(N_g + N_l).$$

Dividing through by N_l and solving for the ratio N_g/N_l , we obtain

$$x_a \left(\frac{N_g}{N_l} \right) + x_b = x \left(\frac{N_g}{N_l} \right) + x, \quad \text{or} \quad \frac{N_g}{N_l} = \frac{x - x_b}{x_a - x}.$$

The graphical interpretation of this formula is shown on the diagram below. Draw a horizontal line connecting the points representing the states of the liquid and gas. Break this line into two segments, separated by a point at the overall composition x . The segment to the left represents the proportion of liquid, while the segment to the right represents the proportion of gas. The ratio of liquid to gas is the same as the ratio of the lengths of these segments.

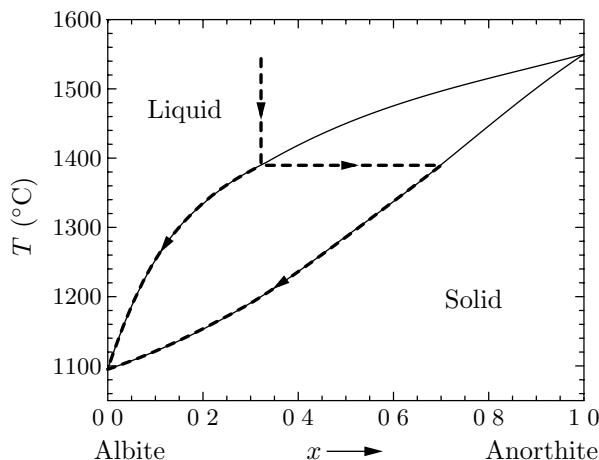


Problem 5.63. As the pressure increases, the boiling points of oxygen and nitrogen, as well as both curves representing the boiling of mixtures, should shift to higher temperature. The best way to see this is to consider the Gibbs free energy, which increases with pressure according to $(\partial G/\partial P)_T = V$. Since the gas has a much greater volume than the liquid, its entire free energy curve $G(x)$ shifted upward, relative to that of the liquid, at any given temperature. Raising the temperature shifts this curve downward again, as shown in Figure 5.30. But at high pressure, a higher temperature is needed to make the curves intersect.

Problem 5.64. (Crystallization of plagioclase feldspar.)

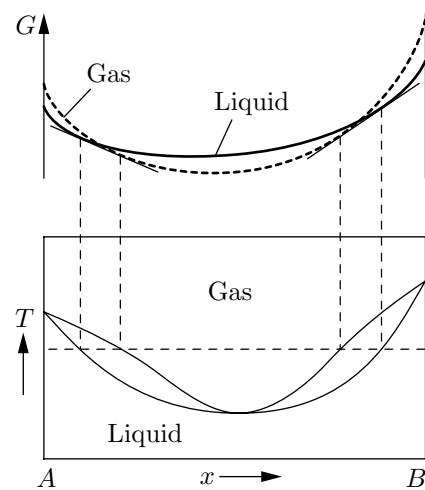
- a) The cooling sequence is indicated by the heavy dashed lines on the phase diagram on the following page. The initial composition of the magma must approximately 32% anorthite, because at this composition, the first crystals to form as the magma cools will have a composition of 70% anorthite. As these crystals form, the magma becomes

more albite-rich, so its composition moves down and to the left along the upper phase boundary curve. Meanwhile, the outermost portions of the crystals follow the lower phase boundary curve, down and to the left. Apparently, the crystals formed quickly enough to inhibit any diffusion of atoms within them, so the cores of the oldest crystals remain at their original composition, 70% anorthite. Although the overall composition of the solid crystals was never less than 32% anorthite, it is still quite possible for the youngest parts of the crystals to consist of essentially pure albite, as the crystallization ended at the bottom-left corner of the phase boundary curves.

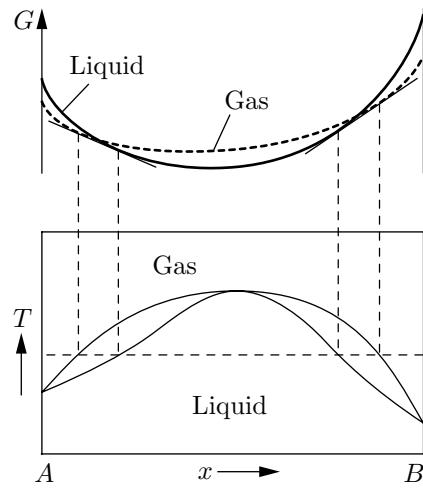


- b) As we have already seen in part (a), the earliest crystals to form as the magma cools will be anorthite-rich, while the latest crystals to form will be albite-rich. Apparently, in this rock body, the earlier crystals settled toward the bottom, leaving an albite-rich magma at the top which then cooled further to form the albite-rich crystals.

Problem 5.65. The illustration at right shows the free energy graphs of the gas and liquid at one particular temperature. Because the liquid's free energy curve is less concave than that of the gas, the curves can intersect in two places, as shown. Therefore there are two composition ranges at which a combination of gas and liquid is most stable (at this temperature). At higher temperatures, the gas's free energy curve moves down relative to that of the liquid ($\partial G / \partial T = -S$), so the intersections move farther apart. At lower temperatures, the gas's free energy curve moves up relative to that of the liquid, so the intersections move closer together until finally the two curves just kiss each other at a single point. The composition at that point is the azeotrope; a mixture of this composition condenses abruptly at a well-defined temperature, just as a pure substance would.



Problem 5.66. The illustration at right shows the free energy graphs of the gas and liquid at one particular temperature. Because the liquid's free energy curve is more concave than that of the gas, the curves can intersect in two places, as shown. Therefore there are two composition ranges at which a combination of gas and liquid is most stable (at this temperature). At lower temperatures, the gas's free energy curve moves up relative to that of the liquid ($\partial G/\partial T = -S$), so the intersections move farther apart. At higher temperatures, the gas's free energy curve moves down relative to that of the liquid, so the intersections move closer together until finally the two curves just kiss each other at a single point. The composition at that point is the azeotrope; a mixture of this composition condenses abruptly at a well-defined temperature, just as a pure substance would.



Problem 5.67. (Analytic treatment of phase changes of an ideal mixture.)

- a) We can compute the chemical potential of species A by differentiating the Gibbs free energy with respect to N_A . Starting with equation 5.61 for the Gibbs free energy of an ideal mixture, note that $x = N_B/(N_A + N_B)$ and $1 - x = N_A/(N_A + N_B)$. Furthermore, $G_A^\circ = N_A^\circ$ and $G_B^\circ = N_B^\circ$, where $N = N_A + N_B$ is assumed to equal Avogadro's number in equation 5.61. Therefore,

$$\begin{aligned} G &= N_A^\circ + N_B^\circ + kT \left[N_B \ln \frac{N_B}{N_A + N_B} + N_A \ln \frac{N_A}{N_A + N_B} \right] \\ &= N_A^\circ + N_B^\circ + kT [N_A \ln N_A + N_B \ln N_B - (N_A + N_B) \ln(N_A + N_B)]. \end{aligned}$$

Differentiating with respect to N_A and N_B then gives

$$\begin{aligned} {}_A \frac{\partial G}{\partial N_A} &= {}_A^\circ + kT [\ln N_A + 1 - \ln(N_A + N_B) - (N_A + N_B)/(N_A + N_B)] \\ &= {}_A^\circ + kT \ln \frac{N_A}{N_A + N_B} = {}_A^\circ + kT \ln(1 - x); \\ {}_B \frac{\partial G}{\partial N_B} &= {}_B^\circ + kT [\ln N_B + 1 - \ln(N_A + N_B) - (N_A + N_B)/(N_A + N_B)] \\ &= {}_B^\circ + kT \ln \frac{N_B}{N_A + N_B} = {}_B^\circ + kT \ln x. \end{aligned}$$

- b) Diffusive equilibrium of the A molecules between the liquid and gas phases implies that the chemical potentials of the A molecules in the two phases are equal to each other:

$${}_{A,l} = {}_{A,g}, \quad \text{or} \quad {}_{A,l}^\circ + kT \ln(1 - x_l) = {}_{A,g}^\circ + kT \ln(1 - x_g).$$

This equation can be rearranged to give

$$\frac{1 - x_l}{1 - x_g} = e^{({}_{A,g}^\circ - {}_{A,l}^\circ)/kT} = e^{-G_A^\circ/RT}, \quad (1)$$

where $\Delta G_A^\circ = N_{Av} (\overset{\circ}{A,g} - \overset{\circ}{A,l})$ is the change in Gibbs free energy when a mole of the pure liquid converts to gas. Similarly, diffusive equilibrium of the B molecules between the liquid and gas phases implies

$$x_l = x_g, \quad \text{or} \quad \overset{\circ}{B,l} + kT \ln x_l = \overset{\circ}{B,g} + kT \ln x_g.$$

This equation can be rearranged to give

$$\frac{x_l}{x_g} = e^{(\overset{\circ}{B,g} - \overset{\circ}{B,l})/kT} = e^{-G_B^\circ/RT}. \quad (2)$$

c) Equation (1) can be written

$$\ln \frac{1 - x_l}{1 - x_g} = \frac{\Delta G_A^\circ}{RT} = \frac{\Delta H_A^\circ}{RT} - \frac{\Delta S_A^\circ}{R}.$$

Assuming that ΔS_A° is independent of temperature, we can evaluate it at the boiling temperature T_A . At this temperature, the boiling of pure A is a reversible process that creates no extra entropy beyond that due to the heat input, $Q/T = \Delta H_A^\circ/T_A$. So, assuming also that ΔH_A° is independent of temperature, we have simply

$$\ln \frac{1 - x_l}{1 - x_g} = \frac{\Delta H_A^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_A} \right), \quad \text{or} \quad \frac{1 - x_l}{1 - x_g} = \exp \left[\frac{\Delta H_A^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_A} \right) \right] \equiv A(T),$$

where the last equality defines the abbreviation $A(T)$. Similarly, equation (2) can be written

$$\begin{aligned} \ln \frac{x_l}{x_g} &= \frac{\Delta G_B^\circ}{RT} = \frac{\Delta H_B^\circ}{RT} - \frac{\Delta S_B^\circ}{R} = \frac{\Delta H_B^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_B} \right) \\ \text{or} \quad \frac{x_l}{x_g} &= \exp \left[\frac{\Delta H_B^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_B} \right) \right] \equiv B(T), \end{aligned}$$

again assuming that ΔH_B° and ΔS_B° are independent of temperature. Solving this equation for x_l and plugging into the previous one a formula for x_g alone,

$$x_g = \frac{A(T)}{A(T) - B(T)},$$

while x_l is simply

$$x_l = x_g B(T).$$

d) To plot the phase diagram using *Mathematica*, I first defined the following functions:

```
a[t_] := Exp[hA((1/t)-(1/tA))]; b[t_] := Exp[hB((1/t)-(1/tB))];
xg[t_] := (a[t]-1)/(a[t]-b[t]); xl[t_] := xg[t]*b[t];
```

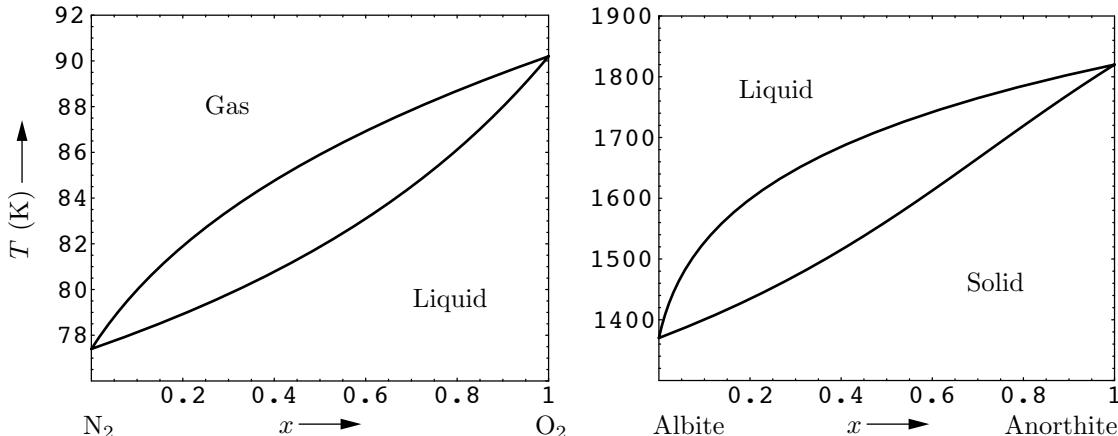
(The constants hA and hB are actually $\Delta H_A^\circ/R$ and $\Delta H_B^\circ/R$.) I then defined the numerical constants for the nitrogen-oxygen system:

```
tA = 77.4; tB = 90.2; hA = 5570/8.315; hB = 6820/8.315;
```

Finally, I issued the following plot command:

```
ParametricPlot[{{xg[t],t},{x1[t],t}}, {t,77.4,90.2},
  PlotRange->{{0,1},{76,92}}, AspectRatio->.8, Frame->True]
```

This produced the plot shown at left below, which is quite similar to Figure 5.31, and almost certainly within the range of uncertainty of the data used to plot Figure 5.31.



- e) To reproduce the phase diagram for plagioclase feldspar, all I had to do was change the numerical constants in the *Mathematica* code used in part (d). The melting temperatures of the pure substances can be read off Figure 5.32. To find the corresponding enthalpies of melting, I just tried various numbers until the plot approximately matched Figure 5.32. I found that the two curves moved farther apart as the enthalpy values increased, and grew more asymmetrical as the two values became more different. The plot above (right), which matches the data pretty well, was produced with the following values:

$$t_A = 1370; t_B = 1820; h_A = 50000/8.315; h_B = 115000/8.315;$$

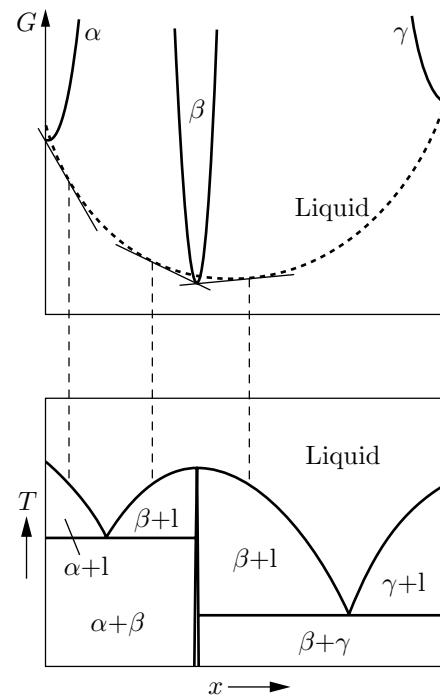
Incidentally, this same calculation and t was done by N. L. Bowen in his 1913 paper, cited in the caption to Figure 5.32. The paper is an outstanding and historical example of both experimental and theoretical applied thermodynamics. It is also very readable, and I highly recommend it.

Problem 5.68. According to Figure 5.34, a liquid mixture of 67% lead and 33% tin (by weight) should begin to crystallize when it cools to about 250°C. The first crystals to form will be about 85% lead. The liquid consequently becomes more tin-rich, so its composition moves to the left of the phase diagram as the temperature drops further, until it reaches the eutectic point where the remaining liquid solidifies. Therefore, unlike electrical solder, this mixture hardens gradually, becoming progressively “thicker” as the temperature drops and the crystals grow. The advantage is that the plumber can still make small adjustments as the solder thickens and hardens.

Problem 5.69. Solid salt crystals in contact with ice, at a temperature not too far below 0°C, are out of thermal equilibrium; the equilibrium state is instead a liquid mixture of salt and water (possibly with some solid present, depending on the proportions of each). In other words, adding salt reduces the freezing point of the water, just as adding lead reduces the freezing point of tin. However, this procedure is useless if the temperature is below the eutectic point, -21°C for this system.

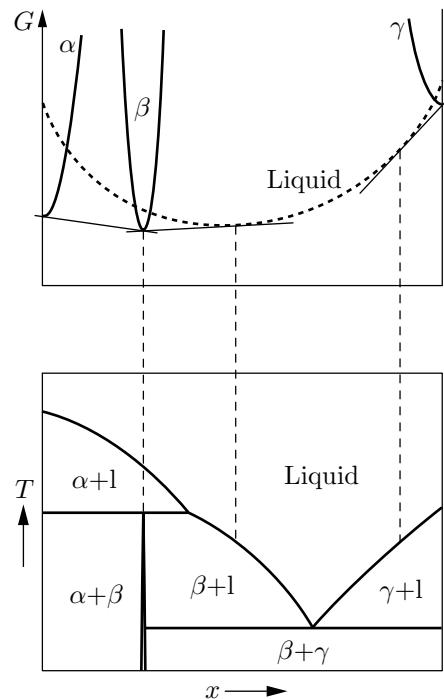
Problem 5.70. The ice bath in an ice cream maker needs to be significantly colder than 0°C, so salt is added to lower the freezing point, just as adding lead to tin lowers its freezing point. Assuming that the mixture is well insulated and the salt crystals aren't too warm to begin with, the mixture will actually cool spontaneously below the initial temperature of the ice, because breaking the chemical bonds in the solid crystals requires energy, and this energy comes from the kinetic energies of the particles. In other words, it's the fastest-moving salt ions and water molecules that escape from the crystals into the liquid, but they slow down as they escape, because of the attractive forces that held them in. This process is analogous to evaporative cooling of liquids such as water.

Problem 5.71. At the temperature shown in the free energy graph, I've drawn three tangent lines to determine the composition ranges where the stable state is inhomogeneous. Starting at small values of x , there is first a range over which α plus liquid is stable, then a range of just liquid, then β plus liquid, then a very narrow range of just β , then β plus liquid again, and finally just liquid (again). If we raise the temperature, the free energy graph of the liquid moves down relative to those of the solids ($\partial G / \partial T = S$), so the stability ranges of β and then γ soon disappear. If we lower the temperature, a stability range of γ plus liquid appears at large x . Meanwhile, the stability ranges of the liquid become narrower until they disappear at eutectic points. At very low temperature the stable phases are $\alpha + \beta$ and $\beta + \gamma$, separated by a narrow range of just β . Theoretically, there are ranges near $x = 0$ and $x = 1$ where just α and just γ are stable, but these ranges are too narrow to show on the diagram.



Problem 5.72. At the temperature shown in the free energy graph, I've drawn three tangent lines to determine the composition ranges where the stable state is inhomogeneous. Starting at small values of x , there is

rst a range over which $\alpha + \beta$ is stable, then a narrow range of just β , then β plus liquid, then just liquid, then γ plus liquid. If we raise the temperature, the free energy graph of the liquid moves down relative to those of the solids ($\partial G / \partial T = -S$), so we soon reach a temperature at which a tangent line from the γ curve to the liquid curve lies entirely below the β curve. The temperature where this rst happens is called the peritectic temperature, and the composition at which the tangent line meets the liquid free energy curve is called the peritectic composition. Above the peritectic temperature, $\gamma + \text{liquid}$ is always more stable than β . At a slightly higher temperature, the stability range of $\gamma + \text{liquid}$ disappears. As the temperature is lowered, on the other hand, the stability range of just liquid narrows until it ends at a eutectic point.



Problem 5.73. Starting with equation 5.68, combine the third and fourth terms into a single logarithm to obtain

$$G = N_A \phi_0(T, P) + N_B f(T, P) + N_B kT \ln(N_B/N_A) - N_B kT.$$

Since the ratio N_B/N_A is intensive, as are T and P , each term in this expression is extensive by virtue of the initial factor of N_A or N_B . That is, if we multiply both N_A and N_B by a common factor c , then each term picks up exactly one such factor, so it can be factored out, yielding the original expression times c .

On the other hand, if we hadn't added the term $kT \ln N_B$! (which accounted for the indistinguishability of the B molecules) to the Gibbs free energy, then the last two terms in equation 5.68 would not be present, so we would have simply

$$G = N_A \phi_0(T, P) + N_B f(T, P) - N_B kT \ln N_A \quad (\text{wrong}).$$

In this expression, multiplying both N_A and N_B by a common factor c would increase the rst two terms by this factor, but the nal term would also pick up a c inside the logarithm. That term, and therefore the entire expression, would not be extensive. (If we really did have a system containing N_B distinguishable solute molecules, then increasing the number of such molecules would not simply increase the size of the system—it would also increase the complexity—so we would expect an additional contribution to the entropy beyond a simple scale factor.)

Problem 5.74. According to equations 5.69 and 5.70,

$$\begin{aligned} N_A \cdot A + N_B \cdot B &= N_A \left(\underset{0}{\circ} - \frac{N_B kT}{N_A} \right) + N_B \left(f + kT \ln \frac{N_B}{N_A} \right) \\ &= N_A \cdot 0 - N_B kT + N_B f + N_B kT \ln(N_B/N_A), \end{aligned}$$

which is the same as expression 5.68 for G . Therefore, $G = N_A \cdot A + N_B \cdot B$.

Problem 5.75. Expression 5.61 (for an ideal mixture) should apply to a dilute solution when the ideal mixture is also dilute—that is, when $N_B \ll N_A$. Expression 5.68 (for a dilute solution) should apply to an ideal mixture when the solution is ideal—that is, when the B molecules “behave” just like A molecules, in terms of their sizes and interactions. To show the agreement between the two expressions under these circumstances, I’ll start with equation 5.61. Recall first that $x = N_B/N_{\text{total}}$, $1-x = N_A/N_{\text{total}}$, so $(1-x)G_A^\circ = N_A G_A^\circ / N_{\text{total}} = N_A \cdot A$, and similarly, $xG_B^\circ = N_B \cdot B$. In the last term, since N_{total} is assumed to be Avogadro’s number, we can write $R = N_{\text{total}} \cdot k$. Equation 5.61 is therefore equivalent to

$$\begin{aligned} G &= N_A \cdot A + N_B \cdot B + kT \left[N_B \ln \frac{N_B}{N_A + N_B} + N_A \ln \frac{N_A}{N_A + N_B} \right] \\ &= N_A \cdot A + N_B \cdot B - kT \left[N_B \ln \left(\frac{N_A}{N_B} + 1 \right) + N_A \ln \left(1 + \frac{N_B}{N_A} \right) \right]. \end{aligned}$$

Now assume that this ideal mixture is also dilute, so $N_B \ll N_A$. Then the 1 in the first logarithm can be dropped, while the second logarithm can be approximated as simply N_B/N_A . With these approximations,

$$G \approx N_A \cdot A + N_B \cdot B - kT [N_B \ln(N_A/N_B) + N_B],$$

up to correction terms that are small compared to the terms that are shown. But this expression is the same as equation 5.68, if we identify

$$f(T, P) = \underset{B}{\circ}(T, P) \quad (\text{ideal, dilute solution}).$$

In other words, the mysterious function $f(T, P)$, in the case of a dilute solution that is also ideal, is just the chemical potential of a system of pure B molecules at the same temperature and pressure.

Problem 5.76. (Osmotic pressure of seawater.)

- a) Let’s take as our system a kilogram of seawater at room temperature. Then the volume is approximately one liter (10^{-3} m^3). The total mass of solute is 35 g, and the average atomic mass of sodium and chlorine is about 29.2 g/mol, so the number of moles of solute is

$$n_B = \frac{35 \text{ g}}{29.2 \text{ g/mol}} = 1.12 \text{ mol.}$$

Therefore, by van't Hoff's formula, the osmotic pressure is

$$P_2 - P_1 = \frac{n_B RT}{V} = \frac{(1.12 \text{ mol})(8.315 \text{ J/mol K})(300 \text{ K})}{10^{-3} \text{ m}^3} = 3.0 \times 10^6 \text{ Pa} \approx 30 \text{ atm.}$$

- b) If you apply an excess pressure just barely greater than the osmotic pressure to the seawater, and force 1 liter of it through an osmotic membrane, the work performed is

$$P \Delta V = (3.0 \times 10^6 \text{ Pa})(10^{-3} \text{ m}^3) = 3000 \text{ J.}$$

This isn't much work—less than 1/1000 of a kilowatt-hour. As usual, though, this number represents the absolute minimum, and in practice the work required will be greater. First, to get the water to go through the membrane at an acceptable rate, you'll need to apply more than the minimum pressure. Second, the membrane probably won't be perfect, so some salt will get through and you'll need to repeat the process several times to reduce the salinity to an acceptable level.

Problem 5.77. When the difference in fluid level between the two sides of the container is Δh , the difference in pressure should be $\rho g \Delta h$, where ρ is the density of the solution (close enough to the density of pure water). Plugging this in for the pressure difference in van't Hoff's formula gives

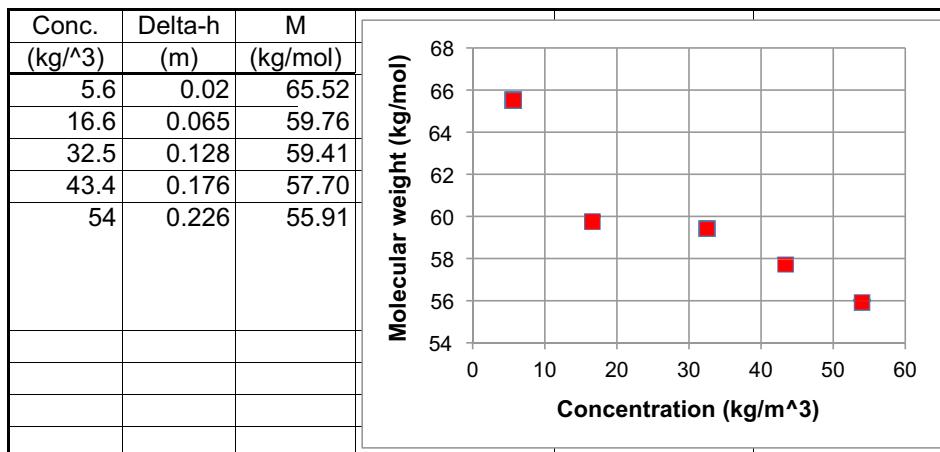
$$\rho g \Delta h = \frac{n_B RT}{V}.$$

But the number of moles of solute, n_B , is equal to mass of the solute, m , divided by its molecular weight, M , in grams per mole. Therefore,

$$\rho g \Delta h = \frac{mRT}{MV}, \quad \text{or} \quad M = \frac{RT}{\rho g} \frac{m/V}{\Delta h}.$$

I used this equation to calculate M for each of the five data points given (see the spreadsheet below). The coefficient $RT/\rho g$ is

$$\frac{RT}{\rho g} = \frac{(8.315 \text{ J/mol K})(276 \text{ K})}{(1000 \text{ kg/m}^3)(9.8 \text{ N/kg})} = 0.234 \text{ m}^4/\text{mol.}$$



From the graph you can see that the calculated value of M does depend somewhat on the concentration, in violation of van't Hoff's formula. However, the trend indicates a value of $M \approx 66,000 \text{ g/mol}$ in the limit of low concentration where the formula should be valid.

Problem 5.78. Imagine plotting a graph of π_0 vs. P (at fixed T). If the slope of this graph is constant over the relevant range of pressures, then we can approximate π_0 as a linear function of P . But the slope of the graph is

$$\frac{\partial \pi_0}{\partial P} = \frac{1}{N_A} \frac{\partial G^\circ}{\partial P} = \frac{1}{N_A} V^\circ,$$

where V° is the volume of the pure solvent. The question, then, is whether this volume varies much with pressure. But liquids are not very compressible; for instance, it takes 200 atm of pressure to reduce the volume of water by 1% (see Problem 1.32). The osmotic pressures in the examples treated here are no more than a few tens of atmospheres, so the slope $\partial \pi_0/\partial P$ should vary by no more than one part in a thousand, and therefore the linear approximation should be excellent.

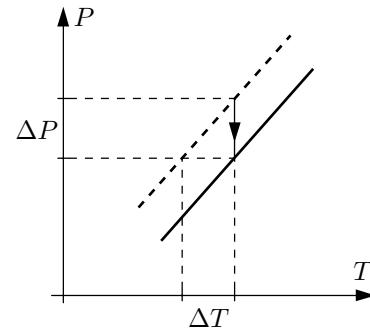
Problem 5.79. According to the label on my salt container, a teaspoon of salt has a mass of about 6 g. The average mass of a sodium or chlorine atom is 29.2 g, so the number of moles of ions in a teaspoon of dissolved salt is $(6 \text{ g})/(29.2 \text{ g/mol}) = 0.205 \text{ mol}$. Suppose that the pot contains only one liter of water. Then according to equation 5.90, the increase in boiling temperature due to the salt is

$$\Delta T = \frac{n_{\text{salt}}RT_0^2}{L} = \frac{(0.205 \text{ mol})(8.31 \text{ J/mol K})(373 \text{ K})^2}{2260 \text{ kJ}} = 0.105 \text{ K} \approx 0.1 \text{ K}.$$

This is not enough to have any appreciable effect on the cooking. Unless the salt participates in some chemical reaction, its only significant effect will be on the flavor.

Problem 5.80. According to Raoult's law, adding a solute lowers the vapor pressure by an amount $\Delta P = (N_B/N_A)P$, where N_B/N_A is the molecular fraction of solute to solvent and P is the original vapor pressure. Graphically, this effect can be represented as shown on the phase diagram at right. Assuming that ΔP is small, we can treat the phase boundary as a straight line. In this case, we could just as well say that the phase boundary has been shifted to the right by some amount ΔT . To relate ΔT to ΔP we can use the Clausius-Clapeyron relation:

$$\Delta T = \frac{T(V_g - V_l)}{L} \Delta P.$$



The volume of the liquid phase is negligible to that of the gas phase, while the volume of gas phase is $N_A kT/P$ by the ideal gas law. Therefore,

$$\Delta T = \frac{T(N_A kT/P)}{L} \frac{N_B P}{N_A} = \frac{N_B kT^2}{L},$$

which is the same upward temperature shift derived in equation 5.90.

Problem 5.81. For a solution of solute B in solvent A , in equilibrium with a solid of pure A , the chemical potentials of A must be equal for the two phases:

$$\mu_A^{\text{liq}} = \mu_A^{\text{solid}}.$$

Using equation 5.69 to rewrite the left-hand side, this condition becomes

$$(T, P) \frac{N_B k T}{N_A} = \mu_{\text{solid}}(T, P).$$

Now let T_0 be the temperature at which the pure liquid would be in equilibrium with the solid (at fixed pressure P). Expanding each chemical potential about T_0 , we have

$$\mu_0(T_0, P) + (T - T_0) \frac{\partial \mu_0}{\partial T} - \frac{N_B k T}{N_A} = \mu_{\text{solid}}(T_0, P) + (T - T_0) \frac{\partial \mu_{\text{solid}}}{\partial T}.$$

The first term on each side of this equation cancels by the assumption that T_0 is the temperature at which the pure liquid is in equilibrium with the solid. Each $\partial \mu / \partial T$ is minus the entropy per particle for that phase, so

$$(T - T_0) \left(\frac{S}{N} \right)_{\text{liq}} - \frac{N_B k T}{N_A} = (T - T_0) \left(\frac{S}{N} \right)_{\text{solid}}.$$

Now set the N under each S equal to N_A , the number of molecules of solvent; the S 's then apply to the same quantity, and our relation becomes

$$(T - T_0)(S_{\text{liq}} - S_{\text{solid}}) = N_B k T, \quad \text{or} \quad T - T_0 = \frac{N_B k T^2}{L},$$

where in the last step I've used $L = \Delta S/T_0 \approx \Delta S/T$, taking L to represent the latent heat for transformation of N_A molecules of solid into liquid. The minus sign in this result indicates that adding a solute *lowers* the freezing point of a liquid. This makes sense because mixing is allowed in the liquid phase but not the solid phase, so we would expect the entropy of mixing to increase the stability of the liquid relative to that of the solid. We saw the same result qualitatively in the last part of Section 5.4.

Problem 5.82. To compute the freezing point of seawater, we need to know that a kilogram of seawater contains 1.2 moles of salt ions, as computed at the bottom of page 207. We also need the latent heat of the ice-water transformation, which from page 33 is 333 J/g or 333,000 J/kg. Plugging these numbers into the formula derived in the previous problem gives

$$\Delta T = \frac{n_B R T^2}{L} = \frac{(1.2 \text{ mol})(8.31 \text{ J/mol K})(273 \text{ K})^2}{333,000 \text{ J/kg}} = 2.2 \text{ K}.$$

The freezing point of seawater should therefore be -2.2°C .

Problem 5.83. For each reaction shown, the equilibrium condition is the same as the reaction equation, with the name of the species replaced by its chemical potential and \leftrightarrow replaced by =:

- a) $2 \text{ H} = \text{H}_2$
- b) $2 \text{ CO} + \text{O}_2 = 2 \text{ CO}_2$
- c) $\text{methane} + 2 \text{ O}_2 = 2 \text{ water} + \text{CO}_2$
- d) $\text{H}_2\text{SO}_4 = 2 \text{ H} + \text{SO}_4^2$
- e) $2 \text{ p} + 2 \text{ n} = \text{He}$

Problem 5.84. I'll use the convention that all pressures are expressed in atmospheres, so $P^\circ = 1$ and the total pressure is 400:

$$P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3} = 400.$$

The initial mixture consists of three parts hydrogen to one part nitrogen, and this proportion is preserved as the reaction takes place, so $P_{\text{H}_2} = 3P_{\text{N}_2}$ and hence

$$4P_{\text{N}_2} + P_{\text{NH}_3} = 400. \quad (1)$$

Meanwhile, the law of mass action tells us that

$$\frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = K.$$

But again, $P_{\text{H}_2} = 3P_{\text{N}_2}$, so

$$\frac{P_{\text{NH}_3}^2}{27P_{\text{N}_2}^4} = K \quad \text{or} \quad P_{\text{NH}_3} = P_{\text{N}_2}^2 \sqrt{27K} = P_{\text{N}_2}^2 \cdot 0.0432,$$

where I've plugged in the value $K = 6.9 \times 10^{-5}$. Plugging this relation into equation 1 then gives the quadratic equation

$$(0.0432)P_{\text{N}_2}^2 + 4P_{\text{N}_2} - 400 = 0,$$

whose solutions are

$$P_{\text{N}_2} = \frac{4 \pm \sqrt{16 + 4(0.0432)(400)}}{2(0.0432)} = 46.3 \pm 106.8 = 153.1 \text{ or } 60.5.$$

The negative solution is obviously unphysical, so the partial pressure of N_2 at equilibrium must be roughly 60 atm. That means the partial pressure of H_2 must be three times as much, or 180 atm, and the partial pressure of ammonia must make up the remaining 160 atm to give 400 atm total. The ratio of nitrogen atoms in ammonia to nitrogen atoms in N_2 is then $160/(2 \cdot 60) = 4/3$, meaning that $4/7$ of all the nitrogen atoms are in ammonia.

Problem 5.85. By the definition (5.107) of the equilibrium constant,

$$\frac{\partial}{\partial T}(\ln K) = \frac{\partial}{\partial T}\left(-\frac{\Delta G^\circ}{RT}\right) = -\frac{1}{R} \frac{T(\partial\Delta G^\circ/\partial T)}{T^2} = -\frac{\Delta G^\circ}{T^2},$$

where all the partial derivatives are taken at fixed pressure. But for either the reactants or the products, $\partial G/\partial T = -S$, so the derivative of ΔG° is just $-\Delta S^\circ$, and therefore,

$$\frac{\partial}{\partial T}(\ln K) = -\frac{1}{R} \frac{T\Delta S^\circ - (\Delta H^\circ - T\Delta S^\circ)}{T^2} = \frac{\Delta H^\circ}{RT^2}.$$

This is van't Hoff's equation. (For an ideal gas reaction, K is independent of pressure so the partial derivative can be written as a total derivative.) This is a separable differential equation, so we can separate it and integrate:

$$\int d(\ln K) = \frac{1}{R} \int \frac{\Delta H^\circ}{T^2} dT,$$

where each integral is taken from the initial to the final temperature. In the approximation that ΔH° is independent of temperature, the right-hand side can be integrated to give

$$\ln K(T_2) - \ln K(T_1) = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} T^{-2} dT = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Problem 5.86. The table on page 405 gives ΔH° for production of a mole of ammonia (from elemental constituents, N₂ and H₂, and at 298 K) as -46.11 kJ. For two moles of ammonia we just multiply this value by 2. The equilibrium constant at 298 K was already computed in equation 5.109. Therefore, in the approximation that ΔH° is independent of temperature,

$$\ln K(773 \text{ K}) = \ln(5.9 \times 10^5) + \frac{92.2 \text{ kJ}}{8.31 \text{ J/K}} \left(\frac{1}{298 \text{ K}} - \frac{1}{773 \text{ K}} \right) = 13.29 - 22.94 = -9.65.$$

Exponentiating this number gives $K = 6.4 \times 10^{-5}$, only slightly less than the value quoted in the text.

Problem 5.87. (Sulfuric acid.)

- a) The law of mass action for the first dissociation reaction is

$$\frac{m_{\text{H}} m_{\text{HSO}_4}}{m_{\text{H}_2\text{SO}_4}} = 10^2.$$

Since the equilibrium constant is so huge compared to that for dissociation of water, we can neglect any H⁺ ions that come from dissociation of water and assume that the molalities of H⁺ and HSO₄⁻ are equal. Then

$$m_{\text{HSO}_4}^2 = 10^2 m_{\text{H}_2\text{SO}_4}, \quad \text{or} \quad m_{\text{HSO}_4} = 10\sqrt{m_{\text{H}_2\text{SO}_4}}.$$

Now let's try some numbers. If the molality of H_2SO_4 is 1, then the molality of HSO_4^- is 10, so more than 90% of the acid is dissociated. If the molality of H_2SO_4 is less than 1, then the square root gives a number greater than its argument, so the molality of HSO_4^- is *more* than ten times that of H_2SO_4 . Only when the molality of H_2SO_4 is somewhat greater than 1 do the two concentrations become comparable. But an HSO_4^- molality of 10 implies an H^+ molality of 10, that is, a pH of 1. This is a *very* acidic solution, and can hardly be considered dilute. Conclusion: In all situations we are likely to encounter, this reaction will have gone almost to completion, so essentially all the sulfuric acid will be dissociated.

- b) The law of mass action for the second dissociation reaction is

$$\frac{m_{\text{H}} \quad m_{\text{SO}_4^2}}{m_{\text{HSO}_4}} = 10^{-1.9} = 0.013.$$

To check whether this reaction essentially goes to completion at a sulfate concentration of 5×10^{-5} mol/kg, let's just plug in this number for the molality of SO_4^{2-} and check that the molality of HSO_4^- is much less:

$$m_{\text{HSO}_4} = \frac{m_{\text{H}} \quad m_{\text{SO}_4^2}}{0.013} = \frac{(10^{-4})(5 \times 10^{-5})}{0.013} = 4 \times 10^{-7}.$$

(Note that the molality of H^+ is twice that of sulfate, since each sulfuric acid molecule gives up two H^+ ions.) Apparently, the concentration of HSO_4^- is about 100 times less than that of SO_4^{2-} , so indeed, this reaction has also gone essentially to completion. In this case the molality of H^+ is 10^{-4} , so water with this sulfate concentration has a pH of 4.

- c) The law of mass action for dissociation of water is

$$m_{\text{H}} \quad m_{\text{OH}} = 10^{-14}.$$

With $m_{\text{H}} = 10^{-4}$, this implies $m_{\text{OH}} = 10^{-10}$, quite negligible compared to the other ion concentrations. Under these conditions, water dissociates even less than it would when pure, so the dissociation of water is insignificant here.

- d) Looking again at the law of mass action for the second dissociation reaction in part (b), we see that for the two sulfate ion concentrations to be equal, we must have

$$m_{\text{H}} = 10^{-1.9},$$

that is, a pH of 1.9. That's a pretty strong acid.

Problem 5.88. For the solution of either the reactants or the products, we can write $(\partial G / \partial P)_T = V$, or $dG = V dP$ at fixed temperature. Taking differences between reactants and products then gives

$$d(\Delta G^\circ) = (V_{\text{products}} - V_{\text{reactants}})dP.$$

But in a dilute solution, the volume isn't going to change much as a reaction takes place among the solutes. For instance, suppose that in a 1-molal solution with a kilogram of

solvent the volume changes by as much as 0.1 liter. Then the change in ΔG° with pressure is

$$d(\Delta G^\circ) = (10^{-4} \text{ m}^3)dP,$$

or about 10 J per atmosphere of additional pressure. But typical values of ΔG° are at 10^4 J, so to change the value of ΔG° by even 1%, we would need at least ten atmospheres of pressure, and in most cases we would need hundreds or thousands of atmospheres. Such pressures are common in geological applications, but in most situations we can de nitely ignore the pressure dependence of ΔG° and hence of K , the equilibrium constant.

Problem 5.89. The equilibrium constant for oxygen dissolving in water at 25°C was computed in equation 5.124: $K = 0.00133$, or $\ln K = -6.62$. Assuming that the value $\Delta H^\circ = 11.7 \text{ kJ}$ is approximately independent of temperature, we then have for any temperature T_2 ,

$$\ln K(T_2) = \ln K(T_1) + \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = -6.62 - \frac{11.7 \text{ kJ}}{8.31 \text{ J/K}} \left(\frac{1}{298 \text{ K}} - \frac{1}{T_2} \right).$$

For $T_2 = 0^\circ\text{C}$, this formula gives

$$\ln K(273 \text{ K}) = -6.62 - (1407 \text{ K}) \left(\frac{1}{298 \text{ K}} - \frac{1}{273 \text{ K}} \right) = -6.62 + 0.43 = -6.19,$$

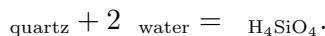
or $K = e^{-6.19} = 0.0021$. For $T_2 = 100^\circ\text{C}$, the formula gives

$$\ln K(373 \text{ K}) = -6.62 - (1407 \text{ K}) \left(\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}} \right) = -6.62 - 0.95 = -7.57,$$

or $K = e^{-7.57} = 5.2 \times 10^{-4}$. The negative value of ΔH° implies that the equilibrium constant decreases with increasing temperature. That is, less oxygen will dissolve in water at high temperature than at low temperature.

Problem 5.90. (Dissolution of silica.)

a) The equilibrium condition for this reaction is



The chemical potentials of the quartz and the water are unaffected by the reaction, while that of H_4SiO_4 can be expressed in terms of the molality as usual. So we have

$$\overset{\circ}{\text{quartz}} + 2 \overset{\circ}{\text{water}} = \overset{\circ}{\text{H}_4\text{SiO}_4} + kT \ln m_{\text{H}_4\text{SiO}_4},$$

or simply

$$\ln m_{\text{H}_4\text{SiO}_4} = \frac{\Delta G^\circ}{RT},$$

where ΔG° is the change in G when one mole of quartz undergoes dissolution into a 1-molar solution. (Notice that for this reaction, the law of mass action is simply $m = K$.) From the data on page 405, this ΔG° value is

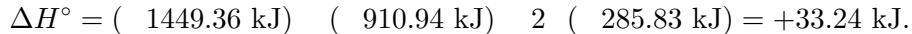
$$\Delta G^\circ = (-1307.67 \text{ kJ}) - (856.64 \text{ kJ}) - 2(-237.13 \text{ kJ}) = +23.23 \text{ kJ}.$$

Therefore, in equilibrium at 298 K,

$$\ln m_{\text{H}_4\text{SiO}_4} = \frac{22.23 \text{ kJ}}{(8.31 \text{ J/K})(298 \text{ K})} = 9.37,$$

or $m_{\text{H}_4\text{SiO}_4} = e^{9.37} = 8.5 \times 10^{-5}$. This means that in a kilogram of water (one liter) there will be 8.5×10^{-5} moles of dissolved silica. Since SiO_2 has a molecular weight of 60 g/mol, that's about 5 mg of quartz dissolved in each kilogram of water.

- b) To apply the van't Hoff equation, we need the ΔH° value for this reaction:



Assuming that this value is approximately independent of temperature, the van't Hoff equation then predicts

$$\ln K(373 \text{ K}) = \ln K(298 \text{ K}) + \frac{33.24 \text{ kJ}}{8.31 \text{ J/K}} \left(\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}} \right) = 9.37 + 2.70 = 6.67.$$

Therefore, at 100°C, $m_{\text{H}_4\text{SiO}_4} = K = e^{6.67} = 0.00127$. This is 15 times greater than at 25°C. Because most rocks are rich in silica, hot water flowing through rocks tends to dissolve quite a bit of silica. As the water flows into cooler rocks the silica then comes out of solution to form deposits of microcrystalline quartz.

Problem 5.91. For the dissolution of carbon dioxide to form H_2CO_3 , the law of mass action is

$$\frac{m_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2}/P^\circ} = K = e^{-G^\circ/RT},$$

where the standard change in G is, according to the data on pages 404–405,

$$\Delta G^\circ = (-623.08 \text{ kJ}) - (394.36 \text{ kJ}) - (237.13 \text{ kJ}) = 8.41 \text{ kJ}$$

at room temperature. Therefore, at $P_{\text{CO}_2}/P^\circ = 3.4 \times 10^{-4}$, the molality of dissolved H_2CO_3 should be

$$m_{\text{H}_2\text{CO}_3} = (3.4 \times 10^{-4}) \exp\left(-\frac{8.41 \text{ kJ}}{(8.31 \text{ J/K})(298 \text{ K})}\right) = 1.14 \times 10^{-5}.$$

Meanwhile, for the dissociation reaction, the law of mass action is

$$\frac{m_{\text{H}} m_{\text{HCO}_3}}{m_{\text{H}_2\text{CO}_3}} = K = e^{-G^\circ/RT},$$

where

$$\Delta G^\circ = (-586.77 \text{ kJ}) + 0 - (623.08 \text{ kJ}) = 36.31 \text{ kJ.}$$

Assuming that essentially all the H^+ ions come from this reaction (rather than from dissociation of water), we can set the molality of H^+ equal to the molality of HCO_3^- to obtain

$$m_{\text{HCO}_3^-} = \sqrt{(1.14 \times 10^{-5}) \exp\left(-\frac{36.31 \text{ kJ}}{(8.31 \text{ J/K})(298 \text{ K})}\right)} = 2.2 \times 10^{-6}.$$

The molality of H^+ would be the same, giving the solution a pH value of $\log_{10}(2.2 \times 10^{-6}) = 5.7$. Because this concentration is about 22 times that in “pure” water, the approximation of neglecting H^+ ions from dissociation of water is reasonably accurate.

Problem 5.92. (Ionization of hydrogen.)

- a) Since the system initially contains nothing but neutral hydrogen, the number of free electrons must always be equal to the number of ionized protons. Therefore the Saha equation becomes

$$\frac{P_p^2}{P_H} = kT \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-I/kT}.$$

Instead of working with partial pressures, let me rewrite each P in terms of the number of particles N , using the ideal gas law. The kT on the right-hand side then cancels, leaving

$$\frac{N_p^2}{N_H} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-I/kT},$$

where V is the volume of the box. Now the problem asks for the *fraction* of ionized atoms, which I'll call x . This fraction is $x = N_p/N_0$, where N_0 is the total number of ionized and un-ionized atoms, that is, the initial number of atoms in the box. The number of un-ionized atoms is $N_H = (1 - x)N_0$, so the Saha equation now becomes

$$\frac{x^2}{1-x} = \frac{V}{N_0} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-I/kT} = \frac{kT_0}{P_0} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-I/kT},$$

where T_0 and P_0 are the initial temperature and pressure. Let me define the symbol α to be an abbreviation for the entire right-hand side of this equation. Then we have simply

$$\frac{x^2}{1-x} = \alpha, \quad \text{or} \quad x^2 + x\alpha = 0.$$

By the quadratic formula, the solution to this equation is

$$x = \frac{\pm \sqrt{\alpha^2 + 4}}{2} = -\frac{\alpha}{2} + \sqrt{\left(\frac{\alpha}{2}\right)^2 + 1},$$

where I've discarded the $-$ in \pm because x must be positive. This is the desired expression for x as a function of temperature. Notice that as the temperature goes to zero, so does α , and therefore so does x , as expected. The limit $T \rightarrow \infty$ is a bit harder to work out; since α then becomes very large, we can write

$$x = -\frac{\alpha}{2} + \frac{1}{2}\sqrt{1 + \frac{4}{\alpha^2}} \approx -\frac{\alpha}{2} + \frac{1}{2}\left(1 + \frac{1}{2} - \frac{4}{\alpha^2}\right) = -\frac{\alpha}{2} + \frac{1}{2} + 1 = 1,$$

that is, fraction of ionized hydrogen approaches 100%, again as expected.

- b) For exactly half of the hydrogen to be ionized, we must have $x = (1 - x) = 1/2$, which implies $\alpha = 1/2$. To find the corresponding temperature, it's easiest to express α in terms of the dimensionless variable $t = kT/I$:

$$= \left[\frac{kT_0}{P_0} \left(\frac{2\pi mI}{h^2} \right)^{3/2} \right] t^{3/2} e^{-1/t}.$$

The bracketed expression, for our initial conditions, is

$$\frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{10^5 \text{ Pa}} \left(\frac{2\pi(9.1 \times 10^{-31} \text{ kg})(2.18 \times 10^{-18} \text{ J})}{(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 6272,$$

so we need to solve the transcendental equation

$$\frac{1}{2} = (6272)t^{3/2}e^{-1/t}.$$

To do so, I used the `FindRoot` function of *Mathematica*:

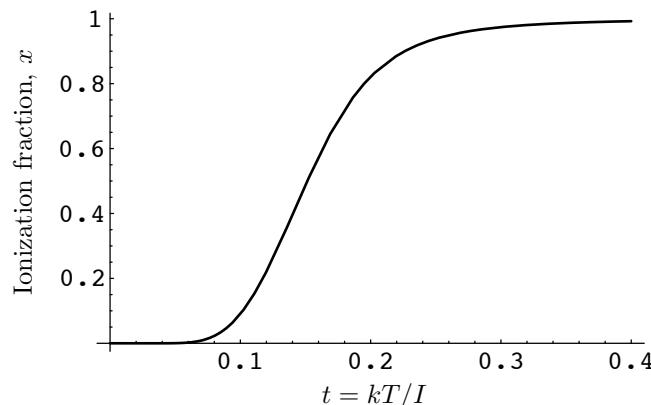
```
FindRoot[.5==6272*t^1.5*Exp[-1/t],{t,1}]
```

The value returned was $t = 0.1514$, corresponding to $T = (0.1514)I/k = 23,900 \text{ K}$ or about 24,000 K. Notice that 50% ionization occurs when kT , and hence the typical kinetic energy of the atoms, is much less than the ionization energy I . Under these conditions, the vast majority of collisions between atoms will not be violent enough to cause ionization. Apparently, recombination of an electron and a proton is also unlikely, due to all the space between particles, that is, due to the larger entropy of the ionized state.

- c) According to Le Chatelier's principle (page 212), increasing the total pressure should inhibit ionization, since there is less pressure when there are fewer free particles. And indeed, the quantity α is inversely proportional to P_0 , and the ionization fraction decreases when α decreases.
- d) To plot the ionization fraction, I used the *Mathematica* instructions

```
alpha = 6272*t^1.5*Exp[-1/t];
Plot[-(alpha/2)+Sqrt[(alpha/2)^2+alpha],{t,0,.4},PlotRange->All]
```

This produced the following graph:



Notice that most of the ionization occurs over a rather narrow range of temperatures, between t values of about 0.1 and 0.2. At lower temperatures, the ionization is exponentially suppressed. At $t = 0.5$, the ionization is essentially complete.

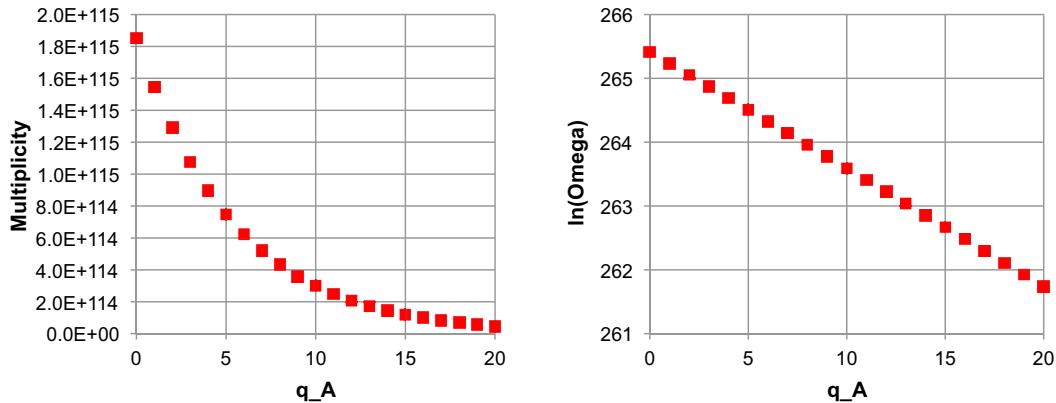
6 Boltzmann Statistics

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Problem 6.1. To make the table and graphs I modified the spreadsheet from Problem 2.10. I changed N_A to 1 and q_{total} to 500, then deleted all but the first 21 rows of the table (up to $q_A = 20$) and added a column for the logarithm of the total multiplicity. Here are the first few rows of the spreadsheet:

Two Einstein Solids					
$N_A = 1$	$N_B = 100$		$q_{\text{total}} = 500$		
q_A	Ω_A	q_B	Ω_B	Ω_{total}	$\ln(\Omega_{\text{total}})$
0	1	500	1.85×10^{115}	1.85×10^{115}	265.41
1	1	499	1.55×10^{115}	1.55×10^{115}	265.23
2	1	498	1.29×10^{115}	1.29×10^{115}	265.05
3	1	497	1.08×10^{115}	1.08×10^{115}	264.87
4	1	496	8.97×10^{114}	8.97×10^{114}	264.69

Here are graphs of the total multiplicity and its logarithm vs. q_A :



Notice that the shape of the first graph closely resembles a decaying exponential function, and the linearity of the second graph verifies that the shape is exponential to a good approximation. This is exactly what we should expect, because this system consists of a small system (A) in thermal contact with a much larger reservoir (B). In the approximation where the reservoir is infinitely larger than the small system, the Boltzmann distribution should apply so the probability of the small system containing q_A units of energy should be proportional to an exponential function of $-q_A$. The multiplicity of the combined system is proportional to the probability of the small system having q_A units of energy, so the multiplicity graph should also be a decaying exponential. According to the Boltzmann distribution, the slope of the graph of $\ln \Omega$ should be $-\epsilon/kT$, where ϵ is the size of an energy unit and T is the temperature of the reservoir. But according to our definition of

temperature, the reservoir temperature is given by

$$\frac{1}{T_B} = \frac{\partial S_B}{\partial U_B} = \frac{\partial S_B}{\partial U_A} = \frac{k}{\epsilon} \frac{\partial(\ln \Omega_B)}{\partial q_A}.$$

The final partial derivative is the slope of the second graph above, so indeed, that slope is ϵ/kT , in accord with the Boltzmann distribution.

Problem 6.2. If a particular energy level has n degenerate states, then the probability of the system being in that level is just n times the probability of being in any one of the states:

$$\mathcal{P}(E) = n\mathcal{P}(s) = n \frac{1}{Z} e^{-E/kT}.$$

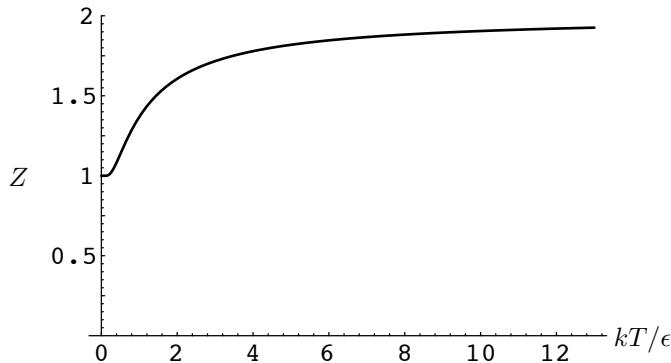
If we write n as $e^{\ln n} = e^{S/k}$ (defining $S = k \ln n$), then this becomes

$$\mathcal{P}(E) = \frac{1}{Z} e^{S/k} e^{-E/kT} = \frac{1}{Z} e^{-(E - TS)/kT} = \frac{1}{Z} e^{-F/kT}.$$

Problem 6.3. For this two-state system,

$$Z = e^0 + e^{-\epsilon/kT} = 1 + e^{-\epsilon/kT},$$

where $\epsilon = 2$ eV is the energy of the excited state. Thus Z varies between 1 (in the limit $T \rightarrow 0$) and 2 (in the limit $T \rightarrow \infty$). To plot the partition function vs. temperature it's convenient to define the dimensionless variable $t = kT/\epsilon$, so $Z = 1 + e^{-1/t}$. The value of t at $T = 300$ K is about $1/80 = .013$, while the value of t at $T = 300,000$ K is about 13. (Recall that at 300 K, $kT = .026$ eV $\approx 1/40$ eV.) Here, then, is a plot of Z vs. t for values of t up to 13:



Problem 6.4. Since the ground state of this system has energy 0, it contributes exactly $e^0 = 1$ to the partition function. The remaining states contribute in proportion to their Boltzmann factors, which are just the heights of the gray bars in the graph. With a ruler I measured the total height of the nine gray bars to be 13.0 cm. The height of the first bar is 4.4 cm, so relative to the height of the first bar, the total of all of them is $13/4.4 = 2.95$, or about 3. Therefore $Z \approx 3$, and the probability of the ground state is $1/Z \approx 1/3$.

Problem 6.5. (A three-state toy model.)

- a) At 300 K, $kT = 0.026$ eV, as computed on page 13. Therefore the partition function for this system is

$$Z = e^{(-0.05/0.026)} + e^0 + e^{(0.05/0.026)} = 6.84 + 1 + 0.15 = 7.99.$$

- b) Numbering the states 1, 2, and 3 in the order listed, the probabilities are

$$\mathcal{P}_1 = \frac{6.84}{7.99} = 0.86; \quad \mathcal{P}_2 = \frac{1}{7.99} = 0.13; \quad \mathcal{P}_3 = \frac{0.15}{7.99} = 0.02.$$

- c) Measuring the energies now relative to the ground state, we have

$$Z = e^0 + e^{(0.05/0.026)} + e^{(0.10/0.026)} = 1 + 0.15 + 0.02 = 1.17.$$

And the probabilities are

$$\mathcal{P}_1 = \frac{1}{1.17} = 0.86; \quad \mathcal{P}_2 = \frac{0.15}{1.17} = 0.13; \quad \mathcal{P}_3 = \frac{0.02}{1.17} = 0.02.$$

So even though the partition function changes, the probabilities are unchanged, as they must be because nature can't possibly care what we use as our zero-point for measuring energy.

Problem 6.6. Let E_1 be the ground-state energy and E_2 the energy of the first excited ($n = 2$) level. The probability of being in any one of the first excited states is

$$\mathcal{P}(s_2) = \frac{e^{-E_2/kT}}{Z} \approx \frac{e^{-E_2/kT}}{e^{-E_1/kT}}.$$

In the last expression I've included only the first term in Z , since it's so much larger than all the other terms, even at 10,000 K. Since there are four such states, the total probability of having energy E_2 is four times as large:

$$\mathcal{P}(E_2) = 4e^{-(E_2 - E_1)/kT} = 4e^{-(10.2\text{ eV})/kT}.$$

At $T = 300$ K we have $kT = .026$ eV, so

$$\mathcal{P}(E_2) = 4e^{-10.2/.026} = 4e^{-395} = 10^{\log_{10}(4e^{-395})} = 10^{(\log_{10} 4) - 395(\log_{10} e)} = 10^{-171}.$$

In other words, you'll never find a hydrogen atom in its first excited level when it's in equilibrium with a reservoir at room temperature. At 9500 K, on the other hand, $kT = .819$ eV, so

$$\mathcal{P}(E_2) = 4e^{-10.2/.819} = 4e^{-12.5} = 1.6 \times 10^{-5}.$$

At this temperature, about one atom in 64,000 is in its first excited level.

Problem 6.7. Taking spin degeneracy into account, the ratio of probabilities for the two lowest energy levels would be

$$\frac{\mathcal{P}(E_2)}{\mathcal{P}(E_1)} = \frac{8}{2} \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = 4e^{-(E_2 - E_1)/kT},$$

the same as if we neglected the spin degeneracy.

Problem 6.8. The probability of an atom being ionized is not simply the Boltzmann factor $e^{-I/kT}$, with I being the ionization energy. Instead, to compute the probability using Boltzmann factors, we would have to multiply by the degeneracy of the ionized states, which is practically infinite. This makes the computation ambiguous, but at least it's fair to say that the "infinite" degeneracy will make the set of all ionized states much more probable than we might guess by their Boltzmann factors alone. In fact, the probability of ionization depends not only on the temperature and the ionization energy, but also on the density of free electrons in the environment, as shown in Section 5.6.

Problem 6.9. (Partition function for a hydrogen atom.)

- a) I'll take the ground-state energy (E_1) to be zero, so that the excited-state energies are $E_2 = 10.2$ eV, $E_3 = 12.1$ eV, and so on up to $E_\infty = 13.6$ eV. Also note that kT at $T = 5800$ K is 0.50 eV. Including only the first three levels, the partition function would be

$$\begin{aligned} Z &= e^{-E_1/kT} + 4e^{-E_2/kT} + 9e^{-E_3/kT} \\ &= e^0 + 4e^{-20.4} + 9e^{-24.2} \\ &= 1 + (5.6 \times 10^{-9}) + (2.8 \times 10^{-10}) \\ &= 1.000000059. \end{aligned}$$

- b) Since there are n^2 states with energy E_n , the full partition function is

$$Z = \sum_{n=1}^{\infty} n^2 e^{-E_n/kT}.$$

(This sum includes only bound states, not ionized states; let's say that it's not an atom if it's ionized.) All of the E_n 's are less than $E_\infty = 13.6$ eV, so we can safely conclude that

$$Z > \sum_{n=1}^{\infty} n^2 e^{-E_\infty/kT} = e^{-E_\infty/kT} \sum_{n=1}^{\infty} n^2 = \infty.$$

Even though the Boltzmann factor $e^{-E_\infty/kT}$ might be tiny (for example, at $T = 5800$ K it is only 1.5×10^{-12}), the sum diverges because there are infinitely many states with Boltzmann factors at least this large.

- c) If we keep the PdV term in equation 6.3, then the Boltzmann factor acquires an additional PV term in the exponent:

$$\text{New Boltzmann factor} = e^{-(E+PV)/kT},$$

where V is the volume of the system and P is the pressure of the reservoir. For a hydrogen atom in its ground state, $V \approx (1 \text{ \AA})^3$, so at atmospheric pressure, $PV \approx (10^5 \text{ Pa})(10^{-30} \text{ m}^3) = 10^{-25} \text{ J} \approx 10^{-6} \text{ eV}$. For the $n = 10$ state, however, the radius is 100 times larger so the volume is a million times larger, that is, $PV \approx 1 \text{ eV}$ at atmospheric pressure. (I don't know off-hand what the pressure is at the sun's "surface," where the density of atoms is probably lower than in our atmosphere but the temperature is much higher. At any reasonable pressure, though, there will be some not-too-large n at which $PV \approx 1 \text{ eV}$.) At 5800 K, a PV term of 1 eV reduces the Boltzmann factor by a factor of $e^{-2} = 0.14$, so this term is not negligible. And as n grows, the PV terms cause the Boltzmann factors to decrease exponentially. Therefore the correct partition function will be dominated by the first few energy levels. At the sun's temperature, this means that Z will be very close to 1, as shown in part (a).

Problem 6.10. (Vibrational excitations of H₂O.)

- a) The partition function for this vibrating atom is

$$Z = e^{-hf/2kT} + e^{-3hf/2kT} + e^{-5hf/2kT} + \dots$$

At 300 K,

$$\frac{hf}{kT} = \frac{(4.136 \times 10^{-15} \text{ eV s})(4.8 \times 10^{13} \text{ s}^{-1})}{(8.617 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 7.68,$$

so the partition function is approximately

$$\begin{aligned} Z &= e^{-3.84} + e^{-11.52} + e^{-19.20} + \\ &= 0.0215 + (9.9 \times 10^{-6}) + (4.6 \times 10^{-9}) + \\ &= 0.0215. \end{aligned}$$

The probabilities of the lowest two excited states are therefore

$$\mathcal{P}_1 = \frac{9.9 \times 10^{-6}}{0.0215} = 0.00046, \quad \mathcal{P}_2 = \frac{4.6 \times 10^{-9}}{0.0215} = 2.1 \times 10^{-7}.$$

The probability of the ground state is very nearly 1; more precisely,

$$\mathcal{P}_0 = 1 - 0.00046 = 0.99954.$$

- b) At 700 K, the ratio hf/kT is smaller by a factor of 3/7, so $hf/kT = 3.25$ and the partition function is

$$\begin{aligned} Z &= e^{-1.624} + e^{-4.873} + e^{-8.121} + e^{-11.37} + \\ &= 0.1971 + 0.0077 + 0.0003 + 0.00001 + \\ &= 0.2051. \end{aligned}$$

The probabilities are therefore

$$\mathcal{P}_0 = \frac{0.1971}{0.2051} = 0.961, \quad \mathcal{P}_1 = \frac{0.0077}{0.2051} = 0.038, \quad \mathcal{P}_2 = \frac{0.0003}{0.2051} = 0.001.$$

Problem 6.11. For the parameters given,

$$\frac{B}{kT} = \frac{(1.03 \times 10^{-7} \text{ eV/T})(0.63 \text{ T})}{(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 2.51 \times 10^{-6}.$$

I'll call this quantity x . The Boltzmann factors for the states $m = -3/2, -1/2, 1/2$, and $3/2$ are then

$$e^{-3x/2} = 0.9999962, \quad e^{-x/2} = 0.9999987, \quad e^{x/2} = 1.0000013, \quad e^{3x/2} = 1.0000038.$$

The partition function is almost exactly 4, so the probabilities of the four states are just the Boltzmann factors divided by 4:

$$\mathcal{P}\left(-\frac{3}{2}\right) = 0.24999906, \quad \mathcal{P}\left(-\frac{1}{2}\right) = 0.24999969, \quad \mathcal{P}\left(\frac{1}{2}\right) = 0.25000031, \quad \mathcal{P}\left(\frac{3}{2}\right) = 0.25000094.$$

If the magnetic field is now reversed, we might expect the quantity x to change sign. However, if the reversal is very sudden, the nuclei will not have time to realign themselves during the reversal, so the probabilities of the four states will remain unchanged. This means that x is unchanged, and to account for this, we can simply say that the temperature also changes sign: $x = B/kT$ remains unchanged when both B and T change sign.

Problem 6.12. If the molecules are in equilibrium with a reservoir of temperature T , then the probability of a molecule being in any one of the excited states, relative to the ground state, should be

$$\frac{e^{-E_1/kT}}{e^{-E_0/kT}} = e^{-(E_1 - E_0)/kT}.$$

We are given that this relative probability is approximately 1/10. Therefore,

$$\frac{E_1 - E_0}{kT} = \ln \frac{1}{10} = -2.303,$$

or

$$T = \frac{4.7 \times 10^{-4} \text{ eV}}{(2.303)(8.62 \times 10^{-5} \text{ eV/K})} = 2.4 \text{ K}.$$

The uncertainty in the data, however, is somewhat large. We now know that the temperature is closer to 2.7 K, and that the “reservoir” is the cosmic background radiation, a gas of photons that fills the entire observable universe (see Section 7.4).

Problem 6.13. The ratio of probabilities under these conditions should be

$$\frac{\mathcal{P}(n)}{\mathcal{P}(p)} = \frac{e^{-m_n c^2/kT}}{e^{-m_p c^2/kT}} = e^{-(m_n c^2/kT)} = \exp\left(-\frac{(2.3 \times 10^{-30} \text{ kg})(3 \times 10^8 \text{ m/s})^2}{(1.38 \times 10^{-23} \text{ J/K})(10^{11} \text{ K})}\right) = 0.86.$$

In other words, there should be 86 neutrons for every 100 protons. That makes 186 particles total, so the fraction of protons should be $100/186 = 0.54$, and the fraction of neutrons should be $86/186 = 0.46$.

Problem 6.14. Following the hint, let the system be a single air molecule, with state s_1 at sea level and state s_2 at a height z . Let's also suppose that the two states differ only in this respect; in particular, their energies differ only by the potential energy mgz . Then the relative probability of these two states is

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{E(s_2)/kT}}{e^{E(s_1)/kT}} = e^{(E(s_2) - E(s_1))/kT} = e^{mgz/kT}.$$

In other words, for any given molecular velocity and internal state, a molecule is less likely to be at height z than at sea level by a factor $e^{-mgz/kT}$. But the available velocities and internal states are exactly the same to molecules at any height, so this result tells us that in an isothermal atmosphere, the number of molecules per unit volume at height z is less than at sea level by the same factor:

$$\rho(z) = \rho(0) e^{-mgz/kT}.$$

This is the same result derived in Problems 1.16 and 3.37.

Problem 6.15. (Weberium.)

a)

$$\bar{E} = \frac{4(0 \text{ eV}) + 3(1 \text{ eV}) + 2(4 \text{ eV}) + 1(6 \text{ eV})}{10} = \frac{3 \text{ eV} + 8 \text{ eV} + 6 \text{ eV}}{10} = 1.7 \text{ eV}.$$

b) Each probability is just the number of atoms with that energy, divided by the total number of atoms:

$$\mathcal{P}(0 \text{ eV}) = \frac{4}{10}, \quad \mathcal{P}(1 \text{ eV}) = \frac{3}{10}, \quad \mathcal{P}(4 \text{ eV}) = \frac{2}{10}, \quad \mathcal{P}(6 \text{ eV}) = \frac{1}{10}.$$

c)

$$\begin{aligned} \bar{E} &= \sum_s E(s)\mathcal{P}(s) = (0 \text{ eV}) \cdot \frac{4}{10} + (1 \text{ eV}) \cdot \frac{3}{10} + (4 \text{ eV}) \cdot \frac{2}{10} + (6 \text{ eV}) \cdot \frac{1}{10} \\ &= 0 + \frac{3}{10} \text{ eV} + \frac{8}{10} \text{ eV} + \frac{6}{10} \text{ eV} = 1.7 \text{ eV}. \end{aligned}$$

Problem 6.16. Starting from the definition of Z ,

$$\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} \sum_s e^{-\beta E(s)} = \sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)} = \sum_s (-E(s))e^{-\beta E(s)}.$$

Now just multiply by $-1/Z$, cancel the minus signs, and move the Z inside the sum:

$$\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{Z} \sum_s (-E(s))e^{-\beta E(s)} = \sum_s E(s) \frac{e^{-\beta E(s)}}{Z} = \sum_s E(s)\mathcal{P}(s) = \bar{E}.$$

Problem 6.17. (Standard deviations of the energy.)

- a) The average energy of the five atoms is 3 eV, so the deviations from the average, in order from low energy to high, are -3 eV, -3 eV, 1 eV, 1 eV, and 4 eV.
- b) The squares of the deviations, in eV², are 9, 9, 1, 1, and 16, respectively. The average of these numbers is

$$\frac{9 + 9 + 1 + 1 + 16}{5} = \frac{36}{5} = 7.2.$$

The standard deviation is the square root of this number, about 2.7. Since the magnitudes of the deviations vary from 1 to 4, the number 2.7 does indeed give a reasonable measure of the typical size of the deviations.

c)

$$\begin{aligned}\sigma_E^2 &= \overline{(\Delta E_i)^2} = \frac{1}{N} \sum_i (\Delta E_i)^2 = \frac{1}{N} \sum_i (E_i - \bar{E})^2 = \frac{1}{N} \sum_i (E_i^2 - 2\bar{E}E_i + \bar{E}^2) \\ &= \frac{1}{N} \sum_i E_i^2 - 2\bar{E} \frac{1}{N} \sum_i E_i + \bar{E}^2 \frac{1}{N} \sum_i (1) = \bar{E}^2 - 2\bar{E}\bar{E} + \bar{E}^2 \\ &= \bar{E}^2 - \bar{E}^2.\end{aligned}$$

- d) The squares of the energies in our toy model are 0, 0, 16, 16, and 49 eV². The average of these numbers is 16.2 eV². The square of the average energy, meanwhile, is (3 eV)² = 9 eV². Therefore,

$$\bar{E}^2 - \bar{E}^2 = 16.2 \text{ eV}^2 - 9 \text{ eV}^2 = 7.2 \text{ eV}^2,$$

exactly the same as our computation of σ_E^2 in part (b).

Problem 6.18. Let's just compute the second derivative of Z with respect to β :

$$\begin{aligned}\frac{\partial^2 Z}{\partial \beta^2} &= \frac{\partial^2}{\partial \beta^2} \sum_s e^{-\beta E(s)} = \sum_s \frac{\partial}{\partial \beta} [-E(s)e^{-\beta E(s)}] = \sum_s [E(s)]^2 e^{-\beta E(s)} \\ &= Z \sum_s [E(s)]^2 \frac{e^{-\beta E(s)}}{Z} = Z \bar{E}^2.\end{aligned}$$

Now I'll rearrange this identity and use the result of Problem 6.16 twice:

$$\bar{E}^2 = \frac{1}{Z} \frac{\partial}{\partial \beta} \left(\frac{\partial Z}{\partial \beta} \right) = \frac{1}{Z} \frac{\partial}{\partial \beta} (-Z\bar{E}) = -\frac{1}{Z} \left(\frac{\partial \bar{E}}{\partial \beta} Z + \bar{E} \frac{\partial Z}{\partial \beta} \right) = -\frac{\partial \bar{E}}{\partial \beta} + (\bar{E})^2.$$

In other words,

$$\bar{E}^2 - (\bar{E})^2 = -\frac{\partial \bar{E}}{\partial \beta} = -\frac{\partial T}{\partial \beta} \frac{\partial \bar{E}}{\partial T}.$$

But $\partial T/\partial \beta = (\partial \beta/\partial T)^{-1} = (-1/kT^2)^{-1} = kT^2$, while $\partial \bar{E}/\partial T$ is just the heat capacity at constant volume, C_V . Therefore,

$$\sigma_E^2 = \bar{E}^2 - (\bar{E})^2 = kT^2 C_V,$$

or $\sigma_E = kT \sqrt{C_V/k}$.

Problem 6.19. For a system of N harmonic oscillators in the high-temperature limit, the average energy is NkT and the heat capacity is Nk . Therefore,

$$\sigma_E = kT\sqrt{Nk/k} = kT\sqrt{N}.$$

Dividing by $\bar{E} = NkT$ gives

$$\frac{\sigma_E}{\bar{E}} = \frac{kT\sqrt{N}}{NkT} = \frac{1}{\sqrt{N}}.$$

So relative to the average energy, the typical energy fluctuations are smaller by a factor of \sqrt{N} . For $N = 1$, that's a typical fluctuation of 100%. For $N = 10^4$, that's a typical fluctuation of one part in 100. And for $N = 10^{20}$, that's a typical fluctuation of one part in 10^{10} , quite impossible to measure. For a large system, therefore, we can generally ignore energy fluctuations and just write E (or U), omitting the $\bar{-}$.

Problem 6.20. (Average energy of a harmonic oscillator.)

a)

$$\begin{aligned} & 1 + x + x^2 + \dots \\ 1 - x \sqrt{1 + 0x + 0x^2 + 0x^3 + \dots} & \\ & \frac{1 - x}{x + 0x^2} \\ & \frac{x - x^2}{x^2 + 0x^3} \\ & \vdots \end{aligned}$$

For the series to converge the terms need to keep getting smaller and smaller. This happens when $|x| < 1$.

- b) Taking the ground state energy to be zero, the partition function for a single oscillator is

$$\begin{aligned} Z &= e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \\ &= 1 + e^{-\beta\epsilon} + (e^{-\beta\epsilon})^2 + (e^{-\beta\epsilon})^3 + \\ &= \frac{1}{1 - e^{-\beta\epsilon}}, \end{aligned}$$

by the result of part (a).

c)

$$\begin{aligned} \bar{E} &= \frac{1}{Z} \frac{\partial Z}{\partial \beta} = (1 - e^{-\beta\epsilon}) \frac{\partial}{\partial \beta} (1 - e^{-\beta\epsilon})^{-1} \\ &= (1 - e^{-\beta\epsilon})(-1)(1 - e^{-\beta\epsilon})^{-2} (\epsilon e^{-\beta\epsilon}) \\ &= \frac{\epsilon e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} - 1}. \end{aligned}$$

- d) The total energy of N identical, independent oscillators is just N times the average energy of one oscillator:

$$U = N\bar{E} = \frac{N\epsilon}{e^{\beta\epsilon} - 1}.$$

This is the same result as in Problem 3.25(c).

- e) (See solution to Problem 3.25.)

Problem 6.21. With 16 terms in the partition function, working this problem by hand would take forever, yet it can be done in only a few lines with *Mathematica*. In the following I'll show only my instructions and the graphical output, suppressing the long expressions generated by *Mathematica* for the partition function, average energy, and heat capacity. First I told *Mathematica* to calculate the partition function in terms of ϵ and β , keeping terms through $n = 15$:

```
z = Sum[Exp[-eps*(1.03*n-.03*n^2)*beta],{n,0,15}]
```

To get the average energy, differentiate with respect to β and multiply by $1/Z$:

```
energy = -(1/z)*D[z,beta] /. beta->1/(k*T)
```

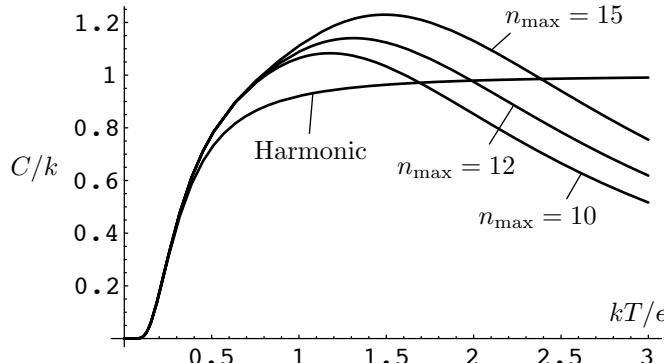
In this instruction I've also substituted $1/kT$ for β in the resulting expression. Now differentiate with respect to T to get the heat capacity:

```
heatcap = D[energy,T] /. T->t*eps/k
```

To facilitate plotting, I've substituted the dimensionless variable $t = kT/\epsilon$. Finally, plot C/k vs. t :

```
Plot[heatcap/k,{t,0,3}]
```

To check how the result depends on the number of energy levels included in the partition sum, I repeated the calculation, changing the maximum n in the first instruction to 12 and then to 10. The plot below shows all the results, as well as the heat capacity of a harmonic oscillator with evenly spaced energy levels.



The divergence of the three curves from each other as n_{\max} changes indicates that we would need to keep still more terms in the sum to predict the heat capacity above $t \approx 1$. For this system, however, there are hardly any more discrete levels beyond $n = 15$, because the molecule dissociates; therefore, $t \approx 1$ must be about the highest temperature at which the bond remains unbroken. Even below $t = 1$, however, we see that all three curves shoot well above the heat capacity of a harmonic oscillator. We therefore have a robust prediction, independent of n_{\max} : The heat capacity of this type of anharmonic oscillator is *larger* than that of a harmonic oscillator at values of kT/ϵ between about 0.5 and 1. Looking at the vibrational portion of Figure 1.13, we see that indeed, the vibrational heat capacity shoots

right up to R , with no sign of leveling off before the molecules dissociate. (The upper portion of the graph is dashed to indicate that rather high pressures would be needed to keep the molecules from dissociating even at somewhat lower temperatures. By the way, this upper portion of the graph was calculated theoretically in the paper of Woolley, et al., using a model similar to the one used here (but more sophisticated in the way it treated molecular rotation). There doesn't seem to be any good experimental data on the heat capacity of hydrogen at such high temperatures.)

Problem 6.22. (An n -state paramagnet.)

- a) First the induction proof. For $n = 0$, the formula gives

$$\frac{1+x^1}{1+x} = 1,$$

which is indeed the sum of all powers of x up to x^0 . Now, assuming that the formula works for $n = 1$, the sum of all the powers of x up to x^n is

$$\begin{aligned}(1+x+\dots+x^{n-1})+x^n &= \frac{1}{1-x}x^n + x^n \\ &= \frac{1}{1-x}x^n + \frac{(1-x)x^n}{1-x} \\ &= \frac{1}{1-x}x^n + x^n - \frac{x^{n+1}}{1-x} = \frac{1}{1-x}x^{n+1},\end{aligned}$$

completing the induction step of the proof.

Alternatively, we can write the infinite sum as a difference of infinite sums:

$$\begin{aligned}1+x+\dots+x^n &= (1+x+\dots)(x^{n+1}+x^{n+2}+\dots) \\ &= (1+x+\dots)x^{n+1}(1+x+\dots) \\ &= (1+x+\dots)(1-x^{n+1}) \\ &= \left(\frac{1}{1-x}\right)(1-x^{n+1}),\end{aligned}$$

where in the last step I've evaluated the infinite sum using the result of Problem 6.20(a).

- b) The allowed energies of a single particle are

$$E = j\delta B, (j-1)\delta B, \dots, j\delta B,$$

so the partition function is

$$\begin{aligned}Z &= e^{-j\beta\delta B} + e^{-(j-1)\beta\delta B} + \dots + e^{+j\beta\delta B} \\ &= e^{-jb} + e^{-(j-1)b} + \dots + e^{+jb} \quad (b \equiv \beta\delta B) \\ &= e^{-jb}[1 + e^b + e^{2b} + \dots + e^{2jb}] \\ &= e^{-jb}[1 + e^b + (e^b)^2 + \dots + (e^b)^{2j}].\end{aligned}$$

The sum in brackets can be evaluated using the result of part (a); a few more manipulations then put the answer in terms of sinh functions:

$$\begin{aligned} Z &= e^{-jb} \frac{1 - (e^b)^{2j+1}}{1 - e^b} = \frac{e^{-jb} - e^{(j+1)b}}{1 - e^b} \frac{e^{-b/2}}{e^{-b/2}} \\ &= \frac{e^{-b(j+\frac{1}{2})} - e^{b(j+\frac{1}{2})}}{e^{-b/2} - e^{b/2}} = \frac{\sinh[b(j + \frac{1}{2})]}{\sinh \frac{b}{2}}. \end{aligned}$$

- c) There are several ways to compute the magnetization. One method is to notice that for any particular state, the z component of the particle's magnetic moment is equal to its energy divided by B ; the same relation must hold between the average magnetization and the average energy. Now according to equation 6.25, the average energy of one magnetic particle is

$$\begin{aligned} \bar{E} &= \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \frac{db}{d\beta} \frac{\partial Z}{\partial b} \\ &= \frac{\sinh \frac{b}{2}}{\sinh[b(j + \frac{1}{2})]} (\delta B) \frac{(j + \frac{1}{2}) \sinh \frac{b}{2} \cosh[b(j + \frac{1}{2})] - \frac{1}{2} \sinh[b(j + \frac{1}{2})] \cosh \frac{b}{2}}{\sinh^2 \frac{b}{2}} \\ &= \delta B \left[(j + \frac{1}{2}) \coth[b(j + \frac{1}{2})] - \frac{1}{2} \coth \frac{b}{2} \right]. \end{aligned}$$

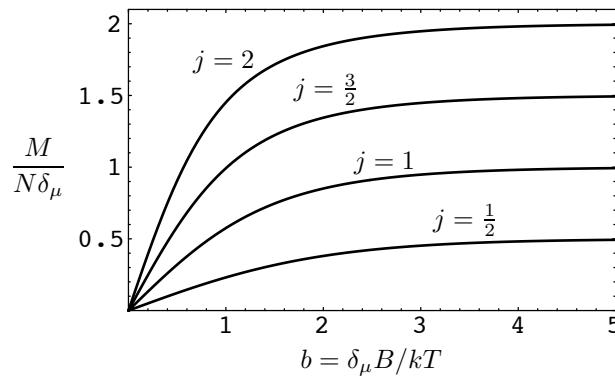
The average z component of the magnetic moment of this particle is given by this expression times $1/B$, so the total magnetization (in the z direction) of a system of N such particles is

$$M = N \delta B \left[(j + \frac{1}{2}) \coth[b(j + \frac{1}{2})] - \frac{1}{2} \coth \frac{b}{2} \right].$$

This formula is known as the Brillouin function. To plot it for $j = \frac{1}{2}, 1, \frac{3}{2}$, and 2 , I gave the following instructions to Mathematica:

```
bril[j_,b_] := (j+.5)/Tanh[b(j+.5)] - .5/Tanh[b/2]
Plot[{bril[.5,b],bril[1,b],bril[1.5,b],bril[2,b]}, {b,0,5},
      PlotPoints->100, Frame->True, PlotRange->{{0,5},{0,2.1}}];
```

Here is the plot:



- d) As $T \rightarrow 0$, the parameter b goes to infinity, so both coth functions go to 1 and the magnetization becomes

$$M = N\delta \left[(j + \frac{1}{2}) - \frac{1}{2} \right] = N\delta j.$$

In other words, all N of the particles are in the lowest-energy state (with $z = j\delta$), as expected. Notice that the graph above confirms this behavior, and also shows that M approaches its asymptotic value more quickly when j is large.

- e) When $x \ll 1$,

$$\begin{aligned} \coth x &= \frac{\cosh x}{\sinh x} = \frac{e^x + e^{-x}}{e^x - e^{-x}} \approx \frac{(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3) + (1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3)}{(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3) - (1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3)} \\ &= \frac{2 + x^2}{2x + \frac{1}{3}x^3} = \frac{1}{x} \left(1 + \frac{x^2}{2}\right) \left(1 + \frac{x^2}{6}\right)^{-1} \approx \frac{1}{x} \left(1 + \frac{x^2}{2}\right) \left(1 - \frac{x^2}{6}\right) \\ &\approx \frac{1}{x} \left(1 + \frac{x^2}{2} - \frac{x^2}{6}\right) = \frac{1}{x} + \frac{x}{3}. \end{aligned}$$

Therefore, as $T \rightarrow \infty$ and $b \rightarrow 0$, the magnetization is approximately

$$\begin{aligned} M &\approx N\delta \left[\left(j + \frac{1}{2}\right) \left(\frac{1}{b(j + \frac{1}{2})} + \frac{b(j + \frac{1}{2})}{3}\right) - \frac{1}{2} \left(\frac{1}{b/2} + \frac{b/2}{3}\right) \right] \\ &= N\delta \left[\frac{1}{b} + \frac{b}{3} \left(j + \frac{1}{2}\right)^2 - \frac{1}{b} - \frac{b}{12} \right] \\ &= \frac{N\delta b}{3} \left[\left(j + \frac{1}{2}\right)^2 - \frac{1}{4} \right] \\ &= \frac{N\delta^2 B j(j+1)}{3kT}. \end{aligned}$$

This is proportional to $1/T$, in accord with Curie's law.

- f) For the special case $j = \frac{1}{2}$, the magnetization becomes

$$M = N\delta \left[\coth b - \frac{1}{2} \coth(b/2) \right].$$

You'd think it would be easy to reduce this to the simple tanh function derived in the text, but I could think of nothing to do short of a brute-force reduction to exponential functions:

$$\begin{aligned} \frac{M}{N\delta} &= \frac{e^b + e^{-b}}{e^b - e^{-b}} - \frac{1}{2} \frac{e^{b/2} + e^{-b/2}}{e^{b/2} - e^{-b/2}} \\ &= \frac{2(e^{b/2} - e^{-b/2})(e^b + e^{-b}) - (e^{b/2} + e^{-b/2})(e^b - e^{-b})}{2(e^b - e^{-b})(e^{b/2} - e^{-b/2})} \\ &= \frac{1}{2} \frac{e^{3b/2} - 3e^{b/2} + 3e^{-b/2} - e^{-3b/2}}{e^{3b/2} - e^{b/2} - e^{-b/2} + e^{-3b/2}} = \frac{1}{2} \frac{(e^{b/2} - e^{-b/2})^3}{(e^{b/2} - e^{-b/2})^2(e^{b/2} + e^{-b/2})} \\ &= \frac{1}{2} \frac{e^{b/2} - e^{-b/2}}{e^{b/2} + e^{-b/2}} = \frac{1}{2} \tanh \frac{b}{2}. \end{aligned}$$

Setting $\delta = 2$ and $b = \beta\delta$, $B = 2\beta$, we see that this expression does indeed agree with equations 3.32 and 6.28.

Problem 6.23. For the numbers given,

$$\frac{kT}{\epsilon} = \frac{(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})}{.00024 \text{ eV}} = 107.8.$$

This is the approximate value of Z_{rot} according to equation 6.31. To compute the “exact” partition function you need to include terms in the sum up to about $j = 30$. The *Mathematica* instruction `Sum[(2j+1)Exp[-j(j+1)/107.8],{j,0,30}]` returns 108.1, and increasing the upper limit affects only the second decimal place, so it seems that the approximate formula is too low by about 0.3. (You can also carry out the sum with a calculator or a computer spreadsheet program.)

Problem 6.24. The two atoms in an oxygen molecule are identical, and at room temperature, $kT \gg \epsilon$, so we can use equation 6.33:

$$Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{0.026 \text{ eV}}{2(0.00018 \text{ eV})} = 72.$$

Problem 6.25. Because of the symmetry of the CO_2 molecule, a 180° rotation has no effect on its state, and therefore we should divide its rotational partition function by 2 just as for a diatomic molecule with identical atoms:

$$Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{0.026 \text{ eV}}{2(0.000049 \text{ eV})} = 265.$$

Problem 6.26. Writing out the first two terms ($j = 0$ and $j = 1$) explicitly, the partition function is

$$Z = 1 + 3e^{-2\beta\epsilon} + \dots$$

The remaining terms can be neglected in the limit $T \rightarrow 0$ (or $\beta \rightarrow \infty$). To compute the average energy I’ll just sum the two lowest energies, weighted by their probabilities:

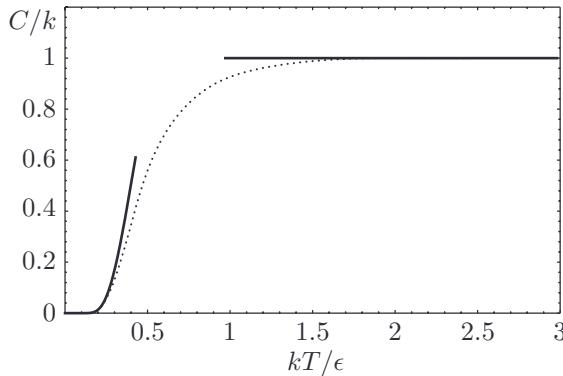
$$\bar{E} = \sum_{j=0}^1 E(j) (2j+1) \frac{e^{-\beta\epsilon j(j+1)}}{Z} = \frac{0 + 3 \cdot 2\epsilon e^{-2\beta\epsilon}}{1 + 3e^{-2\beta\epsilon}} \approx 6\epsilon e^{-2\beta\epsilon}.$$

In the last step I’ve neglected the second term in the denominator, since this term gives a correction that becomes negligible in the limit $\beta \rightarrow \infty$. (If the first term in the numerator were nonzero I couldn’t get away with this.) Finally, the heat capacity per molecule is

$$C = \frac{\partial \bar{E}}{\partial T} = 6\epsilon \frac{\partial}{\partial T} e^{-2\epsilon/kT} = 6\epsilon e^{-2\epsilon/kT} \left(-\frac{2\epsilon}{k} \right) \left(\frac{1}{T^2} \right) = 3k \left(\frac{2\epsilon}{kT} \right)^2 e^{-2\epsilon/kT}.$$

In the last expression I’ve extracted the degeneracy factor of 3. The rest of the result is the standard form for the heat capacity of a two-state system.

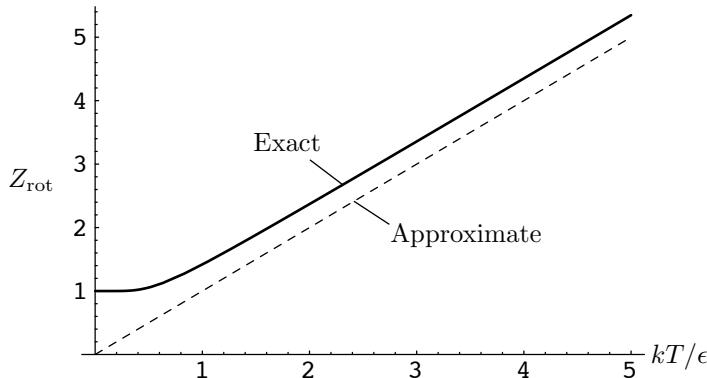
The plot on the following page shows the high- and low-temperature limiting expressions for the heat capacity as solid curves. The dotted line would have been my guess at an interpolation, had I not worked Problem 6.28.



Problem 6.27. To calculate and plot the exact rotational partition function, I used the *Mathematica* instruction

```
Plot[Sum[(2j+1)Exp[-j(j+1)/t],{j,0,20}], {t,.001,5}]
```

Here t represents kT/ϵ . The upper limit of 20 is the sum turned out to be more than necessary to get an accurate plot up to $t = 5$; I checked this by changing the upper limit and verifying that the plot was unaffected. The plot is shown as the solid line below. The dashed line represents the approximate formula, which appears to be less by about $1/3$ in the limit of large t . The reason why the approximation is too low is apparent from Figure 6.7: The approximate formula, which represents the area under the solid curve in the figure, omits the left-hand half of the very first bar in the graph, and the extra area that it takes in, represented by white triangular spaces, is not enough to compensate.



Problem 6.28. This problem is ideally suited for a symbolic algebra program such as *Mathematica*. To sum the partition function I gave the instruction

```
z = Sum[(2j+1)Exp[-j(j+1)*b*eps],{j,0,6}]
```

where b represents β and eps represents ϵ . Then to get the average energy I used equation 6.25:

```
energy = -(1/z)*D[z,b] /. b->1/(k*T)
```

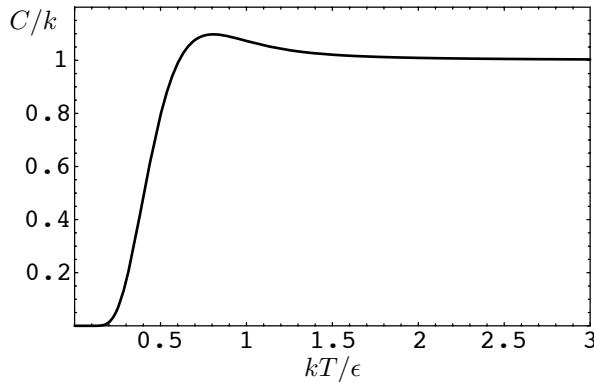
The capital D is the instruction to take the derivative, while the symbols following /. say to evaluate the result “at the point” $\beta = 1/kT$. To get the heat capacity I then differentiated with respect to temperature:

```
heatcap = D[energy,T] /. T->t*eps/k
```

I’ve also substituted the dimensionless variable $t = kT/\epsilon$, for the sake of plotting. I won’t copy the resulting expression, which would fill half a page. The important thing is the plot, which I generated by typing

```
Plot[heatcap/k, {t,.0001,3}, PlotRange->{{0,3},{0,1.2}}, Frame->True];
```

Here it is:



Notice that the heat capacity over-shoots its asymptotic value by about 10% before leveling off at high temperature.

To check whether I’ve included enough terms in the partition function, I increased the “6” in the first line of the calculation to 7 and saw that the graph was unchanged. Alternatively, the instruction

```
Table[(2j+1)Exp[-j(j+1)/3],{j,0,7}] //N
```

generates a table of the numerical values of the terms in the partition function, for $kT/\epsilon = 3$ (the highest temperature shown on the graph), through $j = 7$. The (rounded) values of the terms are

1, 1.54, 0.68, 0.13, 0.011, 5.0×10^{-4} , 1.1×10^{-5} , 1.2×10^{-7} ,

showing that the $j = 7$ term contributes negligibly to the sum.

Problem 6.29. From the graph plotted in the previous problem, we see that the rotational heat capacity falls off steeply when kT/ϵ is between about 0.3 and 0.6; the heat capacity is at about half its asymptotic value when $kT/\epsilon \approx 0.4$. For HD, that translates to a temperature of

$$T = \frac{0.4\epsilon}{k} = \frac{(0.4)(0.0057 \text{ eV})}{8.62 \times 10^{-5} \text{ eV/K}} = 26 \text{ K.}$$

Problem 6.30. (Parahydrogen and orthohydrogen.)

- a) The procedure here is the same as in Problem 6.28, but we keep only the even- j terms in the partition function. To be safe I'll go up to $j = 8$. Here is the sequence of *Mathematica* instructions for computing Z , E , and C , then plotting C :

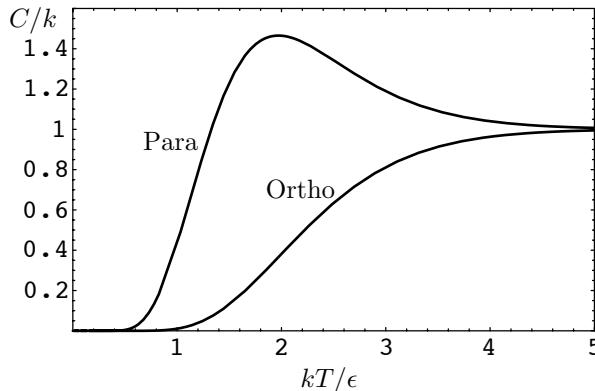
```
zEven = Sum[(2j+1)Exp[-j(j+1)*b*eps],{j,0,8,2}];  
eEven = -(1/zEven)*D[zEven,b] /. b->1/(k*T);  
cEven = D[eEven,T] /. T->t*eps/k;  
Plot[cEven/k,{t,.0001,5},PlotRange->{{0,5},{0,1.6}},Frame->True];
```

In the first line, the list $\{j,0,8,2\}$ says to include j values from 0 through 8 in steps of 2.

- b) The procedure here is exactly the same except we sum over odd values of j . Here's the code:

```
zOdd = Sum[(2j+1)Exp[-j(j+1)*b*eps],{j,1,7,2}];  
eOdd = -(1/zOdd)*D[zOdd,b] /. b->1/(k*T);  
cOdd = D[eOdd,T] /. T->t*eps/k;  
Plot[cOdd/k,{t,.0001,5},PlotRange->{{0,5},{0,1.6}},Frame->True];
```

Here are the plots for both para- and orthohydrogen, shown together for comparison:

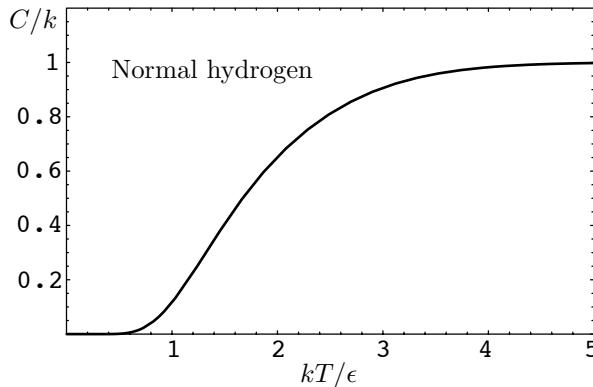


Notice that both graphs rise from zero at temperatures considerably higher than for a molecule of distinguishable atoms (as shown in Problem 6.28). This is because the gap between the lowest and next-lowest energy levels is significantly larger when only half of the levels are accessible.

- c) For a “mixture” of 1/4 parahydrogen and 3/4 orthohydrogen we can just add the separate heat capacities, weighted by these fractions:

```
cNormal = .25*cEven + .75*cOdd;  
Plot[cNormal/k,{t,.0001,5},PlotRange->{{0,5},{0,1.2}},Frame->True];
```

The plot (see the following page) lacks the interesting “bump,” but still rises from zero at rather high temperatures:



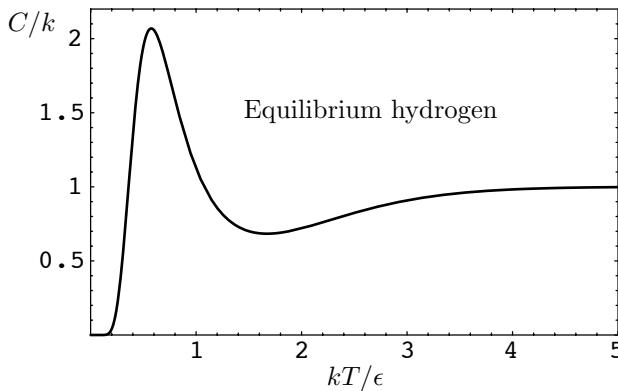
The heat capacity reaches half its asymptotic value at $kT/\epsilon = 1.67$, as you can see from the graph or calculate by typing `FindRoot[cNormal/k==.5, {t,1.5,2}]`. For $\epsilon = 0.0076$ eV, this point occurs at $T = 1.67\epsilon/k = 150$ K, in agreement with the data plotted in Figure 1.13. Note that if the hydrogen atoms were distinguishable, we would predict for this graph not only a rise from zero at lower temperature, but also a slight “bump” as shown in the solution to Problem 6.28.

- d) For a molecule that is truly in equilibrium, we should resum the partition function, weighting the odd- j terms threefold to account for the spin degeneracy. We can then recalculate the energy and the heat capacity as before:

```

zEquil = zEven + 3*zOdd;
eEquil = -(1/zEquil)*D[zEquil,b] /. b->1/(k*T);
cEquil = D[eEquil,T] /. T->t*eps/k;
Plot[cEquil/k,{t,.0001,5},PlotRange->{{0,5},{0,2.2}},Frame->True];

```

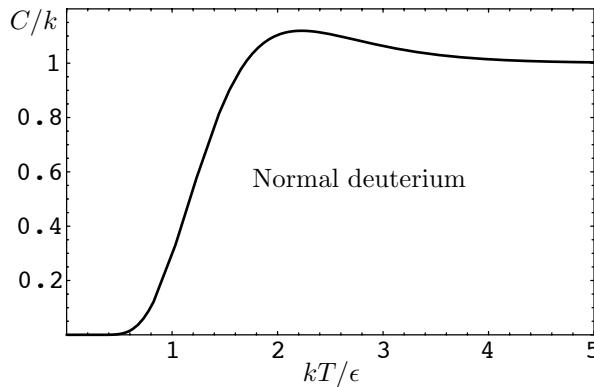


This time the heat capacity contains a huge peak at the temperature where the ninefold-degenerate $j = 1$ level first becomes accessible; there is then a broad valley due to the fact that the $j = 2$ level is only fivefold-degenerate. And, of course, the initial rise occurs at much lower temperature because the first excited state is only 2ϵ above the ground state.

- e) For “normal” deuterium we can compute the heat capacity in the same way as for normal hydrogen, but with the weighting factors $2/3$ for the even- j heat capacity and

1/3 for the odd- j heat capacity:

```
cNormD = (2/3)*cEven + (1/3)*cOdd;
Plot[cNormD/k,{t,.0001,5},PlotRange->{{0,5},{0,1.2}},Frame->True];
```



With the even- j states weighted more heavily than for normal hydrogen, the graph does have a bump this time.

Problem 6.31. If state q has energy $c|q|$, then the Boltzmann factor for this state is $e^{-\beta c|q|}$ and the partition function is the sum of all these Boltzmann factors:

$$Z = \sum_q e^{-\beta c|q|} = \frac{1}{\Delta q} \sum_q e^{-\beta c|q|} \Delta q.$$

In the limit $\Delta q \rightarrow 0$ the sum becomes an integral:

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c|q|} dq = 2 \frac{1}{\Delta q} \int_0^{\infty} e^{-\beta cq} dq = \frac{2}{\Delta q} \left(-\frac{1}{\beta c} \right) e^{-\beta cq} \Big|_0^{\infty} = \frac{2}{\beta c \Delta q} \equiv C \beta^{-1}.$$

(Since the integral is symmetric under $q \rightarrow -q$, I've written it as twice the integral over only positive q values. This trick gets rid of the absolute value bars.) The average energy is therefore

$$\bar{E} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\beta}{C} (-C \beta^{-2}) = \frac{1}{\beta} = kT.$$

Problem 6.32. (A model of thermal expansion.)

- a) Let the “system” be the particle’s position and the associated potential energy, not including the particle’s velocity (and kinetic energy) or any internal state. (As long as the position of the particle does not put any constraints on its other degrees of freedom, we can separate it out as a “system” in this way. To see how the separation works in detail, see Section 6.6.) First pretend that the points x are discretely spaced, like the q values in Figure 6.8. Then the average value of x is

$$\bar{x} = \sum_x x \mathcal{P}(x) = \sum_x x \frac{e^{-\beta u(x)}}{Z},$$

where $u(x)$ is the energy of the system, entirely potential energy in this case. Similarly, the partition function is

$$Z = \sum_x e^{-\beta u(x)}.$$

Plugging this into the expression for \bar{x} and taking the continuum limit, we have

$$\bar{x} = \frac{\sum_x x e^{-\beta u(x)}}{\sum_x e^{-\beta u(x)}} \rightarrow \frac{\int x e^{-\beta u(x)} dx}{\int e^{-\beta u(x)} dx}. \quad (1)$$

- b)** The linear term in the expansion is zero because x_0 is, by definition, a local minimum, and at any local extremum, a smooth function must have a horizontal tangent: $du/dx|_{x_0} = 0$. With this simplification, let me write the expansion as

$$u(x) = u(x_0) + a(x - x_0)^2 + b(x - x_0)^3,$$

where the coefficients a and b can be computed by taking the second and third derivatives of $u(x)$. If we neglect the cubic term and try to truncate the expansion after the quadratic term, then the numerator of equation 1 is

$$\int x e^{-\beta[u(x_0)+a(x-x_0)^2]} dx = e^{-\beta u(x_0)} \int x e^{-\beta a(x-x_0)^2} dx = e^{-\beta u(x_0)} \int (y+x_0) e^{-\beta a y^2} dy,$$

where $y = x - x_0$ and the final integral runs over all y values from $-\infty$ to ∞ . The term $ye^{-\beta ay^2}$ is an odd function and therefore integrates to zero. Meanwhile, the denominator of equation 1 is

$$\int e^{-\beta[u(x_0)+a(x-x_0)^2]} dx = e^{-\beta u(x_0)} \int e^{-\beta a(x-x_0)^2} dx = e^{-\beta u(x_0)} \int e^{-\beta a y^2} dy,$$

which cancels everything but the factor of x_0 in the numerator, leaving us with simply $\bar{x} = x_0$ (in this approximation).

- c)** Keeping the cubic term in the expansion of $u(x)$, let us approximate the Boltzmann factor as

$$e^{-\beta u(x)} = e^{-\beta[u(x_0)+ay^2+by^3]} \approx e^{-\beta u(x_0)} e^{-\beta a y^2} [1 - \beta b y^3],$$

where $y = x - x_0$. Equation 1 then becomes

$$\bar{x} = \frac{e^{-\beta u(x_0)} \int (y+x_0) e^{-\beta a y^2} [1 - \beta b y^3] dy}{e^{-\beta u(x_0)} \int e^{-\beta a y^2} [1 - \beta b y^3] dy} = \frac{\int [x_0 - \beta b y^4] e^{-\beta a y^2} dy}{\int e^{-\beta a y^2} dy},$$

where I've dropped all terms containing odd powers of y , since these are odd functions that integrate to zero. At this point we need the integrals

$$\int_{-\infty}^{\infty} e^{-\beta a y^2} dy = \sqrt{\frac{\pi}{\beta a}}, \quad \int_{-\infty}^{\infty} y^4 e^{-\beta a y^2} dy = \frac{3}{4\beta^2 a^2} \sqrt{\frac{\pi}{\beta a}},$$

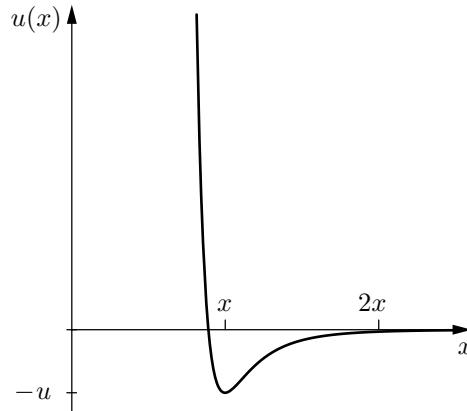
derived in Appendix B (or easily looked up in tables or evaluated by computer). The average position is therefore

$$\bar{x} = x_0 - \beta b \frac{(3/4\beta^2 a^2) \sqrt{\pi/\beta a}}{\sqrt{\pi/\beta a}} = x_0 - \frac{3}{4} \frac{b}{\beta a^2} = x_0 - \frac{3}{4} \frac{b}{a^2} kT.$$

If we think of \bar{x} as the measured length of an object, then the linear thermal expansion coefficient of that object is

$$= \frac{1}{\bar{x}} \frac{\partial \bar{x}}{\partial T} \approx \frac{3b}{4a^2} \frac{k}{x_0}.$$

- d) When $x \ll x_0$, the $(x_0/x)^{12}$ term dominates, so the Lennard-Jones potential is positive and goes to $+\infty$ as $x \rightarrow 0$. When $x \gg x_0$, on the other hand, the $(x_0/x)^6$ term dominates so the Lennard-Jones function is negative, and goes to zero as $x \rightarrow \infty$. In between, there must be a place where $u(x) = 0$, and there must also be a local minimum. Shown at right is a computer-generated plot of $u(x)$, copied from Figure 8.1. To find the location of the minimum, set the derivative equal to zero:



$$0 = \frac{du}{dx} = u_0 [x_0^{12}(-12)x^{-13} - 2x_0^6(-6)x^{-7}] = 12u_0 x_0^6 x^{-7} [-(x_0/x)^6 + 1].$$

The solution is at $x = x_0$, as expected. At this point, the value of $u(x)$ is

$$u(x_0) = u_0 [1 - 2] = -u_0.$$

To compute the Taylor expansion, we need the second and third derivatives of $u(x)$:

$$\begin{aligned} \frac{d^2u}{dx^2} &= u_0 [(-12)(-13)x_0^{12}x^{-14} - 2(-6)(-7)x_0^6x^{-8}]; \\ \frac{d^3u}{dx^3} &= u_0 [(-12)(-13)(-14)x_0^{12}x^{-15} - 2(-6)(-7)(-8)x_0^6x^{-9}]. \end{aligned}$$

The Taylor coefficients are therefore

$$\begin{aligned} a &= \frac{1}{2} \left. \frac{d^2u}{dx^2} \right|_{x_0} = \frac{1}{2} \frac{u_0}{x_0^2} (12)(13) = \frac{36u_0}{x_0^2}; \\ b &= \frac{1}{6} \left. \frac{d^3u}{dx^3} \right|_{x_0} = \frac{1}{6} \frac{u_0}{x_0^3} (-12)[(13)(14) - (7)(8)] = \frac{252u_0}{x_0^3}. \end{aligned}$$

Plugging into the result of part (c), we find for the thermal expansion coefficient

$$= \frac{3}{4} \frac{b}{a^2} \frac{k}{x_0} = \frac{3}{4} \left(\frac{252u_0}{x_0^3} \right) \left(\frac{x_0^2}{36u_0} \right)^2 \frac{k}{x_0} = \frac{7}{48} \frac{k}{u_0} = \frac{1.26 \times 10^{-5} \text{ eV/K}}{u_0}.$$

For argon ($u_0 = 0.010 \text{ eV}$), this formula predicts $= 0.0013 \text{ K}^{-1}$. That's too high by almost a factor of 2, but at least it's of the right order of magnitude.

Problem 6.33. The mass of an oxygen molecule is 32 u, so for oxygen at 300 K,

$$\sqrt{\frac{kT}{m}} = \sqrt{\frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{32(1.66 \times 10^{-27} \text{ kg})}} = 279 \text{ m/s.}$$

The most likely speed, v_{\max} , is just this times $\sqrt{2}$, or 395 m/s. To get the rms speed, we instead multiply by $\sqrt{3}$ to get 484 m/s. And to get the average speed, we multiply by $\sqrt{8/\pi}$ to get 446 m/s.

Problem 6.34. Let me define the constant $v_0 \equiv \sqrt{2kT/m}$ for $T = 300 \text{ K}$. The mass of a nitrogen molecule is 28 u, so

$$v_0 = \sqrt{\frac{2k(300 \text{ K})}{m}} = \sqrt{\frac{2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{28(1.66 \times 10^{-27} \text{ kg})}} = 422 \text{ m/s.}$$

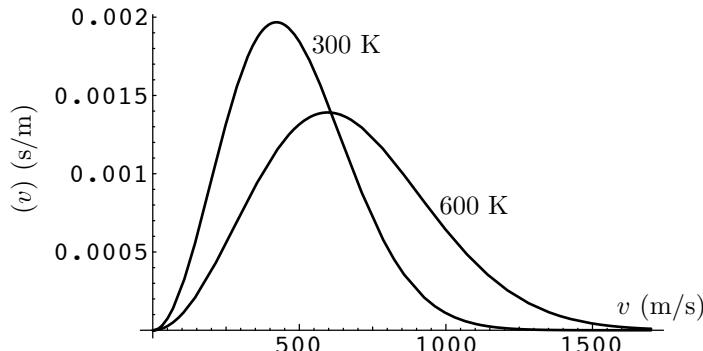
The Maxwell speed distribution can then be written

$$\mathcal{D}(v) = \frac{4}{\sqrt{\pi}} \frac{v^2}{v_0^3} t^{-3/2} e^{-v^2/v_0^2 t},$$

where t is the temperature in units of 300 K. To plot this function for $t = 1$ and $t = 2$, I gave Mathematica the following instructions:

```
v0 = 422;
maxwell[t_, v_] := 2.257*(v^2/v0^3)*t^(-1.5)*Exp[-v^2/(v0^2*t)]
Plot[{maxwell[1, v], maxwell[2, v]}, {v, 0, 1700}]
```

Here's the plot:



Notice that the area under each curve is equal to 1. Therefore, as the location of the peak moves to the right (in proportion to \sqrt{T}), its height must decrease.

Problem 6.35. The most likely speed is the point where the derivative of the Maxwell distribution is equal to 0:

$$0 = \frac{d\mathcal{D}}{dv} \propto \frac{d}{dv} \left(v^2 e^{-mv^2/2kT} \right) = 2ve^{-mv^2/2kT} - v^2 \left(\frac{mv}{kT} \right) e^{-mv^2/2kT} = 2v \left(1 - \frac{mv^2}{2kT} \right) e^{-mv^2/2kT}.$$

This expression is equal to zero at $v = 0$ and at $v = \infty$, but those are the minima of the function. The maximum is at the nontrivial solution, $v^2 = 2kT/m$ or $v = \sqrt{2kT/m}$.

Problem 6.36. As explained in the text, the average speed can be computed as a sum over all speeds, weighted by their probabilities. Therefore,

$$\bar{v} = \sum_v v \mathcal{D}(v) dv = \int_0^\infty v \mathcal{D}(v) dv = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi \int_0^\infty v^3 e^{-mv^2/2kT} dv.$$

This integral can be looked up in tables, or evaluated on a computer. To do it by hand you can start with the integral of ve^{-av^2} (from 0 to infinity) and differentiate with respect to a . By whatever method, the answer is

$$\bar{v} = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi \cdot \frac{1}{2} \left(\frac{2kT}{m} \right)^2 = \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{m} \right)^{1/2} = \sqrt{\frac{8kT}{\pi m}}.$$

Problem 6.37. In analogy with equation 6.51, imagine first that the v values are discretely spaced, then take the continuum limit:

$$\begin{aligned} \bar{v^2} &= \sum_v v^2 \mathcal{D}(v) dv \rightarrow \int_0^\infty v^2 \mathcal{D}(v) dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2kT} dv \\ &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} \left(\frac{2kT}{m} \right)^{5/2} \int_0^\infty x^4 e^{-x^2} dx = \frac{8kT}{\sqrt{\pi} m} \int_0^\infty x^4 e^{-x^2} dx. \end{aligned}$$

The integral over x is worked out in Appendix B, Problem B.2; or you can look it up in a table or ask a computer. The answer is $3\sqrt{\pi}/8$, so finally we have

$$\bar{v^2} = \frac{8kT}{\sqrt{\pi} m} \cdot \frac{3\sqrt{\pi}}{8} = \frac{3kT}{m},$$

in agreement with equation 6.41 and the equipartition theorem.

Problem 6.38. We want to integrate the Maxwell distribution from zero up to $v = 300$ m/s, for N₂ molecules at $T = 300$ K:

$$\int_0^{300 \text{ m/s}} \mathcal{D}(v) dv = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi \int_0^{300 \text{ m/s}} v^2 e^{-mv^2/2kT} dv = \frac{4}{\sqrt{\pi}} \int_0^{x_{\max}} x^2 e^{-x^2} dx.$$

In the last step I've changed variables to $x = v\sqrt{m/2kT}$. The upper limit of the integral then becomes

$$x_{\max} = (300 \text{ m/s}) \sqrt{\frac{(28)(1.66 \times 10^{-27} \text{ kg})}{2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}} = .711.$$

Now I'm ready to do the integral numerically. I typed the instruction

```
(4/Pi^.5)*NIntegrate[x^2*Exp[-x^2], {x, 0, .711}]
```

into Mathematica and it gave me .201. So the fraction of molecules with speeds less than 300 m/s is just over 20%.

Problem 6.39. (Escape of molecules from the upper atmosphere.)

- a) For a nitrogen molecule at 1000 K, the most probable speed is

$$v_{\max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.315 \text{ J/K})(1000 \text{ K})}{0.028 \text{ kg}}} = 771 \text{ m/s.}$$

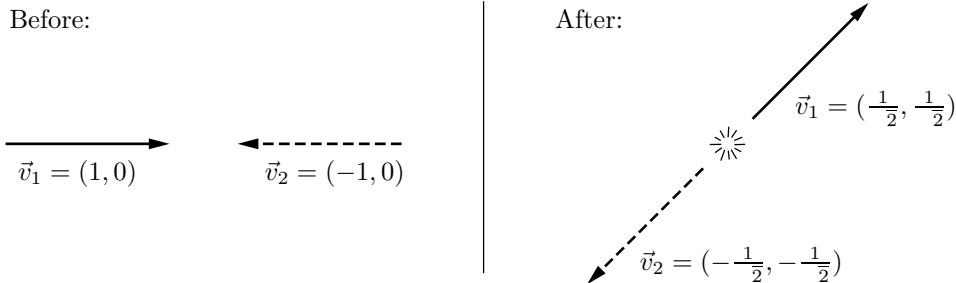
(Here M is the mass of a mole of nitrogen molecules.) The escape speed, 11,000 m/s, exceeds v_{\max} by a factor of $11,000/771 = 14.3$. Following the example in the text on pages 245–246, we can simply plug in this number for x_{\min} in the integral

$$\frac{4}{\sqrt{\pi}} \int_{x_{\min}}^{\infty} x^2 e^{-x^2} dx$$

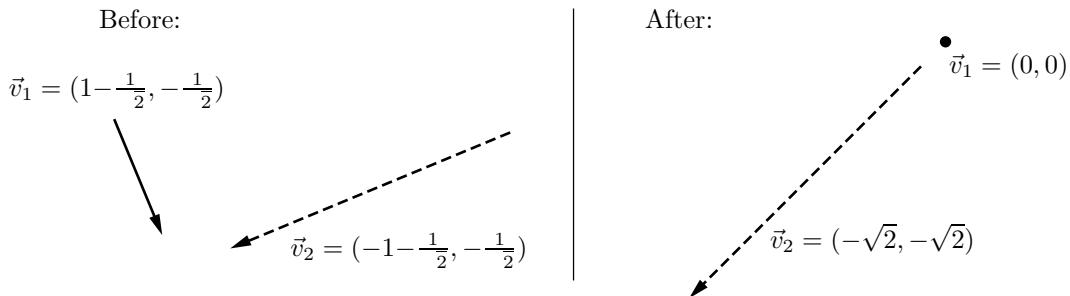
to obtain the probability of a molecule moving faster than escape speed. I used *Mathematica* to do the integral numerically and got the answer 2.5×10^{-88} . (Alternatively, you could use the asymptotic expansion derived in Problem B.5.) The age of the earth is of order 10^{17} seconds, so even if a molecule has a trillion (10^{12}) chances to escape per second over the lifetime of the earth, its chance of escaping by now would be less than one in 10^{58} .

- b) For a hydrogen molecule, M is only 0.002 kg, so v_{\max} is larger by a factor of $\sqrt{14} = 3.7$, that is, $v_{\max} = 2880$ m/s. Escape speed exceeds this number by a factor of $11,000/2880 = 3.81 = x_{\min}$. Evaluating the integral numerically once again, I find that the probability of a hydrogen molecule moving faster than escape speed is 2.2×10^{-6} . This is small but not at all negligible. Over the lifetime of the earth we *would* expect almost every hydrogen molecule to reach the uppermost atmosphere, achieve this speed, and hence escape. For helium, the mass is twice as great as for hydrogen so $v_{\max} = 2030$ m/s, $x_{\min} = 5.39$, and the probability evaluates to 1.5×10^{-12} . Again, this is large enough that every atom should have had plenty of chances to escape by now.
- c) Consider a nitrogen molecule in the moon's (former) atmosphere. Assuming a temperature of 1000 K as in earth's upper atmosphere, the most probable speed is again 771 m/s, but the escape speed of 2400 m/s exceeds this by a factor of only 3.1, and therefore our integral for the probability evaluates to 2.3×10^{-4} . Nitrogen on the moon should therefore escape even faster than hydrogen on earth. Presumably this happened long long ago, leaving the moon with no atmosphere today.

Problem 6.40. The easiest way to ensure energy and momentum conservation is to start in the center-of-mass frame, where (assuming equal masses) the molecules are initially moving directly toward each other with equal speeds, and end up moving directly away from each other with the same equal speeds. I'll take these speeds to equal 1 in some arbitrary unit system. The outgoing direction can be at any angle with respect to the incoming direction; after some experimentation I found that a 45° angle can give the desired result. The first illustration on the following page shows the collision in the center-of-mass frame.



Now let's view this collision from the frame of reference that moves along with particle 1 after the collision. Then, after the collision, particle 2 is moving southwest with speed 2. The initial velocities in this frame can be found by adding a southwest unit-length vector to the velocities in the CM frame. The results are shown in the figure below.



As you can see, particle 1 is initially the slower of the two, and yet it comes to a complete stop after the collision. Particle 2 is initially faster, yet it speeds up after the collision, gaining energy from particle 1. (It is a simple matter to check directly that energy and momentum are conserved in the new frame of reference.)

Problem 6.41. In a two-dimensional “flatland”, the probability of a molecule having velocity vector \vec{v} is still proportional to the Boltzmann factor, $e^{-mv^2/2kT}$. But the velocity vectors now live in a two-dimensional plane, and those with magnitude v have their tips on a circle with radius v . So the number of velocity vectors corresponding to speed v is now proportional to the circumference of a circle, $2\pi v$. With this new geometrical factor, we can write

$$\mathcal{D}(v) = C \cdot 2\pi v \cdot e^{-mv^2/2kT}.$$

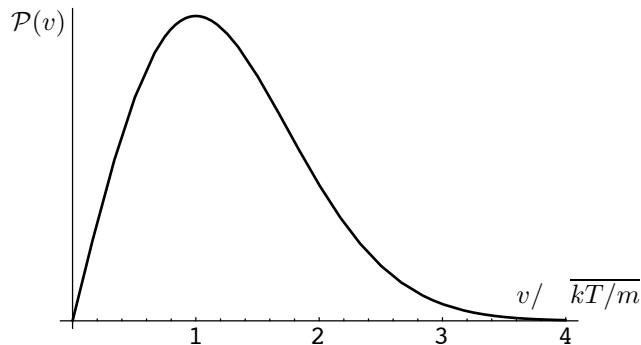
To find the normalization constant, set the integral over all v equal to 1:

$$1 = \int_0^\infty 2\pi C v e^{-mv^2/2kT} dv = 2\pi C \left(\frac{2kT}{m}\right) \int_0^\infty x e^{-x^2} dx = 2\pi C \left(\frac{2kT}{m}\right)^{1/2}.$$

So $C = m/(2\pi kT)$ and the final result for the speed distribution is

$$\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right) 2\pi v e^{-mv^2/2kT}.$$

This distribution function dies exponentially as $v \rightarrow \infty$, just as in three dimensions; as $v \rightarrow 0$, however, it is linear rather than parabolic. Here's a plot:



The most likely velocity *vector* is zero, just as in three dimensions, because its Boltzmann factor is the largest ($e^0 = 1$). But the most likely speed is nonzero. To find it, set $d\mathcal{D}/dv = 0$:

$$0 = \frac{d\mathcal{D}}{dv} \propto e^{-mv^2/2kT} \quad (v) \left(\frac{mv}{kT} \right) e^{-mv^2/2kT} = \left(1 - \frac{mv^2}{kT} \right) e^{-mv^2/2kT}.$$

The solution is $v_{\max} = \sqrt{kT/m}$, which looks right from the plot.

Problem 6.42. (F and S for a harmonic oscillator.)

- a) The Helmholtz free energy of a single harmonic oscillator is

$$F_1 = kT \ln Z_1 = kT \ln(1 - e^{-\beta\epsilon})^{-1} = kT \ln(1 - e^{-\beta\epsilon}),$$

so since F is an extensive quantity, the Helmholtz free energy for N oscillators is

$$F = NkT \ln(1 - e^{-\beta\epsilon}).$$

- b) To find the entropy just differentiate with respect to T :

$$\begin{aligned} S &= \left(\frac{\partial F}{\partial T} \right)_N = Nk \ln(1 - e^{-\beta\epsilon}) - NkT(1 - e^{-\beta\epsilon})^{-1}\epsilon e^{-\beta\epsilon} \left(\frac{d\beta}{d\epsilon} \right) \\ &= Nk \ln(1 - e^{-\beta\epsilon}) + Nk \frac{\epsilon/kT}{e^{\beta\epsilon} - 1}. \end{aligned}$$

Problem 6.43. (Alternative definition of entropy.)

- a) For an isolated system, $\mathcal{P}(s) = 0$ unless s is an accessible state, so we can restrict the sum to accessible states which gives

$$S = k \sum_s \frac{1}{\Omega} \ln \frac{1}{\Omega} = \frac{k \ln \Omega}{\Omega} \sum_s (1).$$

The number of terms in the sum is just Ω , so this expression reduces to the familiar one, $S = k \ln \Omega$.

b) For a system in thermal contact with a reservoir at temperature T , we can write

$$\ln \mathcal{P}(s) = \ln(e^{-\beta E(s)}/Z) = -\beta E(s) - \ln Z = \frac{1}{kT}(-E(s) + F),$$

by equation 6.56. Therefore the alternative definition of entropy reduces to

$$S = k \sum_s \frac{e^{-\beta E(s)}}{Z} \frac{1}{kT} (-E(s) + F) = \frac{1}{T} \sum_s E(s) \frac{e^{-\beta E(s)}}{Z} - \frac{F}{T} \sum_s \frac{e^{-\beta E(s)}}{Z} = \overline{E} - \frac{F}{T},$$

which is equivalent to the original definition of F , that is, $F = \overline{E} - TS$.

Problem 6.44. For N indistinguishable, noninteracting molecules that can exchange places with each other,

$$Z = \frac{1}{N!} Z_1^N,$$

so

$$\begin{aligned} F &= kT \ln Z = kT [N \ln Z_1 - \ln N!] \\ &= kT [N \ln Z_1 - N \ln N + N] = NkT \left[\ln \frac{Z_1}{N} + 1 \right]. \end{aligned}$$

Therefore the chemical potential is

$$= \left(\frac{\partial F}{\partial N} \right)_{T,V} = kT \left[\ln \frac{Z_1}{N} + 1 \right] - NkT \frac{\partial}{\partial N} (\ln N) = kT \ln \frac{Z_1}{N}.$$

Problem 6.45. The free energy is given by equation 6.90,

$$F = NkT [\ln V - \ln N - \ln v_Q + 1] + F_{\text{int}}.$$

Before differentiating with respect to T to get the entropy, note that $v_Q = (h^2/2\pi mkT)^{3/2}$, so $\ln v_Q = \frac{3}{2} \ln T$ plus a temperature-independent constant. Therefore the entropy is

$$\begin{aligned} S &= \left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk [\ln(V/Nv_Q) + 1] + NkT \left[\frac{3}{2} \frac{1}{T} - \frac{\partial F_{\text{int}}}{\partial T} \right] \\ &= Nk \left[\ln \left(\frac{V}{Nv_Q} \right) + \frac{5}{2} \right] - \frac{\partial F_{\text{int}}}{\partial T}. \end{aligned}$$

The chemical potential is

$$\begin{aligned} &= \left(\frac{\partial F}{\partial N} \right)_{T,V} = kT [\ln(V/Nv_Q) + 1] + NkT \left[\frac{1}{N} + \frac{\partial F_{\text{int}}}{\partial N} \right] \\ &= kT \ln(V/Nv_Q) - kT \ln Z_{\text{int}} = kT \ln \left(\frac{VZ_{\text{int}}}{Nv_Q} \right), \end{aligned}$$

where in the second line I've used the definition $F_{\text{int}} = NkT \ln Z_{\text{int}}$.

Problem 6.46. As an “ordinary” gas, consider nitrogen at room temperature and atmospheric pressure. The quantum length is

$$\ell_Q = \frac{h}{\sqrt{2\pi mkT}} = \frac{6.63 \times 10^{-34} \text{ J s}}{\sqrt{2\pi(28)(1.66 \times 10^{-27} \text{ u})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}} = 1.91 \times 10^{-11} \text{ m},$$

and therefore the quantum volume is $6.91 \times 10^{-33} \text{ m}^3$. The volume per particle, however, is much larger:

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{10^5 \text{ Pa}} = 4.14 \times 10^{-26} \text{ m}^3.$$

So the ratio V/Nv_Q works out to a fairly large number, about 6×10^6 . The internal partition function, Z_{int} , is always greater than 1, and is typically a few hundred for a small molecule like N₂. Therefore the argument of either logarithm is a number much *larger* than 1, implying that the logarithm itself is always positive under ordinary conditions. To make the logarithm negative we would have to make v_Q much larger (by lowering the temperature or using lower-mass particles) and/or make V/N much smaller (by lowering the temperature and/or raising the pressure). Gases for which $V/Nv_Q < 1$ do exist, as discussed at length in Chapter 7, but these are not considered “ordinary” gases.

Problem 6.47. A degree of freedom freezes out when kT is less than or comparable to the spacing between the lowest energy levels. In a one-dimensional box, the energy levels are $E_n = h^2 n^2 / 8mL^2$, so for nitrogen in a 1-cm box, the spacing between the two lowest levels is

$$E_2 - E_1 = \frac{3}{8} \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(28)(1.66 \times 10^{-27} \text{ kg})(0.01 \text{ m})^2} = 3.5 \times 10^{-38} \text{ J} = 2.2 \times 10^{-19} \text{ eV}.$$

The freeze-out temperature would therefore be approximately

$$T = \frac{E_2 - E_1}{k} = \frac{2 \times 10^{-19} \text{ eV}}{8.6 \times 10^{-5} \text{ eV/K}} = 2.6 \times 10^{-15} \text{ K},$$

or less than 3 femtokelvins. That’s much colder than they’ve reached even in Lounasmaa’s lab in Helsinki, so in all realistic situations we can assume that the translational motion of molecules in macroscopic boxes is nowhere near freezing out and therefore can be treated “classically” by converting the partition sum into an integral.

Problem 6.48. (*S* and *F* for a diatomic gas.)

- a) For a collection of N rotating diatomic molecules, the internal contribution to the free energy is

$$F_{\text{int}} = NkT \ln(Z_e Z_{\text{rot}}),$$

where (at ordinary temperatures) Z_{rot} is kT/ϵ for a molecule composed of two different atoms, or $kT/2\epsilon$ for a molecule composed of identical atoms. Either way, Z_{rot} is simply a constant times T , so

$$\frac{\partial F_{\text{int}}}{\partial T} = Nk \ln(Z_e Z_{\text{rot}}) - NkT \frac{1}{T} = Nk[\ln(Z_e Z_{\text{rot}}) + 1].$$

Therefore, according to equation 6.92,

$$S = Nk \left[\ln \left(\frac{V}{Nv_Q} \right) + \frac{5}{2} \right] + Nk[\ln(Z_e Z_{\text{rot}}) + 1] = Nk \left[\ln \left(\frac{VZ_e Z_{\text{rot}}}{Nv_Q} \right) + \frac{7}{2} \right].$$

The rotational partition function for oxygen at room temperature is

$$Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{(8.617 \times 10^{-5} \text{ eV/K})(298 \text{ K})}{2(.00018 \text{ eV})} = 71,$$

while the quantum volume is

$$\begin{aligned} v_Q &= \left(\frac{h}{\sqrt{2\pi mkT}} \right)^3 = \left(\frac{6.63 \times 10^{-34} \text{ J s}}{\sqrt{2\pi(32)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}} \right)^3 \\ &= (1.79 \times 10^{-11} \text{ m})^3 = 5.73 \times 10^{-33} \text{ m}^3 \end{aligned}$$

and the average volume per particle (at atmospheric pressure) is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 4.07 \times 10^{-26} \text{ m}^3.$$

From these numbers we can compute the logarithm

$$\ln \left(\frac{VZ_e Z_{\text{rot}}}{Nv_Q} \right) = \ln \left(\frac{(4.07 \times 10^{-26} \text{ m}^3)(3)(71)}{5.73 \times 10^{-33} \text{ m}^3} \right) = 21.14.$$

Thus the entropy under these conditions is

$$S = Nk[21.14 + 3.50] = (24.6)nR = 205 \text{ J/K},$$

precisely in agreement with the measured value (to the number of significant figures used in the calculation).

- b)** The chemical potential is kT times the same logarithm:

$$= (8.62 \times 10^{-5} \text{ eV/K})(298 \text{ K})(21.1) = 0.54 \text{ eV.}$$

Problem 6.49. As shown in Section 6.2, the rotational energy of a diatomic molecule at room temperature is kT , corresponding to two degrees of freedom. Therefore the total thermal energy of a mole of N_2 is

$$U = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT = \frac{5}{2}nRT = \frac{5}{2}(1 \text{ mol})(8.31 \text{ J/mol K})(298 \text{ K}) = 6190 \text{ J.}$$

The enthalpy is just $U + PV = U + nRT$, so it's larger by

$$nRT = (1 \text{ mol})(8.31 \text{ J/mol K})(298 \text{ K}) = 2480 \text{ J,} \quad \text{that is,} \quad H = 8670 \text{ J.}$$

To compute the remaining quantities we need the internal partition function, which in this case is purely rotational:

$$Z_{\text{int}} = Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{(8.617 \times 10^{-5} \text{ eV/K})(298 \text{ K})}{2(0.00025 \text{ eV})} = 51.$$

We also need the quantum volume,

$$\begin{aligned} v_Q &= \left(\frac{h}{\sqrt{2\pi mkT}} \right)^3 = \left(\frac{6.63 \times 10^{-34} \text{ J s}}{\sqrt{2\pi(28)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}} \right)^3 \\ &= (1.91 \times 10^{-11} \text{ m})^3 = 6.98 \times 10^{-33} \text{ m}^3, \end{aligned}$$

and the average volume per particle,

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 4.07 \times 10^{-26} \text{ m}^3.$$

From these numbers we can compute the logarithm

$$\ln\left(\frac{VZ_{\text{int}}}{Nv_Q}\right) = \ln\left(\frac{(4.07 \times 10^{-26} \text{ m}^3)(51)}{6.98 \times 10^{-33} \text{ m}^3}\right) = 19.5.$$

The Helmholtz free energy is therefore

$$F = nRT \left[\ln\left(\frac{VZ_{\text{int}}}{Nv_Q}\right) + 1 \right] = (2480 \text{ J})[19.5 + 1] = 50.8 \text{ kJ},$$

while the Gibbs free energy is

$$G = F + PV = 50.8 \text{ kJ} + 2480 \text{ J} = 48.3 \text{ kJ}.$$

The easiest way to get the entropy is from the definition $F = U - TS$:

$$S = \frac{U - F}{T} = \frac{(6190 \text{ J}) - (50,800 \text{ J})}{298 \text{ K}} = 191 \text{ J/K}$$

(in agreement with the measured value tabulated on page 405). And the easiest way to get the chemical potential is from $G = N \mu$:

$$\mu = \frac{G}{N} = \frac{48.3 \text{ kJ}}{6.02 \times 10^{23}} = 8.03 \times 10^{-20} \text{ J} = .501 \text{ eV}.$$

Problem 6.50. To get the Gibbs free energy, just add $PV = NkT$ to equation 6.90 for the Helmholtz free energy:

$$G = F + PV = NkT \left[\ln\left(\frac{VZ_{\text{int}}}{Nv_Q}\right) + 1 \right] + NkT = NkT \ln\left(\frac{VZ_{\text{int}}}{Nv_Q}\right).$$

Notice that the 1 term inside the square brackets conveniently cancels, leaving us with an expression identical to equation 6.93 for μ , but with an extra factor of N (to make it extensive). Therefore, $G = N \mu$.

Problem 6.51. Because the translational kinetic energy does not depend on position, the integrand is independent of r and therefore the d^3r integral simply gives a factor of V , the volume of the box. The momentum integrals can be evaluated either in rectangular or spherical coordinates. I'll use rectangular coordinates; then

$$E_{\text{tr}} = \frac{|\vec{p}|^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m},$$

and the exponential of E_{tr}/kT can be factored to give

$$Z_{\text{tr}} = \frac{V}{h^3} \int dp_x \int dp_y \int dp_z e^{-p_x^2/2mkT} e^{-p_y^2/2mkT} e^{-p_z^2/2mkT}.$$

But these are just ordinary Gaussian integrals, for which the general formula is

$$\int e^{-p^2} dp = \sqrt{\frac{\pi}{-}}.$$

In our case each integral gives $\sqrt{\pi/2mkT}$, so

$$Z_{\text{tr}} = \frac{V}{h^3} (2\pi mkT)^{3/2} = \frac{V}{v_Q},$$

in agreement with equation 6.82.

Problem 6.52. As in the nonrelativistic case, the allowed wavelengths (in one dimension) are $\lambda_n = 2L/n$, and therefore the allowed momenta are $p_n = h/\lambda_n = hn/2L$. Now, however, the relation between energy and momentum is $E = pc$, so the allowed energies are $E_n = hc n/2L$. Therefore the single-particle partition function is

$$Z_{1d} = \sum_n e^{-E_n/kT} = \sum_n e^{-hc n/2LkT}.$$

When L is macroscopic the number of terms in the sum that are significant is very large, so we can convert the sum to an integral to obtain

$$Z_{1d} = \int_0^\infty e^{-hc n/2LkT} dn = \left. \frac{2LkT}{hc} e^{-hc n/2LkT} \right|_0^\infty = \frac{2LkT}{hc}.$$

As expected, the partition function is directly proportional to L and increases with increasing temperature.

Problem 6.53. As shown in Section 5.6, the equilibrium condition for a chemical reaction is the same as the reaction equation, with the name of each species replaced by its chemical potential and \leftrightarrow replaced by $=$. Therefore, if the dissociation of hydrogen is at equilibrium, we must have $\mu_{H_2} = 2\mu_H$. Treating each species as an ideal gas, the chemical potentials are given by equation 6.93, almost. This formula assumes that each molecule has energy zero when it is at rest, whereas the energy of an H_2 molecule at rest is actually less than that of

two H atoms at rest, the difference being the dissociation energy calculated in Problem 1.53, $\epsilon_d = 4.49$ eV. I'll take the energy of an H atom at rest to be zero; then the energy of an H_2 molecule at rest is ϵ_d , and the chemical potential is shifted accordingly. Thus, the equilibrium condition for the dissociation reaction is

$$kT \ln\left(\frac{VZ_{\text{int},H_2}}{N_{H_2}v_{Q,H_2}}\right) - \epsilon_d = 2kT \ln\left(\frac{VZ_{\text{int},H}}{N_Hv_{Q,H}}\right).$$

Dividing through by kT and exponentiating both sides gives

$$\frac{VZ_{\text{int},H_2}}{N_{H_2}v_{Q,H_2}} e^{\epsilon_d/kT} = \left(\frac{VZ_{\text{int},H}}{N_Hv_{Q,H}}\right)^2.$$

To simplify this expression, consider first the internal partition functions. For H_2 , the internal partition function is a product of rotational and vibrational contributions. There is no electronic spin degeneracy, and electronic excited states are unimportant at the temperatures of interest. There is also a nuclear spin degeneracy of 4, 2 for each spin-1/2 proton. Meanwhile, the internal partition function for atomic hydrogen consists of a nuclear spin degeneracy factor of 2, multiplied by an electronic spin degeneracy factor of 2. Excited electronic states again contribute negligibly. When this partition function is squared, we see that the nuclear degeneracy factor of 4 cancels between the two sides, leaving us with only the electronic degeneracy factor of $2^2 = 4$. The equilibrium condition is therefore

$$\frac{VZ_{\text{rot}}Z_{\text{vib}}}{N_{H_2}v_{Q,H_2}} e^{\epsilon_d/kT} = \frac{4V^2}{N_H^2 v_{Q,H}^2}.$$

Next, recall that the quantum volume of a particle is proportional to its mass to the $-3/2$ power. Since the mass of H_2 is twice the mass of H, we can write $v_{Q,H_2} = v_{Q,H}/2^{3/2}$ and cancel a factor of $v_{Q,H}$ to obtain

$$\frac{VZ_{\text{rot}}Z_{\text{vib}}}{N_{H_2}} e^{\epsilon_d/kT} = \frac{\sqrt{2}V^2}{N_H^2 v_{Q,H}}.$$

Now let me use the ideal gas law to replace each V/N with kT/P , where P is the partial pressure of that species:

$$\frac{kTZ_{\text{rot}}Z_{\text{vib}}}{P_{H_2}} e^{\epsilon_d/kT} = \frac{\sqrt{2}(kT)^2}{P_H^2 v_{Q,H}}, \quad \text{or} \quad \frac{P_H^2}{P_{H_2}} = \frac{\sqrt{2}kT e^{-\epsilon_d/kT}}{Z_{\text{rot}}Z_{\text{vib}} v_{Q,H}}.$$

Dividing through by the reference pressure P° to make each side dimensionless, we finally obtain the law of mass action written in the conventional way:

$$\frac{P_H^2}{P^\circ P_{H_2}} = K, \quad \text{where} \quad K = \frac{\sqrt{2}kT e^{-\epsilon_d/kT}}{P^\circ v_{Q,H} Z_{\text{rot}} Z_{\text{vib}}}.$$

To facilitate numerical computations, let me define

$$K_0(T) \equiv \frac{\sqrt{2}kT}{P^\circ v_{Q,H}} = \frac{\sqrt{2}kT}{P^\circ} \left(\frac{2\pi m_H k T}{h^2} \right)^{3/2}.$$

At $T = 300$ K, this expression evaluates to 57,950. Since it is proportional to $T^{5/2}$, we can write

$$K_0(T) = (57,950)t^{5/2},$$

where $t = T/(300 \text{ K})$. To calculate the rotational partition function I'll use equation 6.33,

$$Z_{\text{rot}} \approx \frac{kT}{2\epsilon_r} = (1.70)t,$$

where I've used the value $\epsilon_r = 0.0076 \text{ eV}$ from Problem 6.30. (This formula really isn't very accurate until $Z_{\text{rot}} \gg 1$, but improving on it would be a lot of work and we'll see that the exact value of K at temperatures around 300 K isn't critical anyway.) The vibrational partition function was computed in Problem 6.20:

$$Z_{\text{vib}} = \frac{1}{1 - e^{-\epsilon_v/kT}} = \frac{1}{1 - e^{-(17.0)/t}},$$

where I've used the value $\epsilon_v = 0.44 \text{ eV}$ estimated in Problem 3.26. Finally, let's write the exponential factor involving the dissociation energy as

$$e^{-\epsilon_d/kT} = e^{-(173.7)/t}.$$

Combining all these expressions, we have for the equilibrium constant

$$K = \frac{K_0(T) e^{-\epsilon_d/kT}}{Z_{\text{rot}} Z_{\text{vib}}} = \frac{(57,950)t^{5/2} e^{-(173.7)/t}}{(1.70)t \left(1 - e^{-(17.0)/t}\right)^{-1}} = (34,090)t^{3/2}(1 - e^{-(17.0)/t})e^{-(173.7)/t}.$$

Rather than evaluating this whole expression at once, though, I entered the various pieces of it into a spreadsheet so I could see how each of them depends on temperature. Here are the results:

T (K)	K_0	Z_rot	Z_vib	e^(-eps_d/kT)	K
300	57950	1.7	1.00	3.66E-76	1.25E-71
1000	1.18E+06	5.7	1.01	2.34E-23	4.82E-18
3000	1.83E+07	17.0	1.22	2.86E-08	0.025
6000	1.04E+08	34.0	1.75	1.69E-04	295
10000	3.72E+08	56.7	2.50	5.46E-03	14300

As you can see, the exponential factor of the dissociation energy is by far the most important contribution to K . At 300 K, this factor is so tiny that the equilibrium constant is utterly negligible, implying that H_2 is never dissociated (when in equilibrium). For example, even if the partial pressure of H_2 is only 10^{-10} bar , the partial pressure of atomic hydrogen would be negligible in comparison:

$$P_{\text{H}} = \sqrt{K P^{\circ} P_{\text{H}_2}} = 3.5 \times 10^{-31} \text{ bar}.$$

At higher total pressures, the ratio of H/H_2 would be even less. (This implies that cold interstellar clouds containing atomic hydrogen are not in thermodynamic equilibrium.) On the other hand, at the surface of the sun, where $T \approx 6000 \text{ K}$, an H_2 partial pressure of 1 bar would imply an atomic hydrogen partial pressure of

$$P_{\text{H}} = \sqrt{K P^{\circ} P_{\text{H}_2}} = 17 \text{ bar},$$

so nearly 90% of the hydrogen would be ionized, and this percentage would be even higher at lower total pressures.

7

Quantum Statistics

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Problem 7.1. The probability of a heme site being occupied by oxygen is

$$\mathcal{P} = \frac{e^{-(\epsilon -)/kT}}{\mathcal{Z}} = \frac{e^{-(\epsilon -)/kT}}{1 + e^{-(\epsilon -)/kT}} = \frac{1}{e^{(\epsilon -)/kT} + 1}.$$

For the hypothetical ideal gas that the blood is assumed to be in equilibrium with,

$$e^{-/kT} = \frac{VZ_{\text{int}}}{Nv_Q} = \frac{kTZ_{\text{int}}}{Pv_Q},$$

where P is the partial pressure. Therefore,

$$\mathcal{P} = \frac{1}{P_0/P + 1},$$

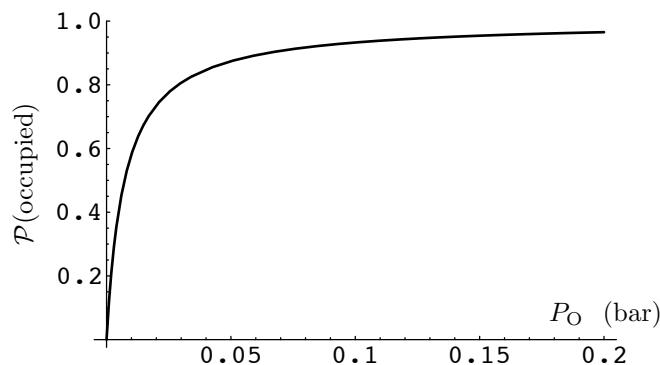
where P_0 is an abbreviation for $kTZ_{\text{int}}e^{\epsilon/kT}/v_Q$, a function of temperature but not pressure. At 310 K, $kT = 4.3 \times 10^{-21}$ J = 0.0267 eV, so for oxygen, assuming $\epsilon = 0.7$ eV, this constant is

$$\begin{aligned} P_0 &= (4.3 \times 10^{-21} \text{ J})(223)(e^{-0.7/0.0267}) \left(\frac{2\pi(32)(1.66 \times 10^{-27} \text{ kg})(4.3 \times 10^{-21} \text{ J})}{(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} \\ &= 740 \text{ Pa} = 0.0072 \text{ bar}. \end{aligned}$$

To plot the probability of the site being occupied, I typed into *Mathematica*

```
Plot[1/(.0072/p + 1), {p, 0, .2}]
```

and it produced the following:



Problem 7.2. This system has four different states, with occupation numbers 0, 1, 1, and 2, and corresponding energies 0, ϵ_1 , ϵ_1 , and ϵ_2 , where $\epsilon_1 = -0.55$ eV and $\epsilon_2 = -1.30$ eV. The grand partition function is

$$\mathcal{Z} = 1 + 2e^{-(\epsilon_1)/kT} + e^{-(\epsilon_2 - 2)/kT},$$

and the average number of oxygen molecules in the system is

$$\overline{N} = \sum_s N(s) \mathcal{P}(s) = 1 \cdot \mathcal{P}(N=1) + 2 \cdot \mathcal{P}(N=2) = \frac{2e^{-(\epsilon_1)/kT}}{\mathcal{Z}} + \frac{2e^{-(\epsilon_2 - 2)/kT}}{\mathcal{Z}}.$$

The average fraction of *sites* that are occupied is just half the average number of oxygens present:

$$\text{occupancy} = \frac{1}{\mathcal{Z}} [e^{-(\epsilon_1)/kT} + e^{-(\epsilon_2 - 2)/kT}] = \frac{e^{-(\epsilon_1)/kT} + e^{-(\epsilon_2 - 2)/kT}}{1 + 2e^{-(\epsilon_1)/kT} + e^{-(\epsilon_2 - 2)/kT}}.$$

To simplify this expression, note that the first Gibbs factor can be written

$$e^{-(\epsilon_1)/kT} = e^{-\epsilon_1/kT} e^{\delta/kT} = e^{-\epsilon_1/kT} \frac{P v_Q}{k T Z_{\text{int}}} = \frac{P}{P_0},$$

where $P_0 = k T Z_{\text{int}} e^{\epsilon_1/kT} / v_Q$. The numerical evaluation of P_0 is the same as in the previous problem, except for the value of ϵ_1 which is much less negative; I find $P_0 = 2.03$ bar. Meanwhile, if we write $\epsilon_2 = 2\epsilon_1 - \delta$, where $\delta = +2$ eV, then the second Gibbs factor can be written

$$e^{-(\epsilon_2 - 2)/kT} = e^{-(2\epsilon_1 - 2)/kT} e^{\delta/kT} = (e^{-(\epsilon_1)/kT})^2 e^{\delta/kT} = (P/P_0) e^{\delta/kT}.$$

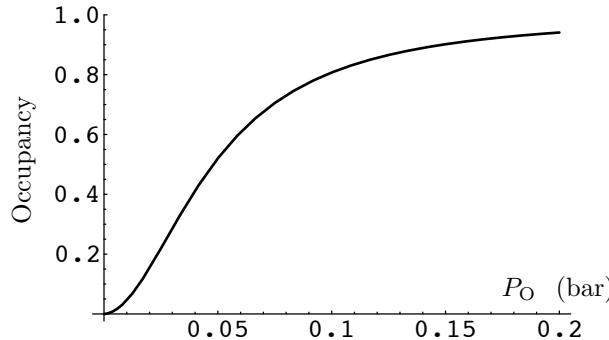
At 310 K, the exponential $e^{\delta/kT}$ equals 1790. In terms of P , P_0 , and δ , the occupancy is

$$\text{occupancy} = \frac{(P/P_0) + e^{\delta/kT} (P/P_0)^2}{1 + 2(P/P_0) + e^{\delta/kT} (P/P_0)^2}.$$

I plotted this formula with the *Mathematica* instruction

```
Plot[((p/2.03)+1790*(p/2.03)^2)/(1+2*(p/2.03)+1790*(p/2.03)^2),{p,0,.2}]
```

which produced the following graph:



As in the independent site model (Problem 7.1), the occupancy in this model is nearly 100% near the lungs where $P = 0.2$ bar. But in this model, the occupancy rises much more gradually at smaller values of P . This means that, with cooperative binding, hemoglobin releases oxygen much more readily in the cells where P is small.

Problem 7.3. Neglecting both spin (which cancels out of the final result) and the excited states of the hydrogen atom (which contribute negligibly even at 10,000 K), this system has just two states:

$$\begin{aligned} \text{unoccupied: } & E = 0, \quad N = 0, \quad \text{Gibbs factor} = e^0 = 1; \\ \text{occupied: } & E = -I, \quad N = 1, \quad \text{Gibbs factor} = e^{(-I - 1)/kT}. \end{aligned}$$

The ratio of the probabilities of these two states is the same as the ratio of partial pressures of ionized to un-ionized atoms:

$$\frac{P_p}{P_H} = \frac{\mathcal{P}(\text{unoccupied})}{\mathcal{P}(\text{occupied})} = \frac{1}{e^{(-I - 1)/kT}} = \frac{e^{-I/kT}}{e^{-1/kT}}.$$

Here I is the chemical potential for electrons. Treating the electrons as an ideal gas and again neglecting spin,

$$= kT \ln \left(\frac{VZ_{\text{int}}}{Nv_Q} \right) = kT \ln \left(\frac{kT}{P_e v_Q} \right),$$

so $e^{-1/kT} = P_e v_Q / kT$, which yields the Saha equation,

$$\frac{P_p}{P_H} = \frac{kT}{P_e v_Q} e^{-I/kT}.$$

Problem 7.4. Taking electron spin into account, the hydrogen atom now has two occupied states, each with the same energy, so the ratio of unoccupied to occupied atoms is

$$\frac{P_p}{P_H} = \frac{\mathcal{P}(\text{unoccupied})}{\mathcal{P}(\text{occupied})} = \frac{1}{2e^{(-I - 1)/kT}} = \frac{e^{-I/kT}}{2e^{-1/kT}}. \quad (1)$$

But now, a free electron has two degenerate states, so the chemical potential of the electron gas is

$$= kT \ln \left(\frac{VZ_{\text{int}}}{Nv_Q} \right) = kT \ln \left(\frac{2kT}{P_e v_Q} \right),$$

implying that $e^{-1/kT} = P_e v_Q / 2kT$. When we plug this into equation 1, the factors of 2 cancel, yielding the Saha equation exactly as derived in the previous problem.

Problem 7.5. (Ionization of donors in a semiconductor.)

- a) Taking the system to be a single donor ion, there are three possible states: one ionized state (no electron present), and two un-ionized states (with one electron present, either spin-up or spin-down). The energies and Gibbs factors of these states are

$$\begin{aligned} \text{ionized: } & E = 0, \quad N = 0, \quad \text{Gibbs factor} = e^0 = 1; \\ \text{un-ionized: } & E = -I, \quad N = 1, \quad \text{Gibbs factor} = e^{(-I - 1)/kT}. \end{aligned}$$

The Grand partition function is therefore

$$\mathcal{Z} = 1 + 2e^{(I+)/kT},$$

and the probability of the ionized state is its Gibbs factor divided by \mathcal{Z} , that is,

$$\mathcal{P}(\text{ionized}) = \frac{1}{1 + 2e^{(I+)/kT}}.$$

- b) For the chemical potential of the conduction electrons we can use equation 6.93 with $Z_{\text{int}} = 2$:

$$= kT \ln\left(\frac{2V}{N_c v_Q}\right),$$

where $v_Q = (h^2/2\pi m_e kT)^{3/2}$.

- c) The answer to part (a) is the ratio of conduction electrons to donor ions, N_c/N_d . Plugging in the result of part (b) for the chemical potential, we obtain for this ratio

$$\frac{N_c}{N_d} = \frac{1}{1 + 2e^{I/kT}(N_c v_Q/2V)} = \frac{1}{1 + N_c v_Q e^{I/kT}/V}.$$

Notice that the 2's cancel, so we would have gotten the same expression if we had neglected the electron spin. Introducing the dimensionless variables $x = N_c/N_d$ and $t = kT/I$, this equation becomes

$$x = \frac{1}{1 + x N_d v_Q e^{1/t}/V}.$$

Notice that we still have another dimensionless quantity in the problem, namely v_Q/V . Let me combine this quantity with some other factors to define $y \equiv N_d e^{1/t} v_Q/V$; this quantity depends on temperature but not on x . Our equation is then

$$x = \frac{1}{1 + xy} \quad \text{or} \quad x^2 y + x - 1 = 0.$$

The solution, according to the quadratic formula, is

$$x = \frac{1}{2y} \quad 1 \pm \sqrt{1 + 4y};$$

since the sign would give a negative x , our desired solution must be the one with the +. More explicitly,

$$N_c = \frac{V}{2v_Q e^{I/kT}} \left(\sqrt{1 + 4N_d v_Q e^{I/kT}/V} - 1 \right).$$

- d) For plotting, it's easiest to write everything in terms of the dimensionless variable t . Note that y can be written as

$$y = \frac{N_d v_Q e^{1/t}}{V} = \frac{N_d}{V} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} e^{1/t} = \frac{N_d}{V} \left(\frac{h^2}{2\pi m I} \right)^{3/2} \frac{e^{1/t}}{t^{3/2}}.$$

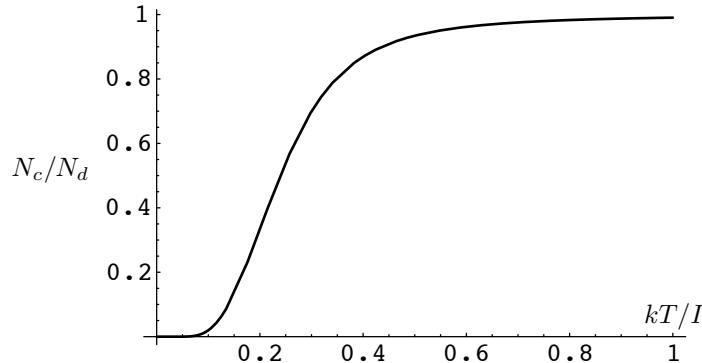
For our parameters, this works out to

$$y = (10^{23} \text{ m}^{-3}) \left(\frac{(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(9.11 \times 10^{-31} \text{ kg})(7.04 \times 10^{-21} \text{ J})} \right)^{3/2} \frac{e^{1/t}}{t^{3/2}} = (0.0036) \frac{e^{1/t}}{t^{3/2}}$$

(where I've converted N_d/V and I to SI units before doing the arithmetic). To plot x as a function of t I used *Mathematica*, first defining the function $y(t)$ with the instruction $y[t_] := 0.0036 * \text{Exp}[1/t] / t^{1.5}$. Then, to draw the actual plot, I typed

```
Plot[(Sqrt[1+4y[t]]-1)/(2y[t]),{t,.01,1}];
```

This produced the following plot:



As expected, the fraction of ionized donors goes to zero at low temperature and to 100% at high temperature. Interestingly, the steep increase occurs when kT is substantially less than the ionization energy. To convert the horizontal scale to kelvins, note that $I/k = (0.044 \text{ eV})/(8.62 \times 10^{-5} \text{ eV/K}) = 511 \text{ K}$. At room temperature, kT/I is about 0.59, and more than 95% of the donors are ionized.

Problem 7.6. It's easiest to start from the right-hand side of the desired relation and work backwards:

$$\begin{aligned} \frac{kT}{Z} \frac{\partial Z}{\partial} &= \frac{kT}{Z} \sum_s \frac{\partial}{\partial} e^{-[E(s) - N(s)]/kT} \\ &= \frac{kT}{Z} \sum_s \frac{N(s)}{kT} e^{-[E(s) - N(s)]/kT} \\ &= \sum_s N(s) \frac{1}{Z} e^{-[E(s) - N(s)]/kT} \\ &= \sum_s N(s) P(s) = \bar{N}. \end{aligned}$$

Similarly, making use of the third line above,

$$\begin{aligned}\frac{(kT)^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial^2} &= \frac{kT}{\mathcal{Z}} \frac{\partial}{\partial} \sum_s N(s) e^{-[E(s) - N(s)]/kT} \\ &= \frac{1}{\mathcal{Z}} \sum_s [N(s)]^2 e^{-[E(s) - N(s)]/kT} \\ &= \sum_s [N(s)]^2 \mathcal{P}(s) = \overline{N^2}.\end{aligned}$$

Notice that these two results can be combined to obtain a formula for $\overline{N^2}$ in terms of \overline{N} :

$$\overline{N^2} = \frac{(kT)^2}{\mathcal{Z}} \frac{\partial}{\partial} \left(\frac{\overline{N} \mathcal{Z}}{kT} \right) = \frac{kT}{\mathcal{Z}} \left(\frac{\partial \overline{N}}{\partial} \mathcal{Z} + \overline{N} \frac{\partial \mathcal{Z}}{\partial} \right) = kT \frac{\partial \overline{N}}{\partial} + (\overline{N})^2.$$

The standard deviation of a quantity can be calculated as the square root of the average of the squares minus the square of the average:

$$\sigma_N = \sqrt{\overline{N^2} - (\overline{N})^2} = \sqrt{kT(d\overline{N}/\partial)}.$$

For an ideal gas, $= kT \ln(VZ_{\text{int}}/Nv_Q)$, where v_Q and Z_{int} are functions of temperature only and the N could just as well be \overline{N} if the number of particles in the gas fluctuates. Therefore $\partial / \partial N = kT/N$ or $\partial \overline{N} / \partial = \overline{N}/kT$, and the standard deviation is simply

$$\sigma_N = \sqrt{kT(\overline{N}/kT)} = \sqrt{\overline{N}}.$$

The appearance of the square root is ubiquitous in formulas for fluctuations, so we could have guessed this result (up to a numerical factor) by dimensional analysis. For a gas of about 10^{23} molecules, the number will typically fluctuate by less than 10^{12} , or about one part in a hundred billion of the total.

Problem 7.7. Recall from Problem 5.23 the partial-derivative relation

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

We can think of N as a function of T , and V ; then this equation is a first-order differential equation for Φ as a function of T , with T and V held fixed. Now define $\tilde{\Phi} \equiv kT \ln \mathcal{Z}$, and differentiate with respect to T :

$$\left(\frac{\partial \tilde{\Phi}}{\partial} \right)_{T,V} = kT \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial} = \overline{N},$$

according to the first result of Problem 7.6. In other words, $\tilde{\Phi}$ obeys exactly the same differential equation as Φ . All that remains is to show that $\tilde{\Phi} = \Phi$ at one particular value of T . Consider both quantities at $T = 0$. Under this condition the Gibbs factor reduces to a simple Boltzmann factor, so the grand partition function reduces to the ordinary partition function (though still summed over states with all possible N) and therefore $\tilde{\Phi} = kT \ln \mathcal{Z} = kT \ln Z = F$, as shown in Section 6.5. On the other hand, the original Φ is simply $U - TS - N = U - TS = F$, when $T = 0$. Since $\tilde{\Phi}$ and Φ obey the same differential equation with the same “initial” condition at $T = 0$, they must be the same function.

Problem 7.8. (A toy 10-state system.)

- a) For a single particle, $Z = Z_1 = \Omega_1 = 10$, the number of states available to the particle (each with energy zero).
- b) For two distinguishable particles, $Z = Z_1^2 = 100$, since each particle independently has ten states available.
- c) For two identical bosons there are 10 ways to put both in the same single-particle state, plus $(10)(9)/2 = 45$ ways to put them into different single-particle states, so the total number of system states is $10+45=55$.
- d) For two identical fermions, the 10 system states with both particles in the same single-particle state are not allowed, so there are only 45 possible system states.
- e) According to equation 7.16, the number of states of this system would be

$$\frac{1}{2}Z_1^2 = \frac{100}{2} = 50.$$

As always, this result interpolates between the correct answer for bosons and the correct answer for fermions. In this case the formula isn't too far off, since the system is not very dense; the fraction of system states for which both particles are in the same single-particle state is fairly small.

- f) For distinguishable particles, 10 (out of 100) of the system states have both particles in the same state, so the probability is $10/100 = 1/10$. For identical bosons there are still 10 such system states, but only 55 system states in total, so the probability is higher, $10/55 = 18\%$. For identical fermions you can't have two particles in the same single-particle state, so the probability is zero.

Problem 7.9. The mass of an N_2 molecule is about 28 atomic mass units, so its quantum volume at room temperature is

$$v_Q = \left(\frac{h^2}{2\pi mkT} \right)^{3/2} = \left(\frac{(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(28)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \right)^{3/2}$$

$$= 6.9 \times 10^{-33} \text{ m}^3 = (1.9 \times 10^{-11} \text{ m})^3.$$

(Since atoms are about 10^{-10} meters wide, this is substantially smaller than the physical volume of the nitrogen molecule.) Now we can use Boltzmann statistics whenever $Z_1 \gg N$, that is, $V \gg Nv_Q$. But at standard temperature and pressure,

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{10^5 \text{ Pa}} = 4.1 \times 10^{-26} \text{ m}^3.$$

This is greater than the quantum volume by a factor of about 6 million, so Boltzmann statistics should be very accurate. On the other hand, Boltzmann statistics would break down when $v_Q \approx V/N$. Holding V/N fixed (i.e., fixed density), this would require that $T^{3/2}$ be lower by a factor of 6 million or that T be lower by a factor of about 30,000. That's 1/100 K. In other words, quantum statistics is irrelevant to an ordinary gas at this density provided that the temperature is higher than .01 K.

Problem 7.10. (A five-particle system with evenly spaced energy levels.)

- a) If the particles are distinguishable, then all five will settle into the lowest energy level. The same will happen if they are indistinguishable bosons. If they are indistinguishable fermions, however, then only one may occupy each level so each of the five lowest levels will contain one particle. The occupancies of the five lowest levels are therefore:

Distinguishable or Bosons	Fermions
5 0 0 0 0	1 1 1 1 1

- b) If the particles are distinguishable or bosons, then the system's first excited state has one of the five particles promoted to the second-lowest level. For distinguishable particles, there are *five* different ways to do this (choose any one of the five particles to promote), while for identical bosons there is only *one* way (it's meaningless to ask which particle has been promoted). For the system of fermions, the first excited state has the highest-energy particle promoted from the fifth state to the sixth (again adding just one unit of energy), and again there is only one way to do this. Graphically,

Distinguishable or Bosons	Fermions
4 1 0 0 0 0	1 1 1 1 0 1

- c) To add another unit of energy to the systems of bosons or distinguishable particles, we can either promote a second particle to the second-lowest level (leaving three in the lowest level) or leave four in the lowest level and promote the fifth up two levels. For bosons, there is only one way to do either of these things, but for distinguishable particles there are ten ways (5 choose 2) of doing the first and five of doing the second, for a total degeneracy of 15. Meanwhile, for the fermionic system there are two ways of putting in two units of energy, as illustrated below:

Distinguishable or Bosons	Fermions
3 2 0 0 0 0 0	1 1 1 0 1 1 0
4 0 1 0 0 0 0	1 1 1 1 0 0 1

To add yet another unit of energy there are basically three choices for each system, which I'll simply illustrate:

Distinguishable or Bosons	Fermions
2 3 0 0 0 0 0 0	1 1 0 1 1 1 0 0
3 1 1 0 0 0 0 0	1 1 1 0 1 0 1 0
4 0 0 1 0 0 0 0	1 1 1 1 0 0 0 1

Again there is a large degeneracy for the system of distinguishable particles: 10 for the first arrangement (5 choose 3), 20 for the second (5 choices for the highest-energy particle and 4 for the next-highest), and 5 for the third for a total of 35.

- d) The probability for the system to be in any particular state is proportional to the Boltzmann factor for that state, $e^{-E/kT}$ (where E is the total energy of all the particles). For any given E value, this quantity is the same for either system (and furthermore the allowed E values are the same). But the probability, say, of finding the system

with three units of energy is also proportional to the degeneracy, which is 3 for the bosonic system but 35 for the system of distinguishable particles. This means that at low temperatures we are much more likely to find a few units of energy in the system of distinguishable particles than in the system of bosons. Put another way, the ground state of the bosonic system is much more probable (relative to collection of all the low-energy excited states) than we might otherwise guess.

Problem 7.11. The probability of a state being occupied is given by the Fermi-Dirac distribution function, $\frac{1}{e^{(\epsilon -)/kT} + 1}$. At room temperature, $kT = .026$ eV, so the probabilities are:

- a) For $\epsilon = 1$ eV, probability = $\frac{1}{e^{-1/.026} + 1} = (1 + 2 \times 10^{-17})^{-1} = 1 - 2 \times 10^{-17} \approx 1$.
- b) For $\epsilon = .01$ eV, probability = $\frac{1}{e^{-.01/.026} + 1} = \frac{1}{1.68} = .59$.
- c) For $\epsilon = 0$, probability = $\frac{1}{e^0 + 1} = \frac{1}{2} = .50$.
- d) For $\epsilon = +.01$ eV, probability = $\frac{1}{e^{+.01/.026} + 1} = \frac{1}{2.47} = .41$.
- e) For $\epsilon = +1$ eV, probability = $\frac{1}{e^{+1/.026} + 1} = \frac{1}{5 \times 10^{16}} = 2 \times 10^{-17}$.

Problem 7.12. According to the Fermi-Dirac distribution, the probability of state B being occupied is

$$\mathcal{P}(B \text{ occupied}) = \frac{1}{e^{(\epsilon_B -)/kT} + 1} = \frac{1}{e^{x/kT} + 1},$$

since $\epsilon_B = -x$. The probability of state A being unoccupied is

$$\begin{aligned} \mathcal{P}(A \text{ unoccupied}) &= 1 - \frac{1}{e^{(\epsilon_A -)/kT} + 1} = 1 - \frac{1}{e^{-x/kT} + 1} = \frac{e^{-x/kT} + 1 - 1}{e^{-x/kT} + 1} \\ &= \frac{e^{-x/kT}}{e^{-x/kT} + 1} = \frac{1}{1 + e^{x/kT}}, \end{aligned}$$

where I've used the fact that $\epsilon_A = -x$. This is exactly the same formula, so the two probabilities are equal as expected.

Problem 7.13. The average occupancy of a state is given by the Bose-Einstein distribution function,

$$\bar{n} = \frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}}, \quad \text{where } x = (\epsilon -)/kT.$$

The probability of a state being occupied by exactly n particles is

$$\mathcal{P}(n) = \frac{e^{-nx}}{\mathcal{Z}} = (e^{-x})^n (1 - e^{-x}).$$

Thus we can compute everything we need from the quantity $e^{-x} = e^{-(\epsilon -)/kT}$, where in this case $kT = .026$ eV.

a) For $\epsilon = .001 \text{ eV}$, $x = .001/.026 = .038$ and $e^{-x} = .962$, so

$$\bar{n} = \frac{.962}{1 - .962} = 25.5; \quad \mathcal{P}(0) = 1 - .962 = .038, \quad \mathcal{P}(1) = (.962)(1 - .962) = .036,$$

$$\mathcal{P}(2) = (.962)^2(1 - .962) = .035, \quad \mathcal{P}(3) = (.962)^3(1 - .962) = .034.$$

b) For $\epsilon = .01 \text{ eV}$, $x = .01/.026 = .38$ and $e^{-x} = .681$, so

$$\bar{n} = \frac{.681}{1 - .681} = 2.13; \quad \mathcal{P}(0) = 1 - .681 = .319, \quad \mathcal{P}(1) = (.681)(1 - .681) = .217,$$

$$\mathcal{P}(2) = (.681)^2(1 - .681) = .148, \quad \mathcal{P}(3) = (.681)^3(1 - .681) = .101.$$

c) For $\epsilon = .1 \text{ eV}$, $x = .1/.026 = 3.8$ and $e^{-x} = .0214$, so

$$\bar{n} = \frac{.0214}{1 - .0214} = .0218; \quad \mathcal{P}(0) = 1 - .0214 = .979, \quad \mathcal{P}(1) = (.0214)\mathcal{P}(0) = .021,$$

$$\mathcal{P}(2) = (.0214)\mathcal{P}(1) = .00045, \quad \mathcal{P}(3) = (.0214)\mathcal{P}(2) = .000010.$$

d) For $\epsilon = 1 \text{ eV}$, $x = 1/.026 = 38$ and $e^{-x} = 2 \times 10^{-17}$, so

$$\bar{n} = \frac{2 \times 10^{-17}}{1 - 2 \times 10^{-17}} = 2 \times 10^{-17}; \quad \mathcal{P}(0) = 1 - 2 \times 10^{-17} \approx 1,$$

$$\mathcal{P}(1) = (2 \times 10^{-17})\mathcal{P}(0) = 2 \times 10^{-17}, \quad \mathcal{P}(2) = (2 \times 10^{-17})\mathcal{P}(1) = 4 \times 10^{-34},$$

$$\mathcal{P}(3) = (2 \times 10^{-17})\mathcal{P}(2) = 8 \times 10^{-51}.$$

Problem 7.14. From Figure 7.7, we see that the three distribution functions more or less coincide when ϵ/kT is at least a few times greater than kT . Under these conditions,

$$\frac{\bar{n}_{\text{BE}}}{\bar{n}_{\text{FD}}} = \frac{e^{(\epsilon - E)/kT} + 1}{e^{(\epsilon - E)/kT} - 1} = \frac{1 + e^{-(\epsilon - E)/kT}}{1 - e^{-(\epsilon - E)/kT}} \approx 1 + 2e^{-(\epsilon - E)/kT},$$

where the last approximation is valid because $(\epsilon - E)/kT \gg 1$. If this ratio is to be within 1% of 1, then $e^{-(\epsilon - E)/kT}$ must be less than 1/200, and therefore it must be the case that

$$\frac{\epsilon}{kT} > \ln 200 = 5.3.$$

(Since the Boltzmann distribution lies between the Fermi-Dirac and Bose-Einstein distributions, it lies within 1% of both of them whenever they lie within 1% of each other.) At any temperature, this inequality will be satisfied for sufficiently large ϵ . Often, however, this inequality is satisfied for all ϵ . For an ordinary gas of particles in a box, with energy levels measured in the usual way (as in Section 6.7), ϵ cannot be negative, while E/kT

is equal to $\ln(VZ_{\text{int}}/Nv_Q)$. The inequality above is therefore satisfied for all energy levels provided that

$$\frac{VZ_{\text{int}}}{Nv_Q} > 200 \quad \text{or} \quad \frac{kTZ_{\text{int}}}{Pv_Q} > 200.$$

For nitrogen at room temperature and atmospheric pressure, the left-hand side of this inequality is

$$\begin{aligned} & \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})(50)}{10^5 \text{ Pa}} \left(\frac{2\pi(28)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} \\ & = 3.0 \times 10^8, \end{aligned}$$

so the inequality is easily satisfied. At 200 K, colder than anywhere on earth, this expression would be less by a factor of only $(3/2)^{7/2} = 4.1$, so the inequality would still be easily met. Even for a gas like hydrogen or helium, with $Z_{\text{int}} \approx 1$ and a mass that is less by an order of magnitude, this expression would evaluate to more than 200. So for ordinary gases under atmospheric conditions, the three distribution functions are always essentially indistinguishable.

Problem 7.15. For a system of particles obeying the Boltzmann distribution, the total number of particles should be

$$N = \sum_{\text{all } s} \bar{n}_{\text{Boltzmann}} = \sum_s e^{-(\epsilon_s - \mu)/kT} = e^{-\mu/kT} \sum_s e^{-\epsilon_s/kT}.$$

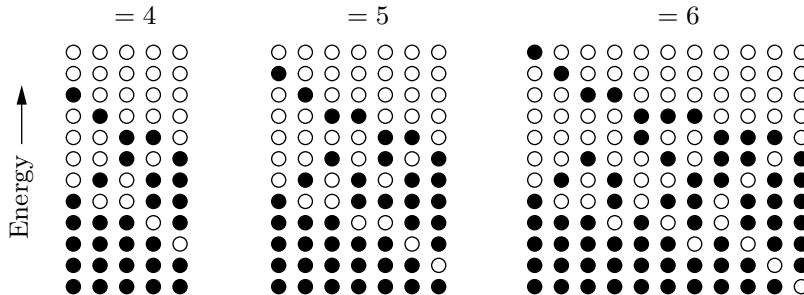
But the sum in the last expression is just the single-particle partition function, Z_1 , and therefore,

$$\frac{N}{Z_1} = e^{-\mu/kT} \quad \text{or} \quad \mu = kT \ln \frac{N}{Z_1} = kT \ln \frac{Z_1}{N}.$$

(I prefer to write $\mu = \ln(Z_1/N)$ rather than $\ln(N/Z_1)$, since $Z_1 \gg N$ whenever the Boltzmann distribution applies.)

Problem 7.16. (Fermionic system with evenly-spaced levels.)

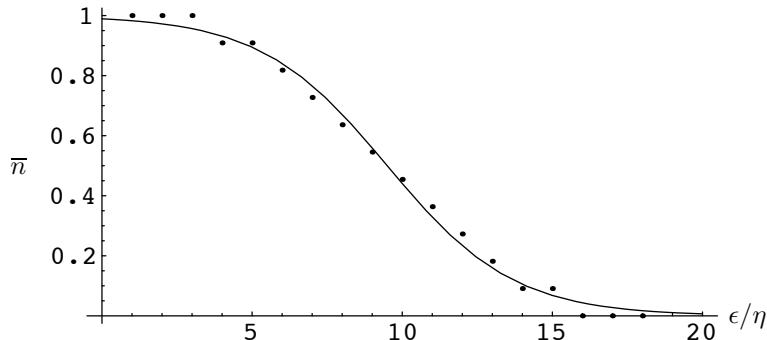
a) Here are the diagrams for $q = 4, 5$, and 6 :



b) For $q = 6$ there are 11 states in total. Counting black dots in each row from bottom to top, I therefore find that the probabilities of the levels being occupied are

$$\frac{10}{11}, \frac{10}{11}, \frac{9}{11}, \frac{8}{11}, \frac{7}{11}, \frac{6}{11}, \frac{5}{11}, \frac{4}{11}, \frac{3}{11}, \frac{2}{11}, \frac{1}{11}, \frac{1}{11}.$$

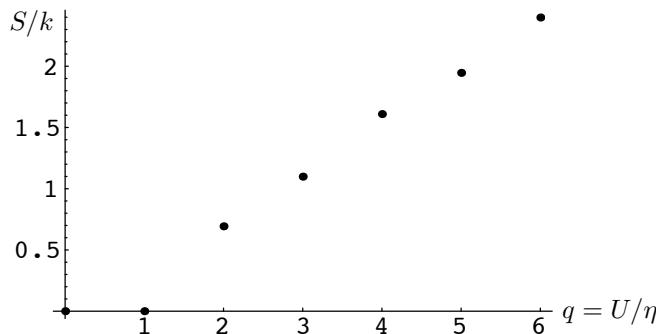
Of course, this list should be preceded by a long list of 11/11, and followed by a long list of 0/11. The following plot includes dots for three such levels on each end:



- c) The chemical potential, μ , should be the symmetry point at which the occupancy is exactly 1/2. This would be the vertical midpoint of the dot diagrams, or 9.5η with the arbitrary zero-point used in the graph in part (b). Given this value, I then adjusted the temperature and plotted the Fermi-Dirac distribution on the same graph, as shown, until I got a good match at $kT = 2.1\eta$. Alternatively, you could just note from Figure 7.7 that the F-D distribution equals about 1/4 when $\epsilon - \mu$ is slightly greater than kT . Our list of probabilities reaches the value 1/4 when $\epsilon - \mu \approx 2.5\eta$, so kT must be about 2η .
- d) In fundamental units, the entropy is just the natural logarithm of the number of system states. Here is a table:

q	Ω	S/k
0	1	0
1	1	0
2	2	0.69
3	3	1.10
4	5	1.61
5	7	1.95
6	11	2.40

And here's a graph:



Calculating the slope from the last two points on the graph, I obtain $T = \Delta U / \Delta S = \eta / 0.45k = 2.2\eta / k$, in rough agreement with the estimate of part (c).

Problem 7.17. (Bosonic system with evenly-spaced levels.)

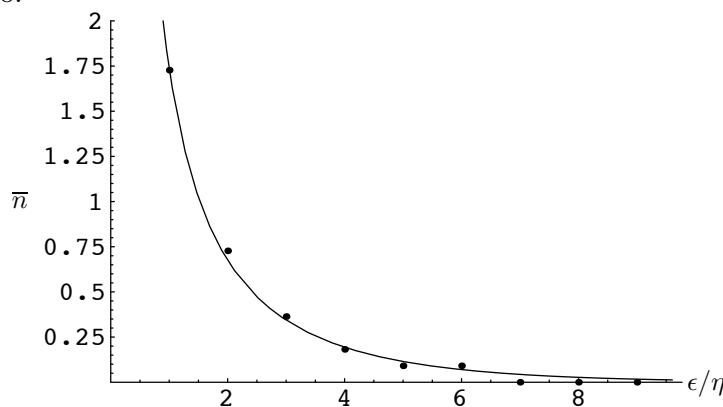
- a) The illustration below shows all system states up to $q = 6$, with each column representing a separate system state, and each row representing a single-particle excited state. The number in each space is the number of particles in that single-particle state, which for bosons is unlimited. The lowest-energy single-particle state (the ground state) is not shown; it contains N particles when $q = 0$, and N minus the total number of particles in excited states when $q > 0$.

	$q = 0$	$q = 1$	$q = 2$	$q = 3$	$q = 4$
Energy ↑	0	0	0 0	0 0 0	0 0 0 0 0
	0	0	0 0	0 0 0	0 0 0 0 0
	0	0	0 0	0 0 0	0 0 0 0 0
	0	0	0 0	0 0 0	1 0 0 0 0
	0	0	0 0	1 0 0	0 1 0 0 0
	0	0	1 0	0 1 0	0 0 2 1 0
	0	1	0 2	0 1 3	0 1 0 2 4
	$q = 5$			$q = 6$	
	0 0 0 0 0 0 0 0			0 0 0 0 0 0 0 0 0 0 0 0	
	0 0 0 0 0 0 0 0			1 0 0 0 0 0 0 0 0 0 0 0	
	1 0 0 0 0 0 0 0			0 1 0 0 0 0 0 0 0 0 0 0	
	0 1 0 0 0 0 0 0			0 0 1 1 0 0 0 0 0 0 0 0	
	0 0 1 1 0 0 0 0			0 0 0 0 2 1 1 0 0 0 0 0	
	0 0 1 0 2 1 0			0 0 1 0 0 1 0 3 2 1 0	
	0 1 0 2 1 3 5			0 1 0 2 0 1 3 0 2 4 6	

- b) Adding the numbers across each row in the $q = 6$ diagram and dividing by 11, we obtain the average occupancy of each level when $q = 6$. From the lowest level to the highest, the results are

$$\frac{19}{11}, \frac{8}{11}, \frac{4}{11}, \frac{2}{11}, \frac{1}{11}, \frac{1}{11}, 0, 0, 0, \dots$$

The average occupancy of the ground state is much larger: $N = (35/11)$. Here's a plot of the average occupancy vs. the energy of the level, taking the lowest level to have energy zero:

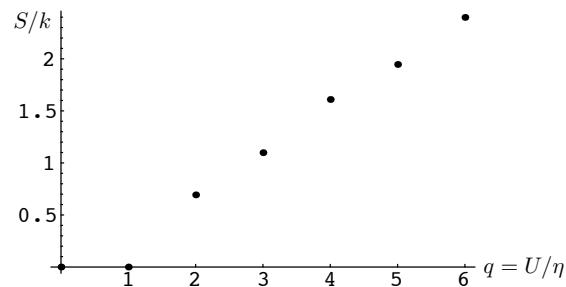


- c) The chemical potential μ is the energy at which the occupancy would be infinite. Assuming that N is large, this is essentially at $\epsilon = 0$, the ground-state energy. To find the best-fit temperature, I plotted the Bose-Einstein distribution on the graph

above, adjusting T until the $\langle t \rangle$ was good. The plot reproduced here is for $T = 2.2\eta/k$. Alternatively, you could just note from Figure 7.7 that at $\epsilon = - + kT$, the occupancy is about 0.6; from our data this point appears to be slightly above $\epsilon = 2\eta$.

- d) In fundamental units, the entropy is just the natural logarithm of the number of system states. Here are a table and graph of the values:

q	Ω	S/k
0	1	0
1	1	0
2	2	0.69
3	3	1.10
4	5	1.61
5	7	1.95
6	11	2.40



(Notice that these values are exactly the same as for the fermionic system treated in the previous problem.) Calculating the slope from the last two points on the graph, I obtain $T = \Delta U / \Delta S = \eta / 0.45k = 2.2\eta/k$, in agreement with the estimate of part (c).

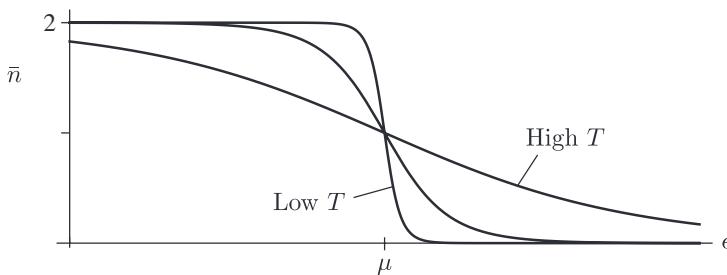
Problem 7.18. If up to two particles of a given type can occupy a state of energy ϵ , then the grand partition function is

$$\mathcal{Z} = e^0 + e^{-(\epsilon - \mu)/kT} + e^{-2(\epsilon - \mu)/kT} = 1 + e^{-x} + e^{-2x},$$

where $x = (\epsilon - \mu)/kT$. Therefore the average number of particles in the state is

$$\bar{n} = \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x} = \frac{1}{1 + e^{-x} + e^{-2x}} \frac{\partial}{\partial x} (1 + e^{-x} + e^{-2x}) = \frac{e^{-x} + 2e^{-2x}}{1 + e^{-x} + e^{-2x}}.$$

A computer-drawn plot of this formula is shown below, for three different temperatures, separated by factors of 4. As you can see, it's qualitatively similar to the Fermi-Dirac distribution, but with \bar{n} ranging from 0 to 2 instead of 0 to 1. (With a bit of algebra you can prove that $\bar{n} - 1$ is an odd function of $\epsilon - \mu$, just as $\bar{n}_{FD} - \frac{1}{2}$ is.)



Problem 7.19. The density of copper (which I looked up in an introductory physics textbook) is 8.93 g/cm³, and the atomic mass (which I got off a periodic table) is 63.5 g/mol. Let's consider a chunk of copper containing one mole of atoms. Then the mass is 63.5 g, and the volume is

$$V = \frac{\text{mass}}{\text{density}} = \frac{63.5 \text{ g}}{8.93 \text{ g/cm}^3} = 7.11 \times 10^{-6} \text{ m}^3.$$

Assuming that each atom contributes one conduction electron, the number of conduction electrons per unit volume is

$$\frac{N}{V} = \frac{6.02 \times 10^{23}}{7.11 \times 10^{-6} \text{ m}^3} = 8.47 \times 10^{28} \text{ m}^{-3},$$

and therefore the Fermi energy is

$$\begin{aligned}\epsilon_F &= \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})} \left(\frac{3}{\pi} \cdot 8.47 \times 10^{28} \text{ m}^{-3} \right)^{2/3} \\ &= 1.13 \times 10^{-18} \text{ J} = 7.05 \text{ eV}.\end{aligned}$$

The Fermi temperature is just this divided by Boltzmann's constant,

$$T_F = \frac{\epsilon_F}{k} = \frac{7.05 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 82,000 \text{ K}.$$

This is 270 times greater than room temperature, so yes, room temperature is sufficiently low for this electron gas to be considered degenerate. The degeneracy pressure for this system is

$$P = \frac{2N}{5V}\epsilon_F = (.4)(8.47 \times 10^{28} \text{ m}^{-3})(1.13 \times 10^{-18} \text{ J}) = 3.8 \times 10^{10} \text{ N/m}^2 = 3.8 \times 10^5 \text{ atm},$$

while the contribution of the degeneracy pressure to the bulk modulus is

$$B = \frac{10U}{9V} = \frac{5}{3}P = 6.4 \times 10^{10} \text{ N/m}^2 = 6.4 \times 10^5 \text{ atm}.$$

Problem 7.20. To determine whether either approximation is valid, let's calculate the Fermi temperature for the electron gas at the center of the sun:

$$\begin{aligned}T_F &= \frac{\epsilon_F}{k} = \frac{h^2}{8mk} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} \left(\frac{3(10^{32} \text{ m}^{-3})}{\pi} \right)^{2/3} \\ &= 9.1 \times 10^6 \text{ K}.\end{aligned}$$

This is quite close to the actual temperature, of order 10^7 K. Since T is neither much greater than nor much less than T_F , neither approximation would be very accurate: We can't treat the gas as degenerate ($T \approx 0$), nor can we treat it as an ordinary "classical" ideal gas ($T \gg T_F$).

Problem 7.21. We need to modify the derivation of the Fermi energy to account for the fact that each spatial wavefunction can hold four nucleons. Looking over pages 274–274, there are no modifications through equation 7.37. Equation 7.38, however, picks up an extra factor of 2:

$$N = \frac{2\pi n_{\max}^3}{3}, \quad \text{or} \quad n_{\max} = \left(\frac{3N}{2\pi} \right)^{1/3}.$$

Therefore the Fermi energy is

$$\epsilon_F = \frac{h^2}{8mL^2} \left(\frac{3N}{2\pi} \right)^{2/3} = \frac{h^2}{8m} \left(\frac{3N}{2\pi V} \right)^{2/3}.$$

Plugging in the numbers for nuclear matter gives

$$\epsilon_F = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(1.67 \times 10^{-27} \text{ kg})} \left(\frac{3(0.18 \times 10^{45} \text{ m}^{-3})}{2\pi} \right)^{2/3} = 6.4 \times 10^{-12} \text{ J} = 40 \text{ MeV}.$$

The Fermi temperature is just this divided by Boltzmann's constant:

$$T_F = \frac{\epsilon_F}{k} = \frac{4 \times 10^7 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 4.6 \times 10^{11} \text{ K}.$$

This is hotter than the center of any ordinary star. Therefore, to the extent that such a small system can be treated using thermodynamics at all, it should be an excellent approximation to treat a nucleus as a degenerate, $T = 0$ Fermi gas, in virtually all circumstances. (Exceptions would include heavy ion collisions, supernova explosions, and the very early universe.)

Problem 7.22. (Relativistic Fermi gas at $T = 0$.)

- a) The allowed wavelengths are the same as for a nonrelativistic particle: If the length of the box in the x direction is L , then the allowed wavelengths in the x direction are $\lambda_x = 2L/n_x$, and similarly for λ_y and λ_z . The momenta are also the same: $p_x = hn_x/2L$, and similarly for p_y and p_z . But now the energy is

$$\epsilon = pc = c\sqrt{p_x^2 + p_y^2 + p_z^2} = \frac{hc}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{hc n}{2L},$$

where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$. Each of the n 's can be any positive integer, so we can visualize the single-particle states as a lattice of points in the first octant of n -space. As in the nonrelativistic case, the energy of a state depends only on its distance from the origin, so at $T = 0$ we simply fill up an eighth-sphere, working our way outward to some maximum radius n_{\max} . The total number of electrons is just the volume of this eighth-sphere times 2 (since there are two spin states for each set of n 's):

$$N = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_{\max}^3 = \frac{\pi}{3} n_{\max}^3.$$

Solving for n_{\max} gives $n_{\max} = (3N/\pi)^{1/3}$. The chemical potential or Fermi energy is just the energy of the last state filled, that is, the energy corresponding to $n = n_{\max}$:

$$\epsilon_F = \epsilon(n_{\max}) = \frac{hc n_{\max}}{2L} = \frac{hc}{2L} \left(\frac{3N}{\pi} \right)^{1/3} = \frac{hc}{2} \left(\frac{3N}{\pi V} \right)^{1/3}.$$

- b) The total energy is the sum of the energies of all the occupied states:

$$U = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(n),$$

where the factor of 2 is for the two spin orientations. As in the nonrelativistic case, convert this sum to an integral in spherical coordinates, being sure to include the “measure” $n^2 \sin \theta$:

$$U = 2 \int_0^{\pi/2} d\phi \int_0^{\pi/2} d\theta \sin \theta \int_0^{n_{\max}} dn n^2 \frac{hc n}{2L}.$$

The angular integrals give $\pi/2$ (the surface area of a unit-radius eighth-sphere), leaving us with

$$U = \pi \frac{hc}{2L} \int_0^{n_{\max}} n^3 dn = \frac{\pi hc}{2L} \frac{1}{4} n_{\max}^4 = \frac{\pi hc}{8L} \left(\frac{3N}{\pi} \right)^{4/3} = \frac{3Nhc}{8} \left(\frac{3N}{\pi V} \right)^{1/3} = \frac{3}{4} N \epsilon_F,$$

where ϵ_F is given by the result of part (a). Thus the average energy is 3/4 of the maximum energy, as compared to 3/5 in the nonrelativistic case.

Problem 7.23. (White dwarf stars.)

- a) We want to make something with units of energy (newton-meters) out of M (kg), R (m), and G ($N m^2/kg^2$). It’s convenient to express all the units as I just have, taking the three basic units to be newtons, kilograms, and meters; none of these three can be written in terms of the other two. How to do it? Well, to get N in the numerator we need exactly one power of G . But then, to cancel the kg^2 in the denominator we need two powers of M . And, since G has m^2 in the numerator and we want just meters, we need to divide by one power of R . Finally, we should put in a minus sign since gravity is attractive: We would have to *add* energy to disassemble the sphere, moving the parts infinitely far apart where they have zero potential energy.

Just for fun, let me now derive the exact formula for the potential energy of a sphere of uniform density ρ . Imagine assembling the sphere by bringing in concentric shells of mass, one at a time, from infinite distance. Suppose, further, that we already have a sphere of radius r and mass $m = 4\pi r^3 \rho / 3$. We now bring in the next shell, whose thickness is dr and whose mass is therefore $dm = 4\pi r^2 dr \rho$. The potential energy of this shell once it arrives is $dU = -Gm dm / r$. Summing over all such shells and converting the sum to an integral, we obtain for the total potential energy

$$\begin{aligned} U_{\text{grav}} &= \int dU = \int \frac{Gm}{r} dm = G \int_0^R \frac{1}{r} \left(\frac{4\pi r^3 \rho}{3} \right) 4\pi r^2 \rho dr \\ &= \frac{16\pi^2 G \rho^2}{3} \int_0^R r^4 dr = \frac{16\pi^2 G \rho^2}{3} \frac{R^5}{5} = \frac{16\pi^2 G R^5}{15} \left(\frac{3M}{4\pi R^3} \right)^2 \\ &= \frac{3}{5} \frac{GM^2}{R}, \end{aligned}$$

where I’ve substituted $\rho = 3M/4\pi R^3$ in the second-to-last step. So the numerical coefficient in the energy formula, for the (probably unrealistic) case of a uniform-density sphere, is 3/5.

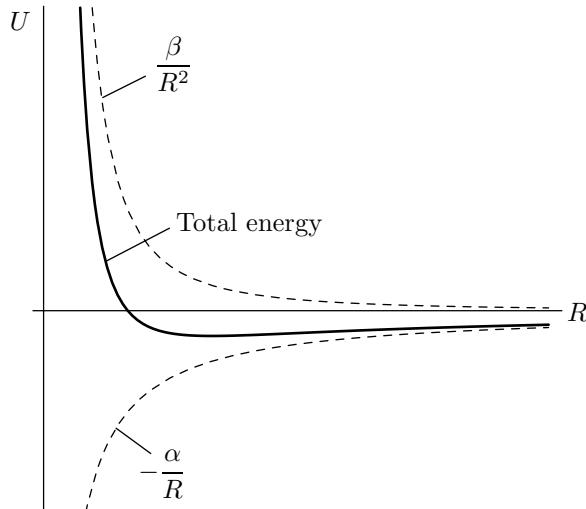
- b) According to equations 7.42 and 7.39, the total energy of a degenerate electron gas is

$$U_{\text{kinetic}} = \frac{3}{5}N\epsilon_F = \frac{3}{5}N \cdot \frac{h^2}{8m_e} \left(\frac{3N}{\pi V}\right)^{2/3},$$

where N is the number of electrons. If the star contains one proton (mass m_p) and one neutron (mass $\approx m_p$) for each electron, then $N = M/2m_p$. Plugging in $\frac{4}{3}\pi R^3$ for the volume then gives

$$U_{\text{kinetic}} = \frac{3h^2}{40m_e} \left(\frac{M}{2m_p}\right)^{5/3} \left(\frac{9}{4\pi^2 R^3}\right)^{2/3} = (0.0088) \frac{h^2 M^{5/3}}{m_e m_p^{5/3} R^2}.$$

- c) The gravitational energy of the star is proportional to $-1/R$, while the kinetic energy of the electrons is proportional to $+1/R^2$. Here's a sketch of these functions and their sum:



To find the minimum in the total energy, set the derivative equal to zero:

$$0 = \frac{d}{dR} \left(-\frac{\alpha}{R} + \frac{\beta}{R^2} \right) = \frac{2\beta}{R^2} - \frac{2\beta}{R^3} = \frac{1}{R^2} \left(\frac{2\beta}{R} \right).$$

The equilibrium radius is therefore at

$$R = \frac{2\beta}{\alpha} = \frac{2(0.0088)h^2 M^{5/3}/m_e m_p^{5/3}}{(3/5)GM^2} = (0.029) \frac{h^2}{G m_e m_p^{5/3}} \frac{1}{M^{1/3}}.$$

Notice that a white dwarf star with a larger mass has a *smaller* equilibrium radius. This does make sense, because adding mass creates more gravitational attraction, allowing the gravitational energy to decrease more than the kinetic energy increases as the star contracts.

- d) For a one-solar-mass white dwarf,

$$\begin{aligned} R &= \frac{(0.029)(6.63 \times 10^{-34} \text{ J s})^2}{(6.67 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(9.11 \times 10^{-31} \text{ kg})(1.67 \times 10^{-27} \text{ kg})^{5/3}(2 \times 10^{30} \text{ kg})^{1/3}} \\ &= 7.2 \times 10^6 \text{ m} = 7200 \text{ km}. \end{aligned}$$

This is just slightly larger than the earth. (For comparison, the sun's radius is more than 100 times the earth's.) The density is the mass divided by the volume:

$$\rho = \frac{M}{\frac{4}{3}\pi R^3} = \frac{2 \times 10^{30} \text{ kg}}{\frac{4}{3}\pi(7.2 \times 10^6 \text{ m})^3} = 1.3 \times 10^9 \text{ kg/m}^3.$$

This is 1.3 million times the density of water.

- e) The Fermi energy is

$$\begin{aligned}\epsilon_F &= \frac{h^2}{8m_e} \left(\frac{3N}{\pi V}\right)^{2/3} = \frac{h^2}{8m_e} \left(\frac{9M}{8\pi^2 m_p}\right)^{2/3} \frac{1}{R^2} \\ &= \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})} \left(\frac{9(2 \times 10^{30} \text{ kg})}{8\pi^2(1.67 \times 10^{-27} \text{ kg})}\right)^{2/3} \frac{1}{(7.2 \times 10^6 \text{ m})^2} \\ &= 3.1 \times 10^{-14} \text{ J} = 1.9 \times 10^5 \text{ eV}.\end{aligned}$$

So the Fermi temperature is

$$T_F = \epsilon_F/k = 2.3 \times 10^9 \text{ K}.$$

This is more than a hundred times hotter than the center of the sun. It seems unlikely that the actual temperature of a white dwarf star would be anywhere near this high. In other words, the thermal energy of the electrons is almost certainly much smaller than the kinetic energy they have even at $T = 0$. For the purposes of the energy calculations in this problem, therefore, simply neglecting the thermal energy and setting $T = 0$ is probably an excellent approximation.

- f) If the electrons are ultra-relativistic, we can use the formulas derived in the previous problem for the Fermi energy and the total kinetic energy:

$$\begin{aligned}U_{\text{kinetic}} &= \frac{3}{4}N\epsilon_F = \frac{3}{4}N \cdot \frac{hc}{2} \left(\frac{3N}{\pi V}\right)^{1/3} \\ &= \frac{3}{8}hc \left(\frac{M}{2m_p}\right)^{4/3} \left(\frac{3}{\pi \frac{4}{3}\pi R^3}\right)^{1/3} = (0.091)hc \left(\frac{M}{m_p}\right)^{4/3} \frac{1}{R}.\end{aligned}$$

The important feature of this formula is that it is proportional to $1/R$, not $1/R^2$. When we add the gravitational potential energy, which is proportional to $-1/R$, we get a total energy function with no stable minimum. Instead, depending on which coefficient is larger, the total energy is simply proportional to either $+1/R$ or $-1/R$. Therefore the "star" will either expand to infinite radius or collapse to zero radius.

- g) First note that the coefficient of the gravitational energy is proportional to M^2 , while that of the kinetic energy is proportional to only $M^{4/3}$, so the star will collapse rather than expand if its mass is sufficiently large. The crossover from expansion to collapse occurs when the coefficients are equal, that is, when

$$(0.091)hc \left(\frac{M}{m_p}\right)^{4/3} = \frac{3}{5}GM^2,$$

or

$$M = \left[(0.091) \frac{5}{3} \frac{hc}{G} \right]^{3/2} \frac{1}{m_p^2} = 3.4 \times 10^{30} \text{ kg},$$

that is, a little under twice the sun's mass. However, the star won't be relativistic to begin with unless the average kinetic energy of the electrons is comparable to their rest energy, $mc^2 = 5 \times 10^5$ eV. For the sun's mass, the average electron energy ($0.6\epsilon_F$) is only 1.2×10^5 eV, too low by a factor of about 4.4. This indicates that a one-solar-mass white dwarf is probably stable, but it's still close enough to being relativistic that we shouldn't expect the nonrelativistic approximation to be terribly accurate. Meanwhile, looking back at part (e), we see that the Fermi energy is proportional to $(M/R^3)^{2/3} \propto (M^2)^{2/3} = M^{4/3}$. Therefore, to increase the Fermi energy by a factor of 4.4, we'd have to increase the mass by only a factor of about 3. Conclusion: A white dwarf star with a mass greater than about three times the sun's mass will be relativistic and hence unstable, collapsing to zero radius (unless it first converts into some other form of matter). (Note: The best modern calculations, which take into account both the exact relativistic energy-momentum relation and the variation of density within the star, put the critical mass for a white dwarf at only 1.4 solar masses.)

Problem 7.24. In a neutron star, the kinetic energy comes from the neutrons, and the number of these is simply $N = M/m_n$, where M is the total mass and m_n is the mass of a neutron. Therefore we can write the kinetic energy as

$$U_{\text{kinetic}} = \frac{3}{5} N \epsilon_F = \frac{3}{5} N \frac{h^2}{8m_n} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{3h^2}{40m_n} \left(\frac{M}{m_n} \right)^{5/3} \left(\frac{9}{4\pi^2 R^3} \right)^{2/3}.$$

Adding the (negative) gravitational potential energy, we have for the total energy

$$U = U_{\text{potential}} + U_{\text{kinetic}} = -\frac{\beta}{R} + \frac{\beta}{R^2},$$

where $\beta = (3/5)GM^2$ and $\beta = (0.028)h^2 M^{5/3} / m_n^{8/3}$. As with a white dwarf star, the equilibrium radius is the one that minimizes the total energy. Setting $dU/dR = 0$ and solving for R gives

$$R = \frac{2\beta}{(0.093)} \frac{(0.093)h^2}{G m_n^{8/3} M^{1/3}}.$$

Here again, the equilibrium radius decreases with increasing mass, due to the greater gravitational attraction. For a one-solar-mass neutron star this model predicts,

$$R = \frac{(0.093)(6.63 \times 10^{-34} \text{ J s})^2}{(6.67 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(1.67 \times 10^{-27} \text{ kg})^{8/3}(2 \times 10^{30} \text{ kg})^{1/3}} = 12.3 \text{ km},$$

about the size of a large city. The density would be

$$\rho = \frac{M}{\frac{4}{3}\pi R^3} = \frac{2 \times 10^{30} \text{ kg}}{\frac{4}{3}\pi(12,300 \text{ m})^3} = 2.6 \times 10^{17} \text{ kg/m}^3,$$

or more than 10^{14} times the density of water. Not surprisingly, this is comparable to the density of an atomic nucleus. The Fermi energy is

$$\begin{aligned}\epsilon_F &= \frac{h^2}{8m_n} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{h^2}{8m_n^{5/3}} \left(\frac{9M}{4\pi^2} \right)^{2/3} \frac{1}{R^2} \\ &= \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(1.67 \times 10^{-27} \text{ kg})^{5/3}} \left(\frac{9(2 \times 10^{30} \text{ kg})}{4\pi^2} \right)^{2/3} \frac{1}{(12,300 \text{ m})^2} \\ &= 9.1 \times 10^{-12} \text{ J} = 5.7 \times 10^7 \text{ eV},\end{aligned}$$

so the Fermi temperature is

$$T_F = \epsilon_F/k = 6.6 \times 10^{11} \text{ K}.$$

This is even higher than for a white dwarf star, so the actual temperature of a neutron star is almost certainly much lower than T_F . Like a white dwarf, a neutron star should become unstable when the neutrons become relativistic, that is, when their average kinetic energy becomes comparable to their rest energy, $mc^2 = 940 \text{ MeV}$. For a one-solar-mass neutron star, the average kinetic energy is only $0.6\epsilon_F = 34 \text{ MeV}$, too small by about a factor of 28. But the Fermi energy is proportional to the mass to the $4/3$ power, so the critical mass should be larger than the sun's mass by a factor of about $28^{3/4} = 12$. (The experts, however, put the critical mass at only about 2 to 3 solar masses, taking into account density variations, nuclear forces, and the full relativistic energy-momentum relation.)

Problem 7.25. According to equation 7.48, the electronic heat capacity of a mole of copper should be

$$C_V = \frac{\pi^2 k T}{2 \epsilon_F} R = \frac{\pi^2}{2} \frac{(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})}{7.05 \text{ eV}} R = (0.018)R = 0.15 \text{ J/K}.$$

For comparison, the heat capacity of lattice vibrations (assuming these are not frozen out) should be roughly $3R = 25 \text{ J/K}$, 166 times greater. So at room temperature, the electrons contribute less than 1% of the total heat capacity of copper.

Problem 7.26. (Liquid helium-3 as a degenerate Fermi gas.)

- a) The Fermi energy of a “gas” of ${}^3\text{He}$ atoms with the given density is

$$\begin{aligned}\epsilon_F &= \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(3)(1.66 \times 10^{-27} \text{ kg})} \left(\frac{3(6.02 \times 10^{23})}{\pi(37 \times 10^{-6} \text{ m}^3)} \right)^{2/3} \\ &= 6.9 \times 10^{-23} \text{ J} = 4.3 \times 10^{-4} \text{ eV}.\end{aligned}$$

The Fermi temperature is therefore

$$T_F = \frac{\epsilon_F}{k} = \frac{4.3 \times 10^{-4} \text{ eV}}{8.62 \times 10^{-5} \text{ J/K}} = 5.0 \text{ K}.$$

That's only a little higher than the boiling point, 3.2 K.

- b) As predicted by equation 7.48, the heat capacity should be

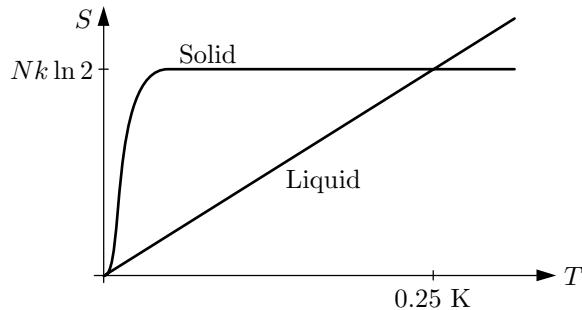
$$\frac{C_V}{NkT} = \frac{\pi^2 k}{2\epsilon_F} = \frac{\pi^2}{2T_F} = 1.0 \text{ K}^{-1}.$$

So although the linear temperature dependence agrees with experiment, the predicted coefficient is too small by almost a factor of 3.

- c) Using the experimental value of the heat capacity coefficient, the entropy of liquid ${}^3\text{He}$ is

$$S = \int_0^T \frac{C_V}{T'} dT' = (2.8 \text{ K}^{-1})Nk \int_0^T dT' = (2.8 \text{ K}^{-1})NkT,$$

exactly equal to the heat capacity, thanks to the linear temperature dependence. The entropy of the solid, meanwhile, should be $k \ln 2^N = Nk \ln 2$, since each nucleus has two possible spin orientations. This constant value should apply down to very low (millikelvin or lower) temperatures, when the nuclear spins finally align and the entropy freezes out. Here is a sketch of both entropy functions:



The intersection point where the entropies are equal should be at approximately

$$Nk \ln 2 = (2.8 \text{ K}^{-1})NkT, \quad \text{or} \quad T = \frac{\ln 2}{2.8 \text{ K}^{-1}} = 0.25 \text{ K}.$$

According to the Clausius-Clapeyron relation, the slope of the solid-liquid phase boundary on a graph of P vs. T should be proportional to the entropy difference, $S_{\text{liquid}} - S_{\text{solid}}$. Our analysis therefore predicts that the slope should be positive at temperatures greater than about 0.25 K, and negative at lower temperatures. The experimental phase diagram (Figure 5.13) shows just this behavior, with the transition from positive to negative slope at about 0.3 K, just slightly higher than our prediction. The discrepancy could be because of lattice vibrations giving the solid some additional entropy, and/or the entropy of the liquid no longer being quite linear at relatively high temperatures. At very low temperature, where the entropy of the solid also goes to zero, the phase boundary becomes horizontal.

Problem 7.27. (Heat capacity of a Fermi system with evenly spaced levels.)

- a) Referring to the dot diagrams of Problem 7.16, imagine starting with $q = 0$ and then constructing a state for higher q by displacing one or more solid dots upward. The total number of upward steps taken by the dots must be q , the total number of units

of energy. This can be accomplished by moving one dot up q steps, or two dots up a number of steps that sum to q , or three dots up a number of steps that sum to q , and so on. In all cases, each successive dot can be moved upward by no more steps than its predecessor. The total number of ways of giving the system q units of energy is therefore just the number of ways of writing nonincreasing lists of integers that add up to q , that is, the number of unrestricted partitions, $p(q)$.

- b) The partitions of 7 are:

$$\begin{aligned} 7, \quad & 6+1, \quad 5+2, \quad 5+1+1, \quad 4+3, \quad 4+2+1, \quad 4+1+1+1, \quad 3+3+1, \quad 3+2+2, \\ & 3+2+1+1, \quad 3+1+1+1+1, \quad 2+2+2+1, \quad 2+2+1+1+1, \\ & 2+1+1+1+1+1, \quad 1+1+1+1+1+1+1. \end{aligned}$$

That's 15 total, so $p(7) = 15$. The partitions of 8 are

$$\begin{aligned} 8, \quad & 7+1, \quad 6+2, \quad 6+1+1, \quad 5+3, \quad 5+2+1, \quad 5+1+1+1, \quad 4+4, \quad 4+3+1, \\ & 4+2+2, \quad 4+2+1+1, \quad 4+1+1+1+1, \quad 3+3+2, \quad 3+3+1+1, \quad 3+2+2+1, \\ & 3+2+1+1+1, \quad 3+1+1+1+1+1, \quad 2+2+2+2, \quad 2+2+2+1+1, \\ & 2+2+1+1+1+1, \quad 2+1+1+1+1+1+1, \quad 1+1+1+1+1+1+1+1. \end{aligned}$$

That's 22 total, so $p(8) = 22$.

- c) *Mathematica* has a built-in function `PartitionsP` for computing unrestricted partitions, so I just made a table with the instruction

```
mult = Table[PartitionsP[q], {q, 0, 100}]
```

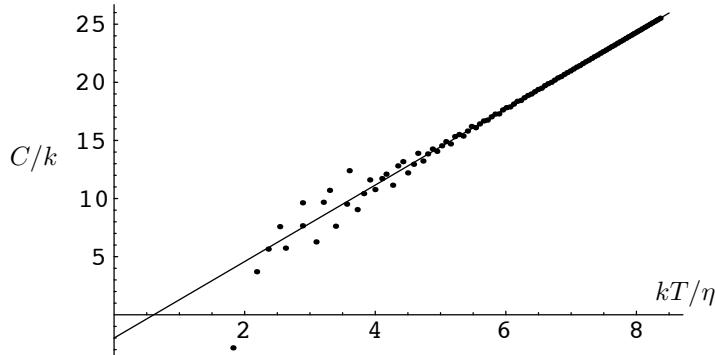
Here's what it returned:

```
{1, 1, 2, 3, 5, 7, 11, 15, 22, 30, 42, 56, 77, 101, 135, 176, 231, 297, 385, 490, 627, 792, 1002, 1255, 1575, 1958, 2436, 3010, 3718, 4565, 5604, 6842, 8349, 10143, 12310, 14883, 17977, 21637, 26015, 31185, 37338, 44583, 53174, 63261, 75175, 89134, 105558, 124754, 147273, 173525, 204226, 239943, 281589, 329931, 386155, 451276, 526823, 614154, 715220, 831820, 966467, 1121505, 1300156, 1505499, 1741630, 2012558, 2323520, 2679689, 3087735, 3554345, 4087968, 4697205, 5392783, 6185689, 7089500, 8118264, 9289091, 10619863, 12132164, 13848650, 15796476, 18004327, 20506255, 23338469, 26543660, 30167357, 34262962, 38887673, 44108109, 49995925, 56634173, 64112359, 72533807, 82010177, 92669720, 104651419, 118114304, 133230930, 150198136, 169229875, 190569292}
```

To compute the entropy, temperature, and heat capacity, I would have preferred to copy this output into a spreadsheet and proceed as in Problem 3.24. But copying the output into a spreadsheet proved to be so awkward that I instead just finished the calculation in *Mathematica*:

```
entropy = Log[mult] //N
temp = Table[2/(entropy[[i+1]] - entropy[[i-1]]), {i, 2, 100}]
heatcap = Table[2/(temp[[i+1]] - temp[[i-1]]), {i, 2, 98}]
ListPlot[Table[{temp[[i]], heatcap[[i-1]]}, {i, 2, 98}]]
```

The `//N` tells *Mathematica* to work with approximate numerical values rather than exact formulas. The temperature and heat capacity are computed by the centered-difference method used in Problem 3.24, with the index ranges carefully chosen to use all the data available and no more. Here's the plot of heat capacity vs. temperature:



As expected, the heat capacity is linear in T , aside from irregularities associated with the small size of the system.

- d) For $q = 10$, the Ramanujan-Hardy formula gives

$$p(10) \approx \frac{e^{\pi\sqrt{20/3}}}{40\sqrt{3}} = 48.1,$$

about 15% higher than the exact value $p(10) = 42$. For $q = 100$, the RH formula gives

$$p(100) \approx \frac{e^{\pi\sqrt{200/3}}}{400\sqrt{3}} = 1.99 \times 10^8,$$

about 5% higher than the exact value $p(100) = 190569292$. So the accuracy does improve with increasing q , although this formula is not nearly as accurate as, say, Stirling's approximation. Working with the RH formula, we have for the entropy of this system

$$\frac{S}{k} = \ln \Omega = \ln p(q) = \pi\sqrt{2q/3} - \ln(4\sqrt{3}q).$$

Since $q = U/\eta$, we can compute the temperature as follows:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{dq}{dU} \frac{\partial S}{\partial q} = \frac{k}{\eta} \frac{d}{dq} [\pi\sqrt{2q/3} - \ln(4\sqrt{3}q)] = \frac{k}{\eta} \left[\frac{\pi}{\sqrt{6q}} - \frac{1}{q} \right].$$

With the abbreviations $t \equiv kT/\eta$ and $s = \sqrt{q}$, this equation becomes

$$t = \frac{s}{(\pi/\sqrt{6})(1/s)} \quad \text{or} \quad s^2 - \frac{\pi t}{\sqrt{6}}s + t = 0.$$

The solutions to this quadratic equation are

$$s = \frac{\pi t}{2\sqrt{6}} \pm \sqrt{\frac{\pi^2 t^2}{24} - t} = \frac{\pi t}{2\sqrt{6}} \left(1 \pm \sqrt{1 - \frac{24}{\pi^2 t}} \right).$$

The plus sign gives the physically relevant solution, since the minus sign would give a value of s that actually decreases with increasing t . Squaring this expression then gives

$$\begin{aligned} q &= \frac{\pi^2 t^2}{24} \left(1 + 1 - \frac{24}{\pi^2 t} + 2 \sqrt{1 - \frac{24}{\pi^2 t}} \right) = \frac{\pi^2 t^2}{12} - t + \frac{\pi^2 t^2}{12} \sqrt{1 - \frac{24}{\pi^2 t}} \\ &= \frac{\pi^2 t^2}{12} - t + \frac{\pi^2 t^2}{12} \left(1 - \frac{12}{\pi^2 t} + \dots \right) = \frac{\pi^2 t^2}{6} - 2t + \dots . \end{aligned}$$

In the second line I've approximated the square root under the assumption that $t \gg 1$, which is true whenever the RH formula applies in the first place. The energy U is just $q\eta$, so the heat capacity is

$$C = \frac{dU}{dT} = k \frac{dq}{dt} \approx k \left(\frac{\pi^2 t}{3} - 2 \right) = k \left(\frac{\pi^2 kT}{3\eta} - 2 \right).$$

The predicted heat capacity is linear in T , as expected, but offset downward by a constant term. This prediction is plotted as the solid line in the graph above. As you can see, it agrees beautifully with the exact numerical calculation as t becomes large.

Why is the heat capacity of this system independent of N ? This may seem like quite a paradox, since heat capacity must be extensive. However, this model system has no explicitly specified volume, so the notion of an extensive vs. intensive quantity is not really meaningful. In real systems, the spacing between energy levels would decrease with increasing volume. So if you like, you can imagine that there is a hidden volume dependence in the constant η . In formula 7.48 for the heat capacity of a Fermi gas in a three-dimensional box, the factor of N really comes from the energy level spacing as well; see equations 7.51 and 7.54.

Problem 7.28. (Two-dimensional Fermi gas.)

- a) In two dimensions, the allowed energy levels are

$$\epsilon = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2).$$

At $T = 0$, fermions settle into the lowest unoccupied levels, so in two-dimensional n -space, they fill a quarter-circle with radius n_{\max} . The Fermi energy is the highest filled level, $\epsilon_F = \hbar^2 n_{\max}^2 / 8mA$. But the total number of fermions in the system is $N = 2\pi n_{\max}^2 / 4$, assuming that the fermions have spin 1/2 and hence two allowed states for each spatial wavefunction. Solving for n_{\max}^2 and plugging into the formula for ϵ_F gives

$$\epsilon_F = \frac{\hbar^2}{8mA} \left(\frac{2N}{\pi} \right) = \frac{\hbar^2 N}{4\pi mA}.$$

To compute the total energy, we add up the energies of all filled states and convert the sum to an integral over a quarter-circle in polar coordinates:

$$U = 2 \sum_{n_x} \sum_{n_y} \epsilon(\vec{n}) = 2 \int_0^{n_{\max}} dn \int_0^{\pi/2} d\phi n \epsilon(\vec{n}) = \pi \int_0^{n_{\max}} n \frac{\hbar^2 n^2}{8mA} dn = \frac{\pi \hbar^2 n_{\max}^4}{32mA}.$$

But $n_{\max}^2 = 2N/\pi$ so this is just

$$U = \frac{\pi h^2}{32mA} \left(\frac{2N}{\pi} \right)^2 = \frac{h^2 N^2}{8\pi mA} = \frac{1}{2} N \epsilon_F.$$

The average energy is just $U/N = \epsilon_F/2$.

- b) To find the density of states, we need to change variables to ϵ in either the integral for the total energy or the integral for the total number of particles. Since the energy integral appears just above, I'll work with it. For the variable change from n to ϵ we need to know that $\epsilon = h^2 n^2 / 8mA$, which implies $d\epsilon = (h^2 n / 4mA) dn$, or $n dn = (4mA/h^2) d\epsilon$. Therefore the energy integral (at $T = 0$) is

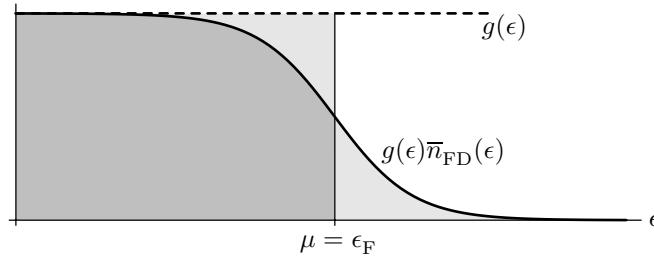
$$U = \int_0^{\epsilon_F} \pi \left(\frac{4mA}{h^2} \right) \epsilon d\epsilon \quad (\text{at } T = 0).$$

We interpret this integral of the sum of all the energies (ϵ) multiplied by the number of states per unit energy ($g(\epsilon)d\epsilon$). Therefore, for this system,

$$g(\epsilon) = \frac{4\pi mA}{h^2} = \frac{N}{\epsilon_F},$$

which is indeed a constant, independent of ϵ .

- c) The illustration below is an adaptation of Figure 7.14 to this two-dimensional system. The solid curve shows the number of particles present, per unit energy; as T increases, the slope of the fall-off becomes shallower. But because $g(\epsilon)$ is constant for this system (and because of the symmetry of the Fermi-Dirac distribution about the point $\epsilon = \mu$), the lightly shaded areas are equal and therefore μ , the point where $\bar{n}_{FD} = 1/2$, remains at its zero-temperature value, ϵ_F . Or almost: At sufficiently high temperatures ($kT \sim \epsilon_F$), the Fermi-Dirac distribution will become significantly less than 1 at negative values of ϵ . Since $g(\epsilon) = 0$ at negative ϵ (there are no negative-energy states), the upper lightly-shaded area will then be smaller than the lower one unless μ decreases. At temperatures much greater than ϵ_F/k , the fall-off in the Fermi-Dirac distribution will be so spread out that μ will have to become negative in order to preserve the equality of the two lightly shaded areas. In summary: When $kT \ll \epsilon_F$, μ remains almost exactly equal to ϵ_F . When $kT \gg \epsilon_F$, μ becomes negative and decreases with increasing temperature.



- d) At nonzero temperature, the integral for the total number of particles is

$$N = \int_0^\infty g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon = g \int_0^\infty \frac{1}{e^{(\epsilon - \mu)/kT} + 1} d\epsilon,$$

since g is a constant. Changing variables to $x = (\epsilon - \mu)/kT$, this integral becomes

$$N = gkT \int_{-\mu/kT}^{\infty} \frac{1}{e^x + 1} dx.$$

The integrand is a composite function involving e^x ; if it were multiplied by the derivative of e^x (which is also e^x), we could integrate it easily with another substitution. But we can almost put it into this form by multiplying numerator and denominator by e^{-x} :

$$N = gkT \int_{-\mu/kT}^{\infty} \frac{e^{-x}}{1 + e^{-x}} dx.$$

Now just substitute $y = e^{-x}$ and $dy = -e^{-x}dx$:

$$\begin{aligned} N &= gkT \int_{e^{-\mu/kT}}^0 \frac{1}{1+y} dy = gkT \ln(1+y) \Big|_{e^{-\mu/kT}}^0 \\ &= gkT \ln\left(\frac{1}{1+e^{-\mu/kT}}\right) = gkT \ln(1 + e^{-\mu/kT}). \end{aligned}$$

Solving for μ as a function of N then gives

$$\mu = kT \ln(e^{N/gkT} - 1) = kT \ln(e^{\epsilon_F/kT} - 1).$$

When $kT \ll \epsilon_F$, the exponential $e^{\epsilon_F/kT}$ is very large, and the 1 is negligible in comparison, so the right-hand side is approximately $kT \epsilon_F/kT = \epsilon_F$, as predicted above. When $kT \gg \epsilon_F$, on the other hand, the exponential is only slightly larger than 1, so the argument of the logarithm is less than 1 and therefore the chemical potential is negative as expected.

- e) When $kT \gg \epsilon_F$, the exponential can be expanded in a power series: $1 + \epsilon_F/kT + \dots$. The 1 cancels, leaving us with

$$\mu \approx kT \ln \frac{\epsilon_F}{kT} = kT \ln\left(\frac{A}{N} \frac{4\pi mkT}{h^2}\right) = kT \ln\left(\frac{A}{N} \frac{2}{\ell_Q^2}\right).$$

This is the two-dimensional analogue of equation 6.93 for the chemical potential of an ordinary (“classical”) ideal gas, with $Z_{\text{int}} = 2$ because the electron has two internal spin states.

Problem 7.29. The energy integral is

$$U = \int_0^\infty \epsilon g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) d\epsilon = g_0 \int_0^\infty \epsilon^{3/2} \bar{n}_{\text{FD}}(\epsilon) d\epsilon.$$

As in equation 7.57, we now integrate by parts:

$$U = \frac{2}{5} g_0 \epsilon^{5/2} \bar{n}_{\text{FD}}(\epsilon) \Big|_0^\infty + \frac{2}{5} g_0 \int_0^\infty \epsilon^{5/2} \left(-\frac{d\bar{n}_{\text{FD}}}{d\epsilon} \right) d\epsilon.$$

The boundary term vanishes at both limits, leaving us with

$$U = \frac{2}{5}g_0 \int_0^\infty \frac{1}{kT} \frac{e^x}{(e^x + 1)^2} \epsilon^{5/2} d\epsilon = \frac{2}{5}g_0 \int_{-kT}^\infty \frac{e^x}{(e^x + 1)^2} \epsilon^{5/2} dx,$$

where $x = (\epsilon - \epsilon_F)/kT$ and I've used equation 7.58 for $d\bar{n}_{FD}/d\epsilon$. Now, because the integrand is negligible when $|x| \gg 1$, and because $kT \ll \epsilon$, we can extend the lower limit of the integral down to $-\infty$. We can also expand the function $\epsilon^{5/2}$ in a Taylor series about $\epsilon = \epsilon_F$:

$$\begin{aligned} \epsilon^{5/2} &= (\epsilon - \epsilon_F)^{5/2} + \frac{5}{2}(\epsilon - \epsilon_F)^{3/2} + \frac{15}{8}(\epsilon - \epsilon_F)^{1/2} + \\ &= (\epsilon - \epsilon_F)^{5/2} + \frac{5}{2}(xkT)^{3/2} + \frac{15}{8}(xkT)^{1/2} + \dots \end{aligned}$$

When we plug this into the energy integral, the first term gives simply $\frac{2}{5}g_0 \epsilon_F^{5/2}$ (see equation 7.62), while the second term gives zero because it is an odd function. To integrate the third term we can again use equation 7.64; therefore,

$$\begin{aligned} U &\approx \frac{2}{5}g_0 \epsilon_F^{5/2} + \frac{2}{5}g_0 \frac{15}{8}(kT)^2 \epsilon_F^{1/2} - \frac{\pi^2}{3} = \frac{2}{5}g_0 \epsilon_F^{5/2} + \frac{\pi^2}{4}g_0(kT)^2 \epsilon_F^{1/2} \\ &= \frac{3}{5}N \frac{\epsilon_F^{5/2}}{\epsilon_F^{3/2}} + \frac{3\pi^2}{8}N \frac{(kT)^2}{\epsilon_F}, \end{aligned}$$

where in the last line I've used the fact that $g_0 = \frac{3}{2}N/\epsilon_F^{3/2}$ and set $\epsilon = \epsilon_F$ in the second term, since that term is already small and the difference between ϵ and ϵ_F would give an even smaller correction. Now all that remains is to plug in equation 7.66 for ϵ . According to that equation,

$$\epsilon_F^{5/2} \approx \epsilon_F^{5/2} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 \right]^{5/2} \approx \epsilon_F^{5/2} \left[1 - \frac{5}{2} \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 \right] = \epsilon_F^{5/2} \left[1 - \frac{5\pi^2}{24} \left(\frac{kT}{\epsilon_F} \right)^2 \right].$$

Plugging this into the previous equation gives

$$U \approx \frac{3}{5}N\epsilon_F - \frac{3}{5}N\epsilon_F - \frac{5\pi^2}{24} \left(\frac{kT}{\epsilon_F} \right)^2 + \frac{3\pi^2}{8}N \frac{(kT)^2}{\epsilon_F} = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N \frac{(kT)^2}{\epsilon_F},$$

as claimed in equation 7.68.

Problem 7.30. If we carry the expansion in equation 7.60 to higher orders, we find terms proportional to $(\epsilon - \epsilon_F)^3$, $(\epsilon - \epsilon_F)^4$, and so on, where $\epsilon - \epsilon_F = xkT$. When integrated as in equation 7.61, however, all terms with odd powers of x vanish by symmetry; thus the next nonzero term would be proportional to $(kT)^4$. The next approximation made was in replacing $\epsilon_F^{1/2}$ with $\epsilon_F^{-1/2}$ in equation 7.65. To be more accurate here, we would have to include the quadratic correction in equation 7.66, which implies

$$\epsilon_F^{1/2} \approx \epsilon_F^{-1/2} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 \right]^{-1/2} \approx \epsilon_F^{-1/2} \left[1 + \frac{\pi^2}{24} \left(\frac{kT}{\epsilon_F} \right)^2 \right].$$

Plugging this into the quadratic term in equation 7.65, we find that the next correction is again proportional to T^4 . Thus, the “ ” in the first line of equation 7.66 represents terms beginning with $(kT/\epsilon_F)^4$. When we apply the binomial expansion to obtain the second line of that equation, we get a quartic contribution from the new quartic term raised to the first power, and also a quartic contribution from the old quadratic term raised to the second power. There is no cubic term, however, so the next correction to ϵ is quartic in temperature.

In the energy integral, the expansion of $\epsilon^{5/2}$ again gives terms proportional to T^3 , T^4 , and so on, but again the terms with odd powers of T also contain odd powers of x , so they integrate to zero. We are left with an expression for U containing terms proportional to $\epsilon^{5/2}$, $(kT)^{2-1/2}$, and $(kT)^{4-3/2}$. Each power of ϵ can be written as a series in (kT/ϵ_F) , but since that series contains only even powers of T , no odd powers can arise in the formula for U . The next correction to the energy is therefore proportional to $(kT\epsilon_F)^4$.

Now let me calculate the next correction explicitly. The first step is to expand $\epsilon^{3/2}$ to fourth order. To do this I used the *Mathematica* instruction

```
Normal[Series[eps^(3/2), {eps, mu, 4}]] /. eps-mu -> x*kT
```

which also converts the truncated series into a “normal” polynomial and substitutes xkT for $(\epsilon - \mu)$. The quartic term in the expansion came out to $3(kT)^4x^4/128^{-5/2}$. Next we need the integral

$$\int_{-\infty}^{\infty} \frac{x^4 e^x}{(e^x + 1)^2} dx = \frac{7\pi^4}{15},$$

which can be evaluated by the same method as in Problem B.21. Equation 7.65 therefore becomes

$$N = N \left(\frac{1}{\epsilon_F} \right)^{3/2} + \frac{\pi^2}{8} N \frac{(kT)^2}{\epsilon_F^{3/2-1/2}} + \frac{7\pi^4}{640} N \frac{(kT)^4}{\epsilon_F^{3/2-5/2}}.$$

The ϵ in the final term can simply be set equal to ϵ_F , since the correction would be sixth order in T . In the second term, we can plug in the formula for ϵ to second order, already calculated in equation 7.66. Solving for ϵ/ϵ_F and expanding everything out in powers of kT/ϵ_F requires a few more steps. I did them by hand and then checked the answer with the *Mathematica* instruction

```
muSeries = Normal[Series[(1 - (Pi^2/8)t^2/(1-Pi^2*t^2/12))^(1/2) - (7*Pi^4/640)t^4)^(2/3), {t, 0, 4}]]
```

where t is an abbreviation for kT/ϵ_F . The formula returned, in ordinary notation, was

$$\frac{1}{\epsilon_F} = 1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 - \frac{\pi^4}{80} \left(\frac{kT}{\epsilon_F} \right)^4.$$

To carry out the energy integral, I similarly expanded $\epsilon^{5/2}$:

```
Normal[Series[eps^(5/2), {eps, mu, 4}]] /. eps-mu -> x*kT
```

Again the cubic term integrates to zero. The quartic term is $-5(kT)^4x^4/128^{-3/2}$, which gets integrated as in the previous problem to give for the energy

$$U = \frac{2}{5} g_0^{-5/2} + \frac{\pi^2}{4} g_0 (kT)^{2-1/2} - \frac{7\pi^4}{960} g_0 \frac{(kT)^4}{\epsilon_F^{3/2}}.$$

In order to do the rest of the algebra with *Mathematica*, I typed in this expression:

$$\text{energy} = (2/5)g_0*\mu^{(5/2)} + (\pi^2/4)g_0*kT^{2*\mu^{(1/2)}} - (7*\pi^4/960)g_0*kT^{4/\mu^{(3/2)}}$$

In the next four steps I plugged in the explicit formula for g_0 , plugged in the previously calculated series for μ , substituted kT/ϵ_F for t , and expanded everything in a series to fourth order in kT :

$$\begin{aligned}\text{energy1} &= \text{energy} /. g_0 \rightarrow (3/2)(n/eF^{(3/2)}) \\ \text{energy2} &= \text{energy1} /. \mu \rightarrow \mu\text{Series}*eF \\ \text{energy3} &= \text{energy2} /. t \rightarrow kT/eF \\ \text{energy4} &= \text{Normal}[\text{Series}[\text{energy3}, \{kT, 0, 4\}]]\end{aligned}$$

The final instruction returned the desired expression for U to fourth order in kT/ϵ_F :

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F} - \frac{3\pi^4}{80}N\frac{(kT)^4}{\epsilon_F^3}.$$

Notice that the fourth-order correction to the energy is negative. The corresponding correction to the heat capacity would also be negative, and cubic in temperature, so a plot of C_V vs. T should become concave-down as T becomes comparable to ϵ_F . (See Problem 7.32.)

Problem 7.31. We saw in Problem 7.28 that the density of states of this two-dimensional system is a constant, N/ϵ_F . Therefore the energy integral is

$$U = \frac{N}{\epsilon_F} \int_0^\infty \epsilon \bar{n}_{FD}(\epsilon) d\epsilon.$$

Unlike the integral for N , this integral cannot be done analytically. So let's integrate by parts as in equation 7.57:

$$U = \frac{N}{\epsilon_F} \frac{\epsilon^2}{2} \bar{n}_{FD}(\epsilon) \Big|_0^\infty - \frac{N}{\epsilon_F} \int_0^\infty \frac{\epsilon^2}{2} \frac{d\bar{n}_{FD}}{d\epsilon} d\epsilon.$$

The boundary term vanishes at both limits, leaving us with

$$U = \frac{N}{2\epsilon_F} \int_0^\infty \epsilon^2 \frac{d\bar{n}_{FD}}{d\epsilon} d\epsilon = \frac{N}{2\epsilon_F} \int_{\epsilon_F/kT}^\infty \frac{e^x}{(e^x + 1)^2} \epsilon^2 dx,$$

where in the last expression I've changed variables to $x = (\epsilon - \epsilon_F)/kT$ and inserted expression 7.58 for $d\bar{n}_{FD}/d\epsilon$. So far this expression is exact. But when $kT \ll \epsilon_F$, we can extend the lower limit of the integral down to $-\infty$ as in the three-dimensional case. Since ϵ^2 contains only integer powers of x , no Taylor expansion is necessary; we have simply

$$U = \frac{N}{2\epsilon_F} \int_{-\infty}^\infty \frac{e^x}{(e^x + 1)^2} \left[\frac{1}{2} + 2 \frac{kTx}{kT} + (kT)^2 x^2 \right] dx.$$

Evaluating the integrals exactly as on page 284, this becomes

$$U = \frac{N}{2\epsilon_F} + \frac{\pi^2}{6} N \frac{(kT)^2}{\epsilon_F} \approx \frac{N\epsilon_F}{2} + \frac{\pi^2}{6} N \frac{(kT)^2}{\epsilon_F}.$$

The heat capacity is therefore

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\pi^2 N k^2 T}{3\epsilon_F},$$

which is linear in T as expected. Here, however, there are no corrections to the linear behavior that are proportional to higher powers of T ; the corrections are instead exponential, just as the deviation of ϵ from ϵ_F is exponentially suppressed by a factor of $e^{-\epsilon_F/kT}$.

Now consider the high temperature limit, $kT \gg \epsilon_F$. In this limit, as shown in Problem 7.28(e), $\epsilon \approx kT \ln(\epsilon_F/kT)$, which is negative. Since $e^{(\epsilon - c)/kT} \gg 1$ for all ϵ , we can neglect the 1 in the denominator of the Fermi-Dirac distribution and write simply

$$U = \frac{N}{\epsilon_F} \int_0^\infty \epsilon e^{-(\epsilon - c)/kT} d\epsilon = \frac{N}{\epsilon_F} \frac{\epsilon_F}{kT} \int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon = \frac{N}{kT} (kT)^2 = NkT,$$

as we would expect for an ordinary ideal gas in two dimensions, according to the equipartition theorem.

Problem 7.32. (Numerical treatment of a Fermi gas.)

- a) Making the substitutions $t = kT/\epsilon_F$, $c = -\epsilon_F/kT$, and $x = \epsilon/\epsilon_F$ in equation 7.53, I obtained the integral

$$1 = \frac{3}{2} \int_0^\infty \frac{\sqrt{x}}{e^{(x-c)/t} + 1} dx.$$

(Here I've used equation 7.51 for $g(\epsilon)$, and canceled the N 's on both sides.) Setting $t = 1$ and $c = 0$, this condition becomes simply

$$1 = \frac{3}{2} \int_0^\infty \frac{\sqrt{x}}{e^x + 1} dx.$$

To evaluate the right-hand side I typed

```
1.5*NIntegrate[Sqrt[x]/(Exp[x]+1),{x,0,Infinity}]
```

into *Mathematica* and got the result 1.017. So ϵ is not exactly zero when $kT = \epsilon_F$, but it's close. To reduce the value of the integral slightly we would want to make the denominator of the integrand larger, which we can do by making c (or ϵ) slightly negative.

- b) First I defined a *Mathematica* function to compute the integral for any values of c and t :

```
fermiN[c_,t_] := 1.5*NIntegrate[Sqrt[x]/(Exp[(x-c)/t]+1),{x,0,Infinity}]
```

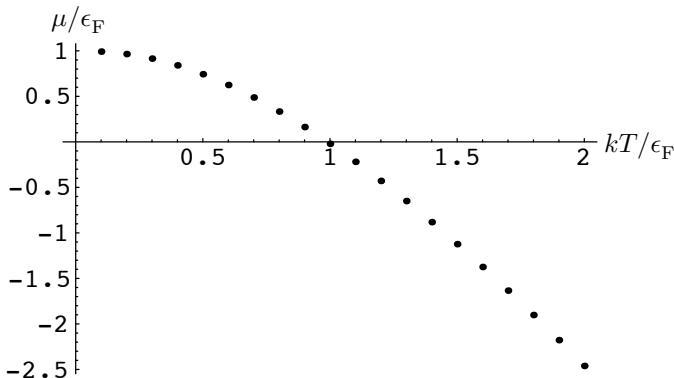
Then, for example, to find the actual value of c when $t = 1$, I typed simply:

```
FindRoot[1 == fermiN[c,1], {c,-1,0}]
```

(The numbers 1 and 0 specify a range of c values to use as initial trials in searching for a solution. The precise numbers used are not critical.) Although *Mathematica* complained with a warning message at this instruction, the answer it gave was quite reasonable: $c = -0.0215$. After this success, I got ambitious and asked for a table of solutions at 20 different t values:

```
mutable = Table[{t,FindRoot[1 == fermiN[c,t],{c,-1,0}][[1,2]]},{t,.1,2,.1}]
```

(Some of the details in this instruction are important only because I wanted to plot the table without retyping it. What it actually produces is a list of ordered pairs (t, c) . The “[1,2]” after the `FindRoot` function strips off some unwanted stuff that would have interfered with plotting.) This time I got several warning messages but still plausible results, so I plotted it with the instruction `ListPlot[mutable]`, which produced the following graph:



- c) In principle, the energy calculation is actually easier than the c calculation, but getting the previously calculated c values into the *Mathematica* formula can be a bit tricky. I did it by defining an “interpolating function”:

```
mu = Interpolation[mutable]
```

The function `mu[t]` can now be used to calculate c (actually $c = \mu/\epsilon_F$) at any temperature. (Figure 7.16 was generated by typing `Plot[mu[t],{t,0,2}]`.) As for the energy integral itself, with the same set of substitutions it becomes

$$\frac{U}{N\epsilon_F} = \frac{3}{2} \int_0^\infty \frac{x^{3/2}}{e^{(x-c)/t} + 1} dx,$$

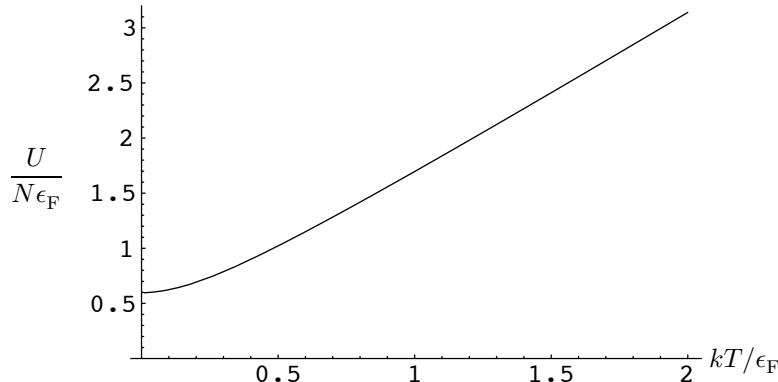
which I programmed by typing

```
energy[t_] := 1.5*NIntegrate[x^1.5/(Exp[(x-mu[t])/t]+1),{x,0,Infinity}]
```

To plot it I gave the instruction

```
Plot[energy[t],{t,.01,2},PlotRange->{All,{0,3.2}}];
```

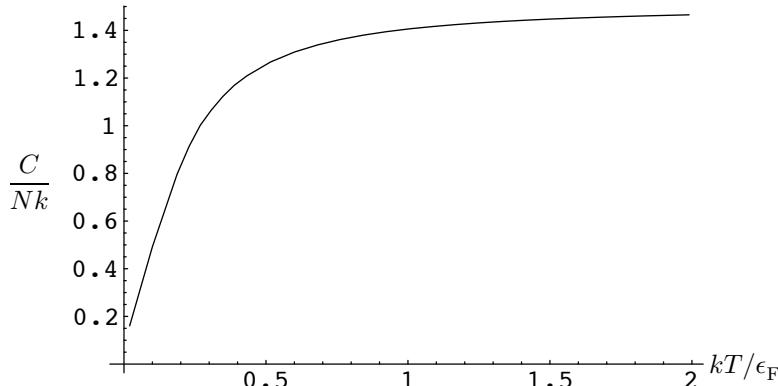
This produced the following graph:



Notice that $U/N\epsilon_F$ goes to $3/5$ at $T = 0$, as expected. To obtain the heat capacity I numerically differentiated the energy function and then plotted the result:

```
heatcap[t_] := (energy[t+.01] - energy[t-.01])/.02
Plot[heatcap[t],{t,.02,1.99}];
```

(Not very elegant, but it does the job.) Note that this “heat capacity” function really calculates C/Nk , since the energy function is really $U/N\epsilon_F$ and t is in units of ϵ_F/k . Here’s the plot:



At temperatures much less than ϵ_F/k , the heat capacity is approximately linear in T , as derived in the text. At temperatures much greater than ϵ_F/k , the heat capacity approaches $\frac{3}{2}Nk$, the value for an ordinary “monatomic” ideal gas.

Problem 7.33. (Simple model of a pure semiconductor.)

- a) At nonzero temperature there will be some electrons in the conduction band and some “holes” (unfilled states) in the valence band. But the numbers of conduction electrons and valence holes must be exactly equal, since raising the temperature can’t change

the total number of electrons. To calculate the number of electrons within any energy range we would integrate the function $g(\epsilon)\bar{n}_{\text{FD}}(\epsilon)$. Now in this simple model, $g(\epsilon)$ is symmetrical about the point $\epsilon = \epsilon_F$. Furthermore, as shown in Problem 7.12, the Fermi-Dirac distribution is symmetrical about the point $\epsilon = \epsilon_c$, in the sense that the probability of a state at ϵ being occupied is equal to the probability of a state at $\epsilon_c - \epsilon$ being unoccupied. In order for the calculated number of conduction electrons to equal the number of valence holes, the produce $g(\epsilon)\bar{n}_{\text{FD}}(\epsilon)$ must also have this property, but this will happen only if the symmetry points ϵ_c and ϵ_F coincide.

- b) The number of electrons in the conduction band is the integral of the density of states times the Fermi-Dirac distribution:

$$N_c = \int_{\epsilon_c}^{\infty} g(\epsilon)\bar{n}_{\text{FD}}(\epsilon) d\epsilon = g_0 \int_{\epsilon_c}^{\infty} \sqrt{\epsilon - \epsilon_c} \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} d\epsilon.$$

If the width of the gap is much greater than kT , then the exponent in the Fermi-Dirac distribution is large over the whole range of integration and we can neglect the $+1$ in comparison to the exponential. The integral then simplifies considerably; we can evaluate it explicitly by changing variables to $x = (\epsilon - \epsilon_c)/kT$:

$$\begin{aligned} N_c &\approx g_0 \int_{\epsilon_c}^{\infty} \sqrt{\epsilon - \epsilon_c} e^{-(\epsilon - \epsilon_F)/kT} d\epsilon \\ &= g_0 \int_{\epsilon_c}^{\infty} \sqrt{\epsilon - \epsilon_c} e^{-(\epsilon - \epsilon_c)/kT} e^{-(\epsilon_c - \epsilon_F)/kT} d\epsilon \\ &= g_0 e^{-(\epsilon_c - \epsilon_F)/kT} (kT)^{3/2} \int_0^{\infty} \sqrt{x} e^{-x} dx \end{aligned}$$

The integral over x can be done by the methods of Appendix B, or looked up in tables or evaluated by computer; it is simply $\sqrt{\pi}/2$. Plugging in the explicit value of g_0 (from equation 7.51) then gives

$$N_c = \frac{\pi(8m)^{3/2}}{2h^3} V(kT)^{3/2} \frac{\sqrt{\pi}}{2} e^{-(\epsilon_c - \epsilon_F)/kT} = \frac{2V}{v_Q} e^{-\epsilon_c/kT},$$

where v_Q is the quantum volume defined in equation 7.18 and $\Delta\epsilon$ is the width of the gap, $2(\epsilon_c - \epsilon_F)$.

- c) At room temperature, $kT \approx 0.026$ eV so the exponential factor is

$$e^{-\epsilon_c/kT} = \exp\left(-\frac{1.11 \text{ eV}}{2(0.026 \text{ eV})}\right) = e^{-21.3} = 5.4 \times 10^{-10}.$$

Meanwhile, the quantum volume is

$$v_Q = \left(\frac{(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(9.11 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \right)^{3/2} = 8.0 \times 10^{-26} \text{ m}^3.$$

Therefore the number of conduction electrons per unit volume should be roughly

$$\frac{N_c}{V} = \frac{2(5.4 \times 10^{-10})}{8.0 \times 10^{-26} \text{ m}^3} = 1.3 \times 10^{16} \text{ m}^{-3} = 1.3 \times 10^{10} \text{ cm}^{-3}.$$

For comparison, the density of conduction electrons in copper is about 8.5×10^{28} per cubic meter, as calculated in Problem 7.19. So copper should conduct electricity roughly a million million times better than (pure) silicon.

- d) A pure semiconductor will conduct much better at higher temperature because there are so many *more* electrons in the conduction band. For example, suppose we raise the temperature of our silicon from 300 K to 350 K. The quantum volume then decreases by a factor of $(350/300)^{3/2} = 1.26$, which isn't very significant. On the other hand, the exponential factor is now

$$e^{-\epsilon/2kT} = \exp\left(-\frac{1.11 \text{ eV}}{2(8.62 \times 10^5 \text{ eV/K})(350 \text{ K})}\right) = e^{-18.4} = 1.0 \times 10^{-8},$$

greater than its value at 300 K by a factor of 19. The number of conduction electrons is therefore more than 20 times larger than at 300 K. (An ordinary metal, on the other hand, has a fixed number of conduction electrons so its conductivity depends only on how readily these electrons can move around. At high temperatures, collisions occur more frequently, so the conductivity is lower. This effect is also present in silicon, but is swamped by the enormously greater number of conduction electrons.)

- e) To get an insulator (with essentially no conduction electrons), we would want the gap to be significantly wider than the 1.11 eV gap in silicon. Doubling this value should pretty much do it, since this would square the exponential factor computed above, multiplying the number of conduction electrons by another factor of 5×10^{-10} to yield only 7 million per cubic meter. For a 3-eV gap, the exponential factor (at room temperature) is

$$e^{-\epsilon/2kT} = \exp\left(-\frac{3 \text{ eV}}{2(0.026 \text{ eV})}\right) = e^{-57.7} = 9 \times 10^{-26},$$

so

$$\frac{N_c}{V} = \frac{2(9 \times 10^{-26})}{8.0 \times 10^{-26} \text{ m}^3} = 2 \text{ m}^{-3},$$

negligible indeed.

Problem 7.34. (Semiconductor: asymmetry of the density of states.)

- a) Suppose that $g_{0v} < g_{0c}$. Then, if were to remain constant as the temperature increases from zero, the symmetry of the Fermi-Dirac distribution would imply that the number of electrons added to the conduction band is less than the number removed from the valence band. To prevent such nonsense, must decrease with temperature. Similarly, if $g_{0v} > g_{0c}$, the chemical potential would have to increase with temperature.
- b) The number of electrons in the conduction band is the integral of the density of states times the Fermi-Dirac distribution:

$$N_c = \int_{\epsilon_c}^{\infty} g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon = g_{0c} \int_{\epsilon_c}^{\infty} \frac{\sqrt{\epsilon - \epsilon_c}}{e^{(\epsilon - \mu)/kT} + 1} d\epsilon \approx g_{0c} \int_{\epsilon_c}^{\infty} \sqrt{\epsilon - \epsilon_c} e^{-(\epsilon - \mu)/kT} d\epsilon,$$

where the last approximation is valid provided that $kT \ll \epsilon_c$. Changing variables to $x = (\epsilon - \epsilon_c)/kT$, this expression becomes

$$N_c = g_{0c}(kT)^{3/2} e^{-(\epsilon_c - \epsilon)/kT} \int_0^\infty \sqrt{x} e^{-x} dx = \frac{\sqrt{\pi}}{2} g_{0c}(kT)^{3/2} e^{-(\epsilon_c - \epsilon)/kT}.$$

(The integral over x is evaluated in Problem B.8. It can also be looked up in tables or done by computer.)

- c) The probability of a state being unoccupied is $1 - \bar{n}_{FD}(\epsilon)$, so the total number of holes is

$$\begin{aligned} N_h &= \int_{-\infty}^{\epsilon_v} g(\epsilon) [1 - \bar{n}_{FD}(\epsilon)] d\epsilon = g_{0v} \int_{-\infty}^{\epsilon_v} \sqrt{\epsilon_v - \epsilon} \left[1 - \frac{1}{e^{(\epsilon - \epsilon_v)/kT} + 1} \right] d\epsilon \\ &= g_{0v} \int_{-\infty}^{\epsilon_v} \frac{\sqrt{\epsilon_v - \epsilon}}{1 + e^{(\epsilon - \epsilon_v)/kT}} d\epsilon \approx g_{0v} \int_{-\infty}^{\epsilon_v} \sqrt{\epsilon_v - \epsilon} e^{-(\epsilon - \epsilon_v)/kT} d\epsilon, \end{aligned}$$

where the last approximation is valid provided that $kT \ll \epsilon_v$. Changing variables to $x = (\epsilon_v - \epsilon)/kT$, this expression becomes

$$\begin{aligned} N_h &= g_{0v} e^{-(\epsilon_v - \epsilon)/kT} \int_{-\infty}^{\epsilon_v} \sqrt{\epsilon_v - \epsilon} e^{-(\epsilon_v - \epsilon)/kT} d\epsilon = g_{0v} e^{-(\epsilon_v - \epsilon)/kT} \int_0^0 \sqrt{xkT} e^{-x} (-kT) dx \\ &= g_{0v}(kT)^{3/2} e^{-(\epsilon_v - \epsilon)/kT} \int_0^\infty \sqrt{x} e^{-x} dx = \frac{\sqrt{\pi}}{2} g_{0v}(kT)^{3/2} e^{-(\epsilon_v - \epsilon)/kT}. \end{aligned}$$

- d) Since every electron excited to the conduction band leaves behind a hole in the valence band, the results of parts (b) and (c) must be equal at any temperature. Canceling the common factors then gives

$$g_{0c} e^{-(\epsilon_c - \epsilon)/kT} = g_{0v} e^{-(\epsilon_v - \epsilon)/kT},$$

or

$$\frac{g_{0c}}{g_{0v}} = \frac{e^{-(\epsilon_c - \epsilon)/kT}}{e^{-(\epsilon_v - \epsilon)/kT}} = e^{(\epsilon_v + \epsilon_c - 2\epsilon)/kT}.$$

Solving for ϵ , we find

$$\epsilon = \frac{\epsilon_v + \epsilon_c}{2} + \frac{kT}{2} \ln \frac{g_{0v}}{g_{0c}}.$$

This formula verifies that at $T = 0$, the chemical potential is still in the exact middle of the band gap. As T increases, ϵ either increases or decreases, depending on whether g_{0v} is greater or less than g_{0c} , respectively.

- e) For silicon, the logarithm is equal to $\ln(0.44/1.09) = -0.91$. So at room temperature, the shift in ϵ is

$$\frac{kT}{2}(-0.91) = -\frac{0.026 \text{ eV}}{2}(0.91) = -0.012 \text{ eV}.$$

This is quite small compared to the band gap of 1.1 eV, so the approximations made above are valid.

Problem 7.35. (Doped semiconductors.)

- a) We saw in Problem 7.33 that for pure silicon at room temperature, the number of electrons excited from the valence band into the conduction band is on the order of 10^{16} per cubic meter, or 10^{10} per cubic centimeter. On the other hand, in Problem 7.5 we saw that for silicon doped with 10^{17} phosphorus atoms per cubic centimeter, nearly every P atom contributes an electron to the conduction band (at room temperature). Therefore, it should be a good approximation to entirely neglect the electrons excited from the valence band, as in Problem 7.5. Under this assumption, the chemical potential is as calculated in Problem 7.5(b):

$$= kT \ln\left(\frac{2V}{N_c v_Q}\right) = kT \ln\left(\frac{2V}{x N_d v_Q}\right),$$

where the energy zero-point is taken to be ϵ_c (the bottom of the conduction band). Here N_c is the number of conduction electrons, equal to the number of donor impurities (N_d) times the dimensionless fraction x that was calculated in Problem 7.5(d):

$$x = \frac{1}{2y} \sqrt{1 + 4y} - 1, \quad y = (0.0036) \frac{e^{1/t}}{t^{3/2}}, \quad t = \frac{kT}{I},$$

where I is the donor ionization energy, 0.044 eV. The number 0.0036, calculated for silicon doped with 10^{17} phosphorus atoms per cm^3 , also comes up in the formula for :

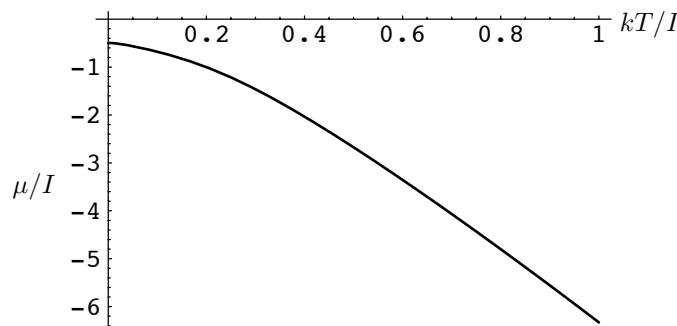
$$\frac{N_d v_Q}{V} = \frac{0.0036}{t^{3/2}}.$$

Therefore we can write the formula for as

$$\frac{\mu}{I} = t \ln\left(\frac{2t^{3/2}}{(0.0036)x}\right).$$

To plot this function, I used the following *Mathematica* code, which produced the graph below:

```
y[t_] := 0.0036 * Exp[1/t] / t^1.5
x[t_] := (Sqrt[1+4y[t]] - 1) / (2y[t])
Plot[-t*Log[2*t^1.5/(0.0036*x[t])], {t, 0, 1}]
```



Notice that at $T = 0$, $= I/2$, halfway between the bottom of the conduction band and the energy of the electrons bound to the donor ions. As the temperature increases, the chemical potential drops, just as for an ordinary ideal gas.

- b) The conduction electrons can be treated as an ordinary ideal gas as long as the 1 in the denominator of the Fermi-Dirac distribution is negligible compared to the exponential function, $e^{(\epsilon - \mu)/kT}$, for all ϵ in the conduction band. This is the same as saying that $\epsilon_c - \mu \gg kT$ for all ϵ in the conduction band, so a sufficient condition is $\epsilon_c - \mu \gg kT$. In the limit $T \rightarrow 0$ this condition definitely holds, since $\epsilon_c - \mu$ goes to a nonzero constant, $I/2$, in this limit. Note also that $\epsilon_c - \mu$ is at least this large at any temperature; furthermore, from the graph in part (a) we see that $\epsilon_c - \mu$ is at least four times greater than kT over the entire range of temperatures plotted. This range includes room temperature, at which $kT = 0.026$ eV so $kT/I = 0.026/0.044 = 0.59$; at this temperature, $\epsilon_c - \mu$ is slightly greater than $3I$, about 5 times greater than kT . Since $e^5 \approx 150$, approximating the Fermi-Dirac distribution by the Boltzmann distribution within the conduction band should be accurate to about the 1% level.
- c) At temperatures around room temperature or lower, the number of valence electrons excited to the conduction band will be quite negligible compared to the number from donor ions, as discussed in part (a). (Actually, the number is even less than in a pure semiconductor, since the chemical potential is considerably higher in this case, implying that occupancies in the valence band are even closer to 1.) At higher temperatures, though, the number of conduction electrons from donor impurities saturates at 10^{17} per cm³, while the number excited from the valence band continues to rise. At what temperature will this number equal 10^{17} per cm³? To make a crude estimate, let's go back to the simplified model of a pure semiconductor used in Problem 7.33. There we calculated that at room temperature, pure silicon contains about 10^{10} conduction electrons per cm³. If we double the temperature to 600 K, the exponential factor increases to

$$e^{-(\epsilon_c - \mu)/2kT} = 2.3 \times 10^{-5},$$

about 40,000 times greater than at 300 K. The quantum volume also decreases by a factor of $2^{3/2} = 2.8$; the combined effect is to increase the density of conduction electrons by only a factor of about 10^5 . At 900 K, however, the exponential factor increases to 8.1×10^{-4} , greater than at 300 K by a factor of 1.5×10^6 . Factor in the decrease in the quantum volume, $(900/300)^{3/2} = 5.2$, and we obtain an increase in the number of conduction electrons by a factor of nearly 10^7 , as desired. Of course, all this assumes that the chemical potential is at the midpoint between the valence and conduction bands. In a doped semiconductor, as we've just seen, the chemical potential is considerably higher at relatively low temperatures. But for our phosphorus-in-silicon example, a temperature of 900 K implies $kT/I = 1.76$, at which the chemical potential should drop below ϵ_c by more than 12 times the ionization energy (extrapolating from the graph in part (a)). That puts μ pretty near the center of the band gap, as needed.

Problem 7.36. (Magnetization of a degenerate Fermi gas.)

- a) In the paramagnetic systems studied in Chapters 3 and 6, every elementary dipole was free to flip its spin from up to down—there were no restrictions from states already being occupied. But in a degenerate Fermi gas, most electrons can't flip from one spin alignment to the other, because the state with opposite spin alignment is already occupied by another electron. Only near the Fermi energy are there a significant

number of unoccupied states, so only a small fraction the electrons are free to flip their spins. Therefore, the magnetization should be relatively small, compared to other paramagnets at the same temperature.

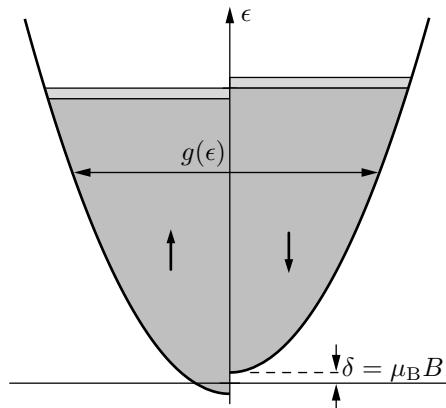
- b) When there is no magnetic field, the density of states is

$$g(\epsilon) = g_0 \sqrt{\epsilon}, \quad \text{where } g_0 = \frac{\pi(8m)^{3/2}}{2h^3} = \frac{3N}{2\epsilon_F^{3/2}}.$$

This formula includes all states with either spin alignment; half of the states at any energy come from each spin alignment. Adding a magnetic field B shifts the energies of half the states (those with positive z , and hence negative z -spin, thanks to the electron's negative charge) down by $\delta \equiv -\mu_B B$, and shifts the energies of the other half of the states up by δ . Thus, the density of states is now

$$g(\epsilon) = \frac{g_0}{2} \sqrt{\epsilon + \delta} + \frac{g_0}{2} \sqrt{\epsilon - \delta},$$

where it is understood that the ϵ values in each term are restricted to those that yield real roots. A clever way to interpret this formula graphically is to turn Figure 7.13 on its side, and plot one term to the left and the other to the right:



- c) As the magnetic field is turned on (at $T = 0$), the number of electrons that flip from one spin alignment to the other is equal to the area of either of the lightly shaded regions in the illustration above. Approximating these areas as rectangles, this number is $\delta \frac{1}{2} g_0 \sqrt{\epsilon_F}$. The number of up-dipoles increases by this amount, while the number of down-dipoles decreases by this amount, so the total magnetization is

$$M = -\mu_B (N_\uparrow - N_\downarrow) = -\mu_B 2 \delta \frac{1}{2} g_0 \sqrt{\epsilon_F} = -\mu_B^2 B g_0 \sqrt{\epsilon_F} = \frac{3N \mu_B^2 B}{2\epsilon_F}.$$

It is interesting to compare this formula to equation 3.35 for an ordinary paramagnet in the regime where Curie's law applies. Aside from the factor of $3/2$, the formulas differ only in the replacement of kT by ϵ_F . Since ϵ_F is normally much larger than kT , the present system has a magnetization much less than that of an ordinary paramagnet.

- d) At nonzero T , we can compute the numbers of up- and down-dipoles by integrating the corresponding portion of the density of states, multiplied by the Fermi-Dirac distribution. Therefore the magnetization is

$$M = {}_B(N_\uparrow - N_\downarrow) = {}_B \left[\int_{-\delta}^{\infty} \frac{g_0}{2} \sqrt{\epsilon + \delta} \bar{n}_{FD}(\epsilon) d\epsilon - \int_{-\delta}^{\infty} \frac{g_0}{2} \sqrt{\epsilon - \delta} \bar{n}_{FD}(\epsilon) d\epsilon \right].$$

To evaluate either integral, we can use the Sommerfeld expansion as on pages 283–284 of the text. For instance, the first integral is

$$\int_{-\delta}^{\infty} \sqrt{\epsilon + \delta} \bar{n}_{FD}(\epsilon) d\epsilon = \frac{2}{3} \int_{-\delta}^{\infty} (\epsilon + \delta)^{3/2} \left(\frac{d\bar{n}_{FD}}{d\epsilon} \right) d\epsilon \approx \frac{2}{3} \int_{-\infty}^{\infty} \frac{e^x}{(e^x + 1)^2} (\epsilon + \delta)^{3/2} dx,$$

where in the first step I've integrated by parts and in the second step I've changed variables to $x = (\epsilon - \mu)/kT$ and extended the lower limit of the integral down to infinity. The next step is to expand $(\epsilon + \delta)^{3/2}$ in a power series about $\epsilon = \mu$:

$$(\epsilon + \delta)^{3/2} = (\mu + \delta)^{3/2} + \frac{3}{2}(\epsilon - \mu)(\mu + \delta)^{1/2} + \frac{3}{8}(\epsilon - \mu)^2(\mu + \delta)^{-1/2} + \dots.$$

Writing $\epsilon - \mu$ as xkT and plugging into the integral above gives (approximately)

$$\begin{aligned} & \frac{2}{3} \int_{-\infty}^{\infty} \frac{e^x}{(e^x + 1)^2} \left[(\mu + \delta)^{3/2} + \frac{3}{2}xkT(\mu + \delta)^{1/2} + \frac{3}{8}(xkT)^2(\mu + \delta)^{-1/2} \right] dx \\ &= \frac{2}{3} \left[(\mu + \delta)^{3/2} + \frac{\pi^2}{8}(kT)^2(\mu + \delta)^{-1/2} \right], \end{aligned}$$

where I've evaluated the integrals as in equations 7.62 through 7.64. The other integral is the same except that δ is replaced by $-\delta$, so the magnetization is approximately

$$M = \frac{{}_B g_0}{2} \left[(\mu + \delta)^{3/2} - (\mu - \delta)^{3/2} + \frac{\pi^2}{8}(kT)^2(\mu + \delta)^{-1/2} - \frac{\pi^2}{8}(kT)^2(\mu - \delta)^{-1/2} \right].$$

Since δ is much smaller than μ , we can now use the binomial expansion as follows:

$$(\mu \pm \delta)^p = \mu^p \left(1 \pm \frac{\delta}{\mu}\right)^p \approx \mu^p \left(1 \pm \frac{p\delta}{\mu}\right),$$

where p is either $3/2$ or $-1/2$. Applying this approximation to each term gives

$$\begin{aligned} M &= \frac{{}_B g_0}{3} \left[{}^{3/2} \left(1 + \frac{3\delta}{2\mu} - 1 + \frac{3\delta}{2\mu} \right) + \frac{\pi^2}{8}(kT)^2 {}^{-1/2} \left(1 - \frac{\delta}{2\mu} - 1 - \frac{\delta}{2\mu} \right) \right] \\ &= \frac{{}_B g_0}{3} \left[{}^{3/2} \left(\frac{3\delta}{2\mu} - \frac{\pi^2}{8}(kT)^2 {}^{-1/2} \right) - \frac{\delta}{2\mu} \right] = {}_B \delta g_0 \left[{}^{-1/2} \left(\frac{\pi^2}{24} \frac{(kT)^2}{\mu^{3/2}} \right) \right]. \end{aligned}$$

Now recall that the chemical potential is given, to order $(kT/\epsilon_F)^2$, by equation 7.66 (plus a correction proportional to $(\delta/\epsilon_F)^2$, which we assume to be small in comparison). In the second term of our formula for M , we can simply plug in $\mu = \epsilon_F$, since the

correction would be proportional to $(kT/\epsilon_F)^4$, which we assume to negligible. In the first term, though, we must carefully plug in the corrected formula for δ and use the binomial expansion once again:

$$\begin{aligned} M &= \frac{B}{\epsilon_F^{1/2}} \left[\left(1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 \right)^{1/2} - \frac{\pi^2}{24} \frac{(kT)^2}{\epsilon_F^{3/2}} \right] \\ &= \frac{B}{\epsilon_F^{1/2}} \left[\left(1 - \frac{\pi^2}{24} \left(\frac{kT}{\epsilon_F} \right)^2 \right) - \frac{\pi^2}{24} \frac{(kT)^2}{\epsilon_F^{3/2}} \right] \\ &= \frac{B}{\epsilon_F^{1/2}} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 \right] = \frac{3N_B^2 B}{2\epsilon_F} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 \right]. \end{aligned}$$

(In the final step I've used the definitions of δ and g_0 .) The prefactor is the same zero-temperature result obtained much more easily in part (c). The correction term shows that as the temperature increases, the magnetization decreases (as one would expect), but only slightly as long as $kT \ll \epsilon_F$.

Problem 7.37. To find the maximum of the Planck function $x^3/(e^x - 1)$, you could just plug in numbers until it becomes clear that $x = 2.82$ gives a larger value than any other x . Or you could use a *Mathematica* instruction such as

```
FindMinimum[-x^3/(Exp[x]-1), {x, 3}]
```

which returns the value 2.82144. The sophisticated method is to set the derivative of the function equal to zero:

$$0 = \frac{d}{dx} \left(\frac{x^3}{e^x - 1} \right) = \frac{3x^2(e^x - 1) - x^3e^x}{(e^x - 1)^2} = \frac{x^2}{(e^x - 1)^2} [3(e^x - 1) - xe^x].$$

The solutions $x = 0$ and $x = \infty$ give the minima of the function. We want the maximum, which is at the nontrivial solution where

$$3e^x - 3 = xe^x, \quad \text{or} \quad e^{-x} = 1 - \frac{x}{3}.$$

But this is a transcendental equation, so we again must resort to numerical methods, such as the *Mathematica* instruction

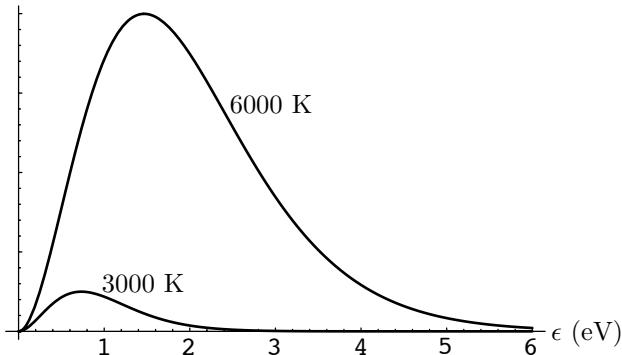
```
FindRoot[Exp[-x]==1-(x/3), {x, 3}]
```

which again returns 2.82144.

Problem 7.38. At $T = 3000$ K, $kT = 0.26$ eV, while at $T = 6000$ K, $kT = 0.52$ eV. To plot the Planck spectrum vs. photon energy at each of these temperatures, I used the *Mathematica* instruction

```
Plot[{e^3/(Exp[e/.26]-1), e^3/(Exp[e/.52]-1)}, {e, 0, 6}]
```

in which I've ignored the overall constant in equation 7.84 since the vertical axis of the graph is so tricky to interpret anyway. Here's the resulting plot:



Note that doubling the temperature shifts the peak in the spectrum to the right, to a photon energy exactly twice as large. Much more dramatic, though, is the height of the spectrum: Doubling the temperature increases the total area under the graph by a factor of $2^4 = 16$, as predicted by equation 7.85 or 7.86.

Problem 7.39. The relation $\lambda = hc/\epsilon$ implies $\epsilon = hc/\lambda$ and $d\epsilon = -(hc/\lambda^2)d\lambda$. Therefore, equation 7.83 becomes

$$\frac{U}{V} = \frac{8\pi}{(hc)^3} \int_0^\infty \frac{\epsilon^3}{e^{\epsilon/kT} - 1} d\epsilon = \frac{8\pi}{(hc)^3} (hc)^4 \int_{\infty}^0 \frac{1/\lambda^5}{e^{hc/kT\lambda} - 1} d\lambda = 8\pi(hc) \int_0^\infty \frac{1/\lambda^5}{e^{hc/kT\lambda} - 1} d\lambda.$$

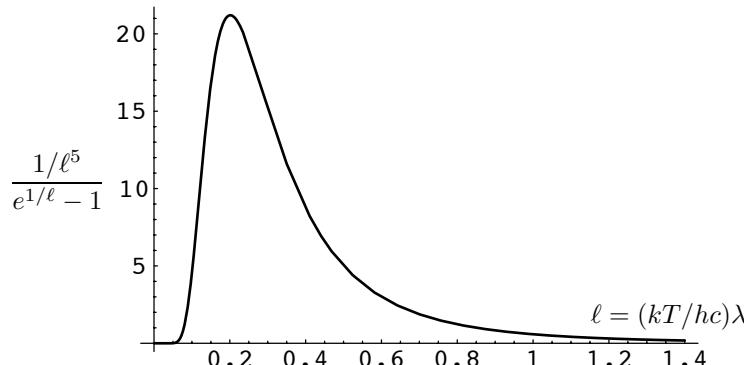
The function whose integral gives the energy density within any desired wavelength range is therefore

$$u(\lambda) = \frac{8\pi hc/\lambda^5}{e^{hc/kT\lambda} - 1}.$$

To plot this function it's easiest to change variables again to the dimensionless variable $\ell = (kT/hc)\lambda$:

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{1/\ell^5}{e^{1/\ell} - 1} d\ell.$$

To plot the integrand I said `Plot[(1/e11^5)/(Exp[1/e11]-1),{e11,0,1.4}]` to *Mathematica*, and it produced the following:



Although this curve may look superficially similar to Figure 7.19, it differs significantly: It goes to zero exponentially as $\ell \rightarrow 0$, and falls off in proportion to $1/\ell^4$ as $\ell \rightarrow \infty$. Notice also that the peak of the curve is at approximately $\ell = 0.2$; to locate it more precisely I used the *Mathematica* instruction `FindMinimum[-(1/e11^5)/(Exp[1/e11]-1),{e11,.2}]`, which returned the value $\ell = 0.201405$. Therefore, as a function of wavelength, the Planck spectrum peaks at the value $\lambda = (0.2014)(hc/kT) = hc/(4.97kT)$. This is *not* the same point where the spectrum peaks as a function of photon energy (or frequency); it is lower in wavelength (or higher in energy) by a factor of $4.97/2.82 = 1.76$. How can this be? The difference occurs because both this spectrum and the one plotted in Figure 7.19 are functions *whose purpose in life is to be integrated*. Either formula will give the same answer when you integrate it appropriately between any two points. However, one gives the energy density per unit photon energy, while the other gives the energy density per unit wavelength, and the *units* of photon energy and wavelength depend on each other in a nonlinear way. For instance, a one-unit photon energy range, say a range of 1 eV, corresponds to a larger range of wavelengths if it's from 2 eV to 3 eV than if it's from 200 eV to 201 eV. Therefore, when we convert the photon-energy spectrum to the wavelength spectrum, we shift the curve upward at short wavelengths (where a unit of wavelength includes a relatively large range of photon energies) and downward at long wavelengths (where a unit of wavelength includes a relatively small range of photon energies).

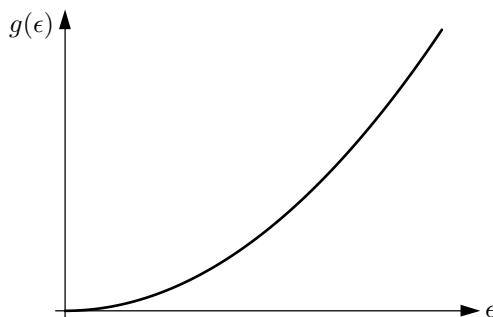
Problem 7.40. Notice that equation 7.83 can be written

$$U = \int_0^\infty \epsilon \left(\frac{8\pi V \epsilon^2}{(hc)^3} \right) \bar{n}_{\text{Pl}}(\epsilon) d\epsilon.$$

This is in the form of an integral of ϵ times $g(\epsilon)$ times the appropriate distribution function, provided that we identify

$$g(\epsilon) = \frac{8\pi V \epsilon^2}{(hc)^3}$$

as the density of states—the number of single-particle states per unit energy. This formula is quadratic in ϵ , so its graph is a parabola opening upward:



Problem 7.41. (Einstein A and B coefficients.)

- a) The number of atoms in state 1 can increase due to spontaneous decay from state 2, and increase due to stimulated emission from state 2, and decrease due to stimulated absorption up to state 2. The rate of each of these processes is equal to the probability for any one atom undergoing the process (as expressed in terms of the definitions of A , B , and B') times the number of atoms currently in the required initial state. Therefore the total rate is

$$\frac{dN_1}{dt} = AN_2 + B'N_2u(f) - BN_1u(f),$$

where $u(f)$ is evaluated at the required frequency, $f = \epsilon/h$.

- b) In equilibrium, $dN_1/dt = 0$ and N_2/N_1 is given by a simple ratio of Boltzmann factors,

$$\frac{N_2}{N_1} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}} = e^{-\epsilon/kT} = e^{-hf/kT}.$$

The function $u(f)$ is obtained by changing variables from ϵ to $f = \epsilon/h$ in equation 7.83:

$$u(f) = \frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT} - 1}.$$

(The extra factor of h in the numerator comes from $d\epsilon = h df$.) Plugging all of these expressions into the result of part (a) and canceling the common factor of N_1 , we obtain

$$0 = Ae^{-hf/kT} + (B'e^{-hf/kT} - B)\frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT} - 1}.$$

Pulling the A term to the left-hand side and multiplying through by $e^{hf/kT}$ gives

$$A = (Be^{hf/kT} - B') \frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT} - 1}.$$

Now this equation must hold for all temperatures T , but the coefficients themselves, being intrinsic properties of the atom, cannot possibly depend on temperature. Therefore, since the left-hand side is independent of temperature, the temperature dependence on the right-hand side must cancel out. The only way this can happen is if $B' = B$. We then have simply

$$A = B(e^{hf/kT} - 1) \frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT} - 1} = B \frac{8\pi hf^3}{c^3},$$

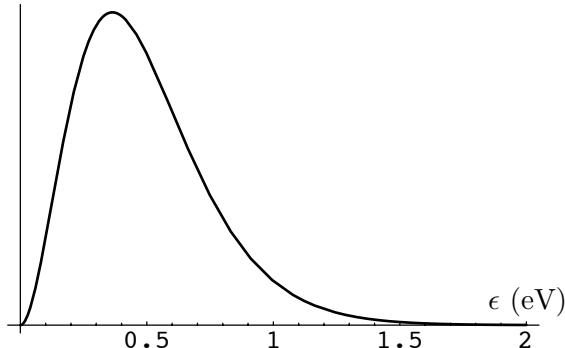
which is Einstein's relation between the rates of spontaneous and stimulated emission.

Problem 7.42. (Electromagnetic radiation in a kiln.)

- a) The total energy of the radiation in a cubic meter of space at 1500 K is

$$U = \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3} V = \frac{8\pi^5}{15} \frac{[(1.38 \times 10^{-23} \text{ J/K})(1500 \text{ K})]^4}{[(6.63 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m/s})]^3} (1 \text{ m}^3) = 0.0038 \text{ J.}$$

- b) A graph of the spectrum should look like Figure 7.19, but with the horizontal axis representing ϵ (in eV). At $T = 1500$ K, the product kT is 0.129 eV, so the spectrum (plotted as a function of photon energy) peaks at $\epsilon = (2.82)(0.129 \text{ eV}) = 0.36 \text{ eV}$. Here's a computer-drawn plot, which I generated by typing the instruction `Plot[eps^3/(Exp[eps/.129]-1), {eps,0,2}]` into *Mathematica*:



(I didn't bother to label the vertical scale because it isn't easy to interpret. The total area under the graph, though, represents the total energy density, 0.0038 J/m^3 .)

- c) The photon energies at the (nominal) limits of the visible spectrum are $\epsilon = hc/\lambda = (1240 \text{ eV nm})/\lambda$, which evaluates to 1.77 eV at 700 nm and 3.1 eV at 400 nm. The corresponding values of $x = \epsilon/kT$ are 13.73 and 24.0. The fraction of all the energy in this range can be computed as

$$\int_{13.7}^{24.0} \frac{x^3 dx}{e^x - 1} / \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{15}{\pi^4} \int_{13.7}^{24.0} \frac{x^3 dx}{e^x - 1}.$$

At this point you could do the integral numerically. Alternatively, since $x \gg 1$ over the entire range of integration, we can approximate the integrand by neglecting the 1 in the denominator to obtain

$$\frac{15}{\pi^4} \int_{13.7}^{24.0} x^3 e^{-x} dx = \frac{15}{\pi^4} \left[-e^{-x} x^3 + 3x^2 + 6x + 6 \right]_{13.7}^{24.0} = .00054.$$

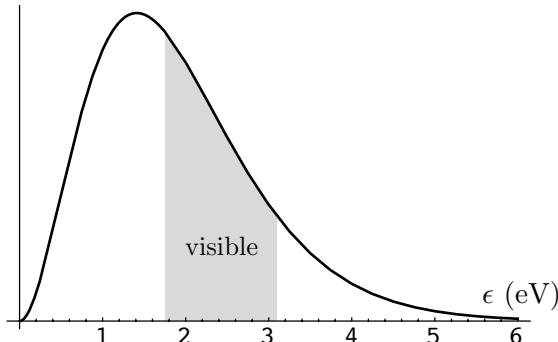
So only about 1/20th of 1% of the energy is in the visible part of the spectrum.

Problem 7.43. (Photons at the surface of the sun.)

- a) The total energy of the radiation in a cubic meter of space at 5800 K is

$$U = \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3} V = \frac{8\pi^5}{15} \frac{[(1.38 \times 10^{-23} \text{ J/K})(5800 \text{ K})]^4}{[(6.63 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m/s})]^3} (1 \text{ m}^3) = 0.855 \text{ J.}$$

- b) To sketch the graph you can just copy Figure 7.19, but recalibrate the horizontal axis. Note that at 5800 K, $kT = 0.50 \text{ eV}$, so $x = 1$ corresponds to $\epsilon = 0.50 \text{ eV}$. Alternatively, you can just replot the graph with ϵ as the horizontal axis. I did so using the *Mathematica* instruction `Plot[eps^3/(Exp[eps/.5]-1), {eps,0,6}]`, which produced the graph on the following page.



To locate the visible portion of the spectrum, note that the red end is at 700 nm which corresponds to a photon energy of $\epsilon = hc/\lambda = 1.77$ eV, while the violet end is at 400 nm which corresponds to a photon energy of 3.1 eV. I've shaded this region in the graph.

- c) Since $kT = 0.50$ eV, the limits of the visible range are at $x = 1.77/0.5 = 3.54$ and $x = 3.1/0.5 = 6.2$. Therefore the fraction of energy in the visible range is

$$\int_{3.54}^{6.2} \frac{x^3}{e^x - 1} dx / \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{15}{\pi^4} \int_{3.54}^{6.2} \frac{x^3}{e^x - 1} dx.$$

I evaluated the integral numerically with the *Mathematica* instruction

```
(15/Pi^4)*NIntegrate[x^3/(Exp[x]-1),{x,3.54,6.2}]
```

which returned the number 0.36831. So about 37% of the sun's energy is within the visible range.

Problem 7.44. (Number of photons in a photon gas.)

- a) To compute the number of photons, we can simply sum the Planck distribution over all "modes," including a factor of 2 to count the two polarization states for each wave shape:

$$N = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \bar{n}_{Pl}(\epsilon) = 2 \sum_{n_x, n_y, n_z} \frac{1}{e^{hc n / 2 L k T} - 1}.$$

(Except for the absence of a factor of ϵ , this is the same as equation 7.81.) The steps from here on are the same as in the text: Convert the sum to an integral, and carry out the integral in spherical coordinates where the measure includes a factor of n^2 and the angular integrals give a factor of $4\pi/8$. Then change variables to $x = hc n / 2 L k T$:

$$\begin{aligned} N &= 2 \cdot \frac{4\pi}{8} \int_0^\infty \frac{n^2}{e^{hc n / 2 L k T} - 1} dn = \pi \left(\frac{2 L k T}{hc} \right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx \\ &= 8\pi V \left(\frac{k T}{hc} \right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx. \end{aligned}$$

I evaluated the integral numerically with *Mathematica*:

```
NIntegrate[x^2/(Exp[x]-1),{x,0,Infinity}]
```

It replied with the answer 2.404.

- b) Combining this result with equation 7.89, I find for the entropy per photon

$$\frac{S}{N} = \frac{(32\pi^5/45)V(kT/hc)^3k}{2.404 \cdot 8\pi V(kT/hc)^3} = \frac{32\pi^5/45}{2.404 \cdot 8\pi} k = 3.60k.$$

So in fundamental units, the entropy per photon is 3.6.

- c) At room temperature,

$$\frac{N}{V} = 2.404 \cdot 8\pi \left(\frac{kT}{hc}\right)^3 = 60.4 \left(\frac{(8.62 \times 10^{-5} \text{ eV/K})(300 \text{ K})}{(4.14 \times 10^{-15} \text{ eV s})(3 \times 10^8 \text{ m/s})}\right)^3 = 5.5 \times 10^{14} \text{ m}^{-3}.$$

(This may seem large, but it's tiny compared to the number of air molecules per cubic meter under atmospheric conditions.) At 1500 K the temperature is 5 times as high so we can simply multiply by 5^3 to obtain $N/V = 6.8 \times 10^{16} \text{ m}^{-3}$. And for 2.73 K we can multiply by $(2.73/300)^3$ to obtain $4.1 \times 10^8 \text{ m}^{-3}$. That's slightly under half a billion photons per cubic meter filling the entire observable universe—huge compared to the average density of ordinary matter.

Problem 7.45. To evaluate $(\partial U / \partial V)_{S,N}$, we need a formula for U in terms of V and S ; we need to eliminate T , and holding S fixed is the same as holding N fixed. Let me abbreviate $= 8\pi^5 k^4 / (15hc)^3$, so

$$U = VT^4 \quad \text{and} \quad S = \frac{4}{3} VT^3.$$

Solving the second equation for T and plugging into the first gives

$$U = V \left(\frac{3S}{4V}\right)^{4/3} = \left(\frac{3S}{4}\right)^{4/3} (-V)^{-1/3}.$$

Now we can compute

$$P = \left(\frac{\partial U}{\partial V}\right)_S = \frac{1}{3} \left(\frac{3S}{4}\right)^{4/3} -1/3 V^{-4/3} = \frac{1}{3} \frac{U}{V} = \frac{1}{3} T^4.$$

At 1500 K, the energy density is 0.0038 J/m^3 , as computed in Problem 7.42(a). The pressure is therefore $1/3$ of this, or 0.0013 Pa . For comparison, the pressure of the air inside an ordinary kiln is the same as outside, approximately 1 atm (if the kiln is at sea level) or 10^5 Pa , greater by a factor of almost 10^8 . On the other hand, at the center of the sun the temperature is greater by a factor of 10^4 , so the radiation pressure should be greater by a factor of $(10^4)^4$, that is, about $1.3 \times 10^{13} \text{ Pa}$. For comparison, the ionized hydrogen would have a pressure of roughly

$$P = \frac{nRT}{V} = 2(10^3 \text{ mol/kg})(10^5 \text{ kg/m}^3)(8.3 \text{ J/mol K})(1.5 \times 10^7 \text{ K}) = 2.5 \times 10^{16} \text{ Pa},$$

where the factor of 2 accounts for the two particles (electron and proton) per ionized atom. This is still greater than the radiation pressure, but “only” by a factor of about 2000. My understanding is that there are some stars in which the radiation pressure is actually larger than the gas pressure.

Problem 7.46. (Free energy of a photon gas.)

- a) From equations 7.86 and 7.89, we have

$$\begin{aligned} F = U - TS &= \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3} V - T \left(\frac{32\pi^5}{45} V \left(\frac{kT}{hc} \right)^3 k \right) \\ &= \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3} V \left(1 - \frac{4}{3} \right) = \frac{8\pi^5}{45} \frac{(kT)^4}{(hc)^3} V = \frac{1}{3} U. \end{aligned}$$

- b) Differentiating this result with respect to T gives

$$\left(\frac{\partial F}{\partial T} \right)_V = \frac{32\pi^5}{45} \frac{k^4 T^3}{(hc)^3} V,$$

which is indeed equal to S , by equation 7.89.

- c) By equation 5.22 and the result of part (a),

$$P = \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{8\pi^5}{45} \frac{(kT)^4}{(hc)^3} = \frac{1}{3} \frac{U}{V},$$

in agreement with the result of the previous problem.

- d) For any particular mode with energy ϵ , the partition function is $Z = (1 - e^{-\epsilon/kT})^{-1}$, as calculated in equation 7.70. Therefore the free energy of this mode is $F = -kT \ln Z = kT \ln(1 - e^{-\epsilon/kT})$. To get the total free energy, we sum this expression over all modes, as in equation 7.81:

$$F = 2 \sum_{n_x, n_y, n_z} kT \ln(1 - e^{-\epsilon/kT}) = 2kT \frac{\pi}{2} \int_0^\infty n^2 \ln(1 - e^{-\epsilon/kT}) dn.$$

In the last expression I've converted the sum to an integral in spherical coordinates over the first octant of n -space, and carried out the angular integrals to obtain $\pi/2$, the area of an eighth of a unit sphere. Changing variables to $x = \epsilon/kT = hc n / 2LkT$ then gives

$$F = \pi kT \left(\frac{2LkT}{hc} \right)^3 \int_0^\infty x^2 \ln(1 - e^{-x}) dx = 8\pi V \frac{(kT)^4}{(hc)^3} \int_0^\infty x^2 \ln(1 - e^{-x}) dx.$$

To put this integral into a more familiar form, integrate by parts; that is, integrate the x^2 to obtain $x^3/3$, and differentiate the logarithm:

$$F = 8\pi V \frac{(kT)^4}{(hc)^3} \left[\frac{x^3}{3} \ln(1 - e^{-x}) \Big|_0^\infty - \int_0^\infty \frac{x^3}{3} \frac{e^{-x}}{1 - e^{-x}} dx \right]$$

The boundary term vanishes at both limits, so we're left with

$$F = \frac{8\pi V}{3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{1}{3} U,$$

by comparison with equation 7.85. This is the same result obtained in part (a).

Problem 7.47. Assuming thermal equilibrium, we can compute the fraction of hydrogen atoms that are ionized using the Saha equation, derived in Section 5.6 and in Problem 7.3:

$$\frac{N_p N_e}{N_H} = \frac{V}{v_Q} e^{-I/kT},$$

where I is the ionization energy, v_Q is the electron's quantum volume, and N_H is the number of un-ionized hydrogen atoms. In our case the number of free electrons is equal to the number of free protons: $N_e = N_p$. Therefore the Saha equation simplifies to

$$\frac{N_p^2}{N_H} = \frac{V}{v_Q} e^{-I/kT}. \quad (1)$$

Meanwhile, we are to assume that the total number of ionized and un-ionized hydrogen atoms is equal to some fixed fraction η times the number of thermal photons:

$$N_p + N_H = \eta N_\gamma = \eta b V \left(\frac{kT}{hc} \right)^3, \quad (2)$$

where b is an abbreviation for the numerical factor $8\pi/2.404$ computed in Problem 7.44. What we want to compute is the fraction of atoms that are ionized, that is,

$$f = \frac{N_p}{N_p + N_H}. \quad (3)$$

Combining these three equations to obtain f as a function of temperature is now just a matter of algebra. From equations 2 and 3 we have

$$N_p = f \eta b V \left(\frac{kT}{hc} \right)^3 \quad \text{and} \quad N_H = (1-f) \eta b V \left(\frac{kT}{hc} \right)^3.$$

Plugging these expressions into equation 1 and canceling the V 's, we obtain

$$\frac{f^2}{1-f} \eta b \left(\frac{kT}{hc} \right)^3 = \frac{1}{v_Q} e^{-I/kT}, \quad \text{or} \quad f^2 + f - 1 = 0,$$

where

$$\equiv \eta b \left(\frac{kT}{hc} \right)^3 v_Q e^{I/kT} = \eta b \left(\frac{kT}{2\pi mc^2} \right)^{3/2} e^{I/kT}$$

is a convenient abbreviation. Solving the quadratic equation gives

$$f = \frac{1 + \sqrt{1+4}}{2},$$

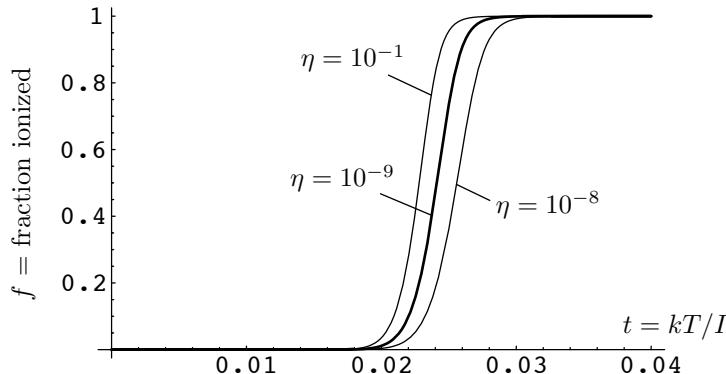
where I've discarded the other root because it is negative and therefore unphysical. To plot this formula, it's convenient to introduce the dimensionless variable $t = kT/I$. Then

$$= \eta b \left(\frac{I}{2\pi mc^2} \right)^{3/2} t^{3/2} e^{1/t} = (5.27 \times 10^{-7}) \eta t^{3/2} e^{1/t},$$

where I've plugged in the numerical values $I = 13.6$ eV and $mc^2 = 511,000$ eV. To plot f as a function of t for $\eta = 10^{-9}$, I used the following Mathematica code:

```
eta = 10^-9;
alpha = eta*(5.27*10^-7)*(t^1.5)*Exp[1/t];
Plot[(Sqrt[1+4*alpha]-1)/(2*alpha),{t,0,.04},PlotRange->All]
```

(The upper limit on the t range corresponds to $T = (0.04)I/k = 6300$ K.) I also repeated the calculation for $\eta = 10^{-8}$ and $\eta = 10^{-10}$. The results are shown in the plot below:



First note that the atoms go from completely ionized to completely un-ionized over a very narrow range of temperatures, and that the temperature of the transition is relatively insensitive to the value of η . A larger value of η means that the atoms are closer together at a given temperature, so there is a greater tendency for them *not* to be ionized. Furthermore, the transition temperature is considerably lower than I/k , basically due to the greater entropy of the ionized state. The temperature at which essentially all the hydrogen is un-ionized is roughly $(0.02)I/k \approx 3000$ K. This is roughly the temperature at which the universe first became transparent. However, this calculation assumes thermal equilibrium, and it turns out that the universe was expanding and cooling too quickly for neutral hydrogen to form at the rate required for equilibrium; see Peebles (1993). More sophisticated calculations show that there was still a small amount of ionized plasma left at temperatures below 3000 K, but not enough to keep the universe opaque to photons. [Note: The formula for f predicts that when $t \gg 1$, f decreases and goes to zero as $t \rightarrow \infty$. This is because we're assuming that the density of hydrogen is proportional to the density of photons, which is extremely high at high temperatures, and the Saha equation says that the atoms prefer not to be ionized at such high density. However, the t value at which the ionization fraction would drop significantly below 1 is of order 10^{10} , that is, $kT \sim 10^{11}$ eV. This temperature is so high that the conditions would be extremely different from those assumed in this problem.]

Problem 7.48. (The cosmic neutrino background.)

- a) According to equation 5.102, the condition for equilibrium is the same as the reaction equation, but with the name of each species replaced by its chemical potential. So, for the reaction $\nu + \bar{\nu} \leftrightarrow 2\gamma$, the equilibrium condition would be

$$\nu + \bar{\nu} = 2\gamma.$$

But the chemical potential for the photons is zero as discussed on page 290, while the chemical potentials of the neutrinos and antineutrinos are equal to each other if they are equally abundant. Therefore we must have $\nu = \bar{\nu} = 0$.

- b) The probability of any single-particle state being occupied by a neutrino should be given by the Fermi-Dirac distribution, with $\bar{\nu} = 0$ as shown in part (a). To find the total energy of all such particles in a box, we multiply by $\epsilon = hc\nu/2L$ (assuming massless neutrinos) and sum over states just as for photons:

$$U = 3 \cdot 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \frac{\epsilon}{e^{hc\nu/2LkT} + 1}.$$

Here the factor of 3 counts the three neutrino species, and the factor of 2 counts the neutrinos and antineutrinos. Now convert the triple sum to an integral in spherical coordinates, evaluate the angular integrals to obtain $4\pi/8$, and change variables to $x = hc\nu/2LkT$ as always:

$$U = 6 \cdot \frac{4\pi}{8} \int_0^\infty \frac{(hc\nu/2L)^n}{e^{hc\nu/2LkT} + 1} dn = 3\pi \left(\frac{2L}{hc}\right)^3 (kT)^4 \int_0^\infty \frac{x^3}{e^x + 1} dx$$

As shown in Appendix B (equation B.36), this integral (with a $+1$ in the denominator) is equal to $7/8$ times the integral we did for the photon gas (which had a -1 in the denominator). Therefore,

$$\frac{U}{V} = \frac{24\pi(kT)^4}{(hc)^3} \cdot \frac{7}{8} \cdot \frac{\pi^4}{15} = \frac{7\pi^5(kT)^4}{5(hc)^3}.$$

This is exactly $21/8$ times the energy density of photons at the same temperature.

- c) The number of neutrinos is given by the same calculation, but without the extra factor of ϵ in the numerator:

$$N = 3\pi \int_0^\infty \frac{n^2}{e^{hc\nu/2LkT} + 1} dn = 3\pi \left(\frac{2LkT}{hc}\right)^3 \int_0^\infty \frac{x^2}{e^x + 1} dx.$$

This integral is $3/4$ times the corresponding integral for photons (evaluated in Problem 7.44), so

$$\frac{N}{V} = 24\pi \left(\frac{kT}{hc}\right)^3 \cdot \frac{3}{4} \cdot 2.404 = (135.9) \left(\frac{kT}{hc}\right)^3.$$

At $T = 1.95$ K, this evaluates to

$$\frac{N}{V} = (135.9) \left(\frac{(8.62 \times 10^{-5} \text{ eV/K})(1.95 \text{ K})}{(4.14 \times 10^{-15} \text{ eV s})(3 \times 10^8 \text{ m/s})} \right)^3 = 3.4 \times 10^8 \text{ m}^{-3},$$

just slightly less than the present density of photons in the universe.

- d) For a single species of neutrino and antineutrino, the present number density would be $1/3$ of the number just calculated, or 1.1×10^8 per cubic meter. The average density of ordinary matter in the universe, on the other hand, is only about one proton per cubic meter, or, multiplying by c^2 to get the energy equivalent, about 1 GeV or 10^9 eV per cubic meter. To equal this energy density, the neutrinos would need an energy (mc^2) of only about 10 eV each, since there are roughly 10^8 of them. This is comparable to the present experimental upper limit on the mass of the electron neutrino, but much less than the experimental limits on the masses of the other two species. (By contrast, the lightest measured particle mass is that of the electron, with $mc^2 = 5 \times 10^5$ eV.)

Problem 7.49. (Electrons and positrons in the early universe.)

- a) The probability of any single-particle state being occupied by an electron or positron should be given by the Fermi-Dirac distribution, with $\epsilon = 0$ as for neutrinos (see part (a) of the previous problem) and with

$$\epsilon = \sqrt{(pc)^2 + (mc^2)^2} = \sqrt{(hcn/2L)^2 + (mc^2)^2}$$

instead of the ultra-relativistic relation given in equation 7.79. The total energy of the e^+e^- radiation should therefore be

$$U = 2 \cdot 2 \sum_{n_x, n_y, n_z} \frac{\epsilon}{e^{\epsilon/kT} + 1} = 4 \cdot \frac{\pi}{2} \int_0^\infty \frac{n^2 \sqrt{(hcn/2L)^2 + (mc^2)^2}}{e^{\sqrt{(hcn/2L)^2 + (mc^2)^2}/kT} + 1} dn,$$

where the two factors of 2 count the electrons and positrons, each with two polarization states. In the second expression I've converted the triple sum to an integral in spherical coordinates and evaluated the angular integrals to obtain $\pi/2$, the area of a unit eighth-sphere. Changing variables to $x = hcn/2LkT$, we then obtain

$$U = 2\pi \left(\frac{2LkT}{hcn} \right)^3 \int_0^\infty \frac{x^2 \sqrt{(xkT)^2 + (mc^2)^2}}{e^{\sqrt{x^2 + (mc^2/kT)^2}} + 1} dx = \frac{16\pi V(kT)^4}{(hc)^3} u(T),$$

where

$$u(T) = \int_0^\infty \frac{x^2 \sqrt{x^2 + (mc^2/kT)^2}}{e^{\sqrt{x^2 + (mc^2/kT)^2}} + 1} dx = \int_0^\infty \frac{x^2 \sqrt{x^2 + (1/t)^2}}{e^{\sqrt{x^2 + (1/t)^2}} + 1} dx,$$

and I've used the abbreviation $t = kT/mc^2$ in the last expression.

- b) When $kT \ll mc^2$, that is, $t \ll 1$, the exponential factor in the denominator is always large, over the entire range of x . Therefore the function $u(T)$ is exponentially suppressed, going to zero as $T \rightarrow 0$. (To make this argument more rigorous, you could divide the integral into two pieces, one from 0 to $1/t$ and the other from $1/t$ to ∞ . Then show that each piece is bounded above by an expression that goes to zero as $t \rightarrow 0$. Alternatively, you can just look at the plot of $u(T)$ in part (d).) This behavior is exactly what we should expect: When $kT \ll mc^2$, the creation of electron-positron pairs in collisions is extremely unlikely, so the number of them in equilibrium should be exponentially suppressed relative to the number of photons or neutrinos.

- c) In the limit $t \rightarrow \infty$, the $1/t$ terms can be neglected so we have simply

$$u(T) \rightarrow \int_0^\infty \frac{x^3}{e^x + 1} dx = \frac{7}{8} \cdot \frac{\pi^4}{15} \approx 5.68,$$

the same integral evaluated in part (b) of the previous problem. Therefore, in this limit,

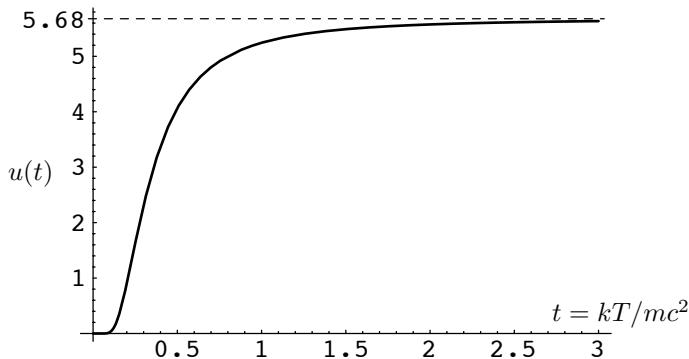
$$\frac{U}{V} \rightarrow \frac{16\pi(kT)^4}{(hc)^3} \cdot \frac{7}{8} \cdot \frac{\pi^4}{15} = \frac{14\pi^5(kT)^4}{15(hc)^3}.$$

This is just $2/3$ the energy density of the neutrino radiation (at any given temperature), with the factor $2/3$ accounting for the four different species and polarization states rather than six.

- d) To plot $u(T)$ I used the *Mathematica* instructions

```
u[t_] := NIntegrate[
  x^2*.Sqrt[x^2+t^2]/(Exp[Sqrt[x^2+t^2]]+1), {x,0,Infinity}]
Plot[u[t],{t,0,3}]
```

which produced the following plot:



(The *Plot* instruction generated several error messages, because the exponential function overflows at small t values. Nevertheless, the plotted curve correctly shows that $u(t)$ is essentially zero below $t = 0.1$.) I added the dashed line to the plot, to show the asymptotic value calculated in part (c).

- e) As in Problem 7.46(d), consider first just a single “mode” (or single-particle state), which can be occupied either by zero particles (with energy zero) or one particle (with energy ϵ). The partition function of this mode is $Z = 1 + e^{-\epsilon/kT}$, and the free energy is $F = -kT \ln Z = -kT \ln(1 + e^{-\epsilon/kT})$. To obtain the *total* free energy, we sum this expression over all modes:

$$\begin{aligned} F &= 4 \sum_{n_x, n_y, n_z} (-kT) \ln(1 + e^{-\epsilon/kT}) = -4kT \frac{\pi}{2} \int_0^\infty n^2 \ln(1 + e^{-\epsilon/kT}) dn \\ &= 2\pi(kT) \left(\frac{2LkT}{hc} \right)^3 \int_0^\infty x^2 \ln(1 + e^{-\epsilon/kT}) dx = -\frac{16\pi(kT)^4}{(hc)^3} f(T), \end{aligned}$$

where

$$f(T) = \int_0^\infty x^2 \ln(1 + e^{-\epsilon/kT}) dx = \int_0^\infty x^2 \ln\left(1 + e^{-\sqrt{x^2 + (1/t)^2}}\right) dx.$$

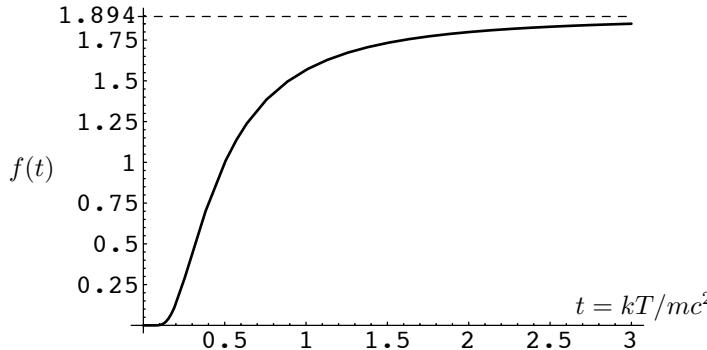
As $T \rightarrow 0$, the exponential factor becomes very small for all x , so we can expand the logarithm: $\ln(1 + e^{-\epsilon/kT}) \approx e^{-\epsilon/kT}$. This exponential factor therefore suppresses the entire expression for $f(T)$, so the free energy, like the energy, vanishes when the temperature is too low to create electron-positron pairs. In the other limit, where $t \gg 1$, we can neglect the $1/t$ term in the exponent to obtain simply

$$\begin{aligned} f(T) &\rightarrow \int_0^\infty x^2 \ln(1 + e^{-x}) dx = \int_0^\infty \frac{x^3}{3} \frac{e^{-x}}{1 + e^{-x}} dx \\ &= \frac{1}{3} \int_0^\infty \frac{x^3}{e^x + 1} dx = \frac{1}{3} \cdot \frac{7}{8} \cdot \frac{\pi^4}{15} = \frac{7\pi^4}{360} \approx 1.894. \end{aligned}$$

(In the second step I've integrated by parts and dropped the boundary term which vanishes at both limits.) To plot $f(T)$ I used the *Mathematica* instructions

```
f[t_] := NIntegrate[x^2*Log[1+Exp[-Sqrt[x^2+t^2]]],{x,0,Infinity}]
Plot[f[t],{t,0,3}]
```

which (after a long list of nonfatal error messages) produced the following:



- f) From the definition $F = U - TS$, we have simply

$$S = \frac{U - F}{T} = \frac{1}{T} \left(\frac{16\pi V(kT)^4}{(hc)^3} u(T) + \frac{16\pi V(kT)^4}{(hc)^3} f(T) \right) = \frac{16\pi V(kT)^3}{(hc)^3} (u(T) + f(T))k.$$

When $T \ll mc^2$, this expression goes exponentially to zero along with $u(T)$ and $f(T)$. In the high-temperature limit, it goes to

$$S \rightarrow 16\pi V \left(\frac{kT}{hc} \right)^3 \frac{7}{8} \frac{\pi^4}{15} \left(1 + \frac{1}{3} \right) k = \frac{56\pi^5}{45} V \left(\frac{kT}{hc} \right)^3 k.$$

Problem 7.50. (Cooling of radiation in the early universe.)

- a) The total entropy of the electrons, positrons, and photons would be given by the sum of equation 7.89 and the result of Problem 7.49(f):

$$\begin{aligned} S_e + S_\gamma &= 16\pi V \left(\frac{kT}{hc} \right)^3 (u(T) + f(T))k + \frac{32\pi^5}{45} V \left(\frac{kT}{hc} \right)^3 k \\ &= 16\pi V \left(\frac{kT}{hc} \right)^3 k \left[u(T) + f(T) + \frac{2\pi^4}{45} \right]. \end{aligned}$$

Because this radiation is in internal equilibrium throughout the expansion process, it is expanding adiabatically and quasistatically, and therefore its total entropy should be conserved as it cools. This implies

$$VT^3 \left[u(T) + f(T) + \frac{2\pi^4}{45} \right] = \text{constant.}$$

- b) Although we didn't compute the neutrino entropy explicitly in Problem 7.48, it isn't necessary to do so; we know that it will be some numerical factor times $V(kT_\nu/hc)^3k$, in analogy with the photon entropy and the high-energy electron-positron entropy. Since the neutrinos don't interact with the other particles during the time period of interest, this entropy (along with the number of neutrinos, which is directly proportional) should be conserved as the universe expands and cools. This implies

$$VT_\nu^3 = \text{constant}.$$

Dividing the final relation of part (a) by this equation cancels the factors of V to give

$$\left(\frac{T}{T_\nu}\right)^3 \left[u(T) + f(T) + \frac{2\pi^4}{45} \right] = \text{constant}.$$

In the high-temperature limit, this equation becomes

$$\text{constant} = (1)^3 \left[\frac{7\pi^4}{8} \left(1 + \frac{1}{3}\right) + \frac{2\pi^4}{45} \right] = \frac{\pi^4}{15} \left[\frac{7}{8} + \frac{4}{3} + \frac{2}{3} \right] = \frac{\pi^4}{45} \left[\frac{7}{2} + 2 \right] = \frac{11\pi^4}{90}.$$

- c) When $T \ll mc^2$, both $u(T)$ and $f(T)$ go to zero exponentially, so we have simply

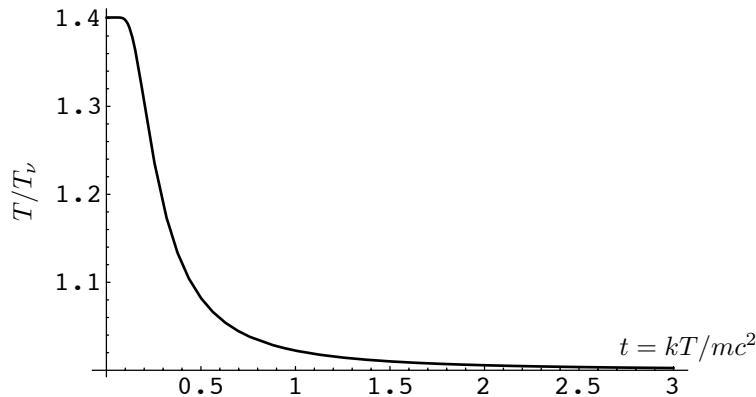
$$\left(\frac{T}{T_\nu}\right)^3 - \frac{2\pi^4}{45} = \frac{11\pi^4}{90}, \quad \text{or} \quad \frac{T}{T_\nu} = \left(\frac{11}{4}\right)^{1/3} = 1.401.$$

Given the present photon temperature of 2.728 K, this implies a neutrino temperature of $(2.728 \text{ K})/1.401 = 1.95 \text{ K}$.

- d) To plot the ratio T/T_ν as a function of T , I simply used the *Mathematica* instruction

```
Plot[((11Pi^4/90)/(u[t]+f[t]+(2Pi^4/45)))^(1/3),{t,0,3}]
```

(which in turn uses the functions $u[t]$ and $f[t]$ defined in the previous problem). After no fewer than 20 nonfatal error messages, it plotted the following:



This graph is most naturally read from right to left: As the temperature of the electrons, positrons, and photons dropped, the annihilation of the electrons and positrons raised the temperature of the photons in comparison to that of the neutrinos, with the ratio ending at the value 1.401 calculated in part (c).

Problem 7.51. (Radiation from an incandescent light.)

- a) The power radiated is $e\sigma AT^4$, so the area is

$$A = \frac{\text{power}}{e\sigma T^4} = \frac{100 \text{ W}}{(1/3)(5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4)(3000 \text{ K})^4} = 6.6 \times 10^{-5} \text{ m}^2 = 66 \text{ mm}^2.$$

So if you spread the lamp's surface out into a square, it would measure about 8 mm across.

- b) The spectrum (plotted vs. photon energy) peaks at $x = 2.82$, where $x = \epsilon/kT$. So the peak is at

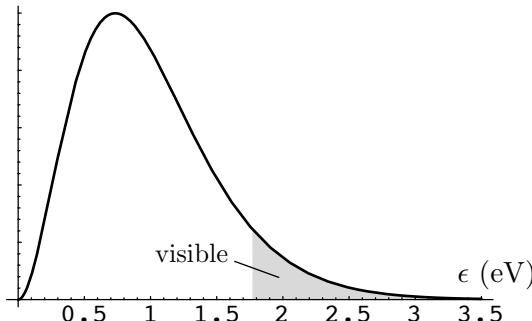
$$\epsilon = (2.82)(8.62 \times 10^{-5} \text{ eV/K})(3000 \text{ K}) = 0.73 \text{ eV.}$$

A photon of this energy has a wavelength of

$$\lambda = \frac{hc}{\epsilon} = \frac{1230 \text{ eV nm}}{0.73 \text{ eV}} = 1700 \text{ nm} = 1.7 \text{ m,}$$

in the infrared.

- c) At 3000 K, $kT = 0.26 \text{ eV}$. So to plot the spectrum as a function of photon energy in eV, I gave Mathematica the instruction `Plot[eps^3/(Exp[eps/.26]-1), {eps, 0, 3.5}]`. It produced the following graph:



To locate the visible range, note that the red end of the spectrum, at 700 nm, corresponds to a photon energy of $\epsilon = hc/\lambda = 1.77 \text{ eV}$, while the violet end (400 nm) corresponds to a photon energy of 3.1 eV. I've shaded this region in the plot. Notice that it's not a particularly large fraction of the whole spectrum, and that the lamp gives off much more energy at the red end of the spectrum than at the violet end.

- d) To integrate the Planck spectrum, it's easiest to work in terms of the dimensionless variable $x = \epsilon/kT = hc/\lambda kT$. At the red end of the visible spectrum, $x = 1.77/0.26 = 6.8$, while at the violet end, $x = 3.1/0.26 = 11.9$. The fraction of energy between these wavelengths is equal to the integral of $x^3/(e^x - 1)$ over this range, divided by the integral over all x :

$$\text{fraction} = \int_{6.8}^{11.9} \frac{x^3}{e^x - 1} dx / \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{15}{\pi^4} \int_{6.8}^{11.9} \frac{x^3}{e^x - 1} dx.$$

I evaluated this expression numerically with the Mathematica instruction

$$(15/\text{Pi}^4)*\text{NIntegrate}[x^3/(Exp[x]-1), \{x, 6.8, 11.9\}]$$

and it returned the value 0.083, indicating that only about 8% of the light is in the visible range. Comparing the shaded portion of the graph to the full area under the curve, this seems about right.

- e) To increase the efficiency (that is, the fraction of energy in the visible range), we would want to increase the temperature of the lamp. This would move the peak in the spectrum to the right (higher photon energies), so the shaded region would fall nearer the peak rather than in the high-energy tail of the spectrum. Unfortunately, the temperature can't be raised much above 3000 K because the tungsten would rapidly deteriorate as its melting temperature, 3695 K, is approached.
- f) To estimate the temperature at which the efficiency would be highest, note that whatever the temperature, the values of $x = \epsilon/kT$ for visible wavelengths range from some value x_r at the red end of the spectrum up to $\frac{7}{4}x_r$ at the violet end. I therefore defined the following *Mathematica* function to compute the efficiency for any given x_r :

```
eff[xr_] := (15/Pi^4)*NIntegrate[x^3/(Exp[x]-1),{x,xr,7*xr/4}]
```

To find the x_r that maximizes this function, I used the instruction

```
FindMinimum[-eff[xr],{xr,2,3}]
```

(where the numbers 2 and 3 are suggested starting points for the search). The x_r value returned was 2.92, corresponding to a temperature of

$$T = \frac{\epsilon}{kx_r} = \frac{1.77 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(2.92)} = 7030 \text{ K.}$$

The efficiency at this temperature is about 39%. By the way, note that even at this temperature, the peak in the blackbody spectrum lies slightly outside the visible range, in the very near infrared (at $x = 2.82$). Raising the temperature further would put the peak in the visible range, but would also broaden the spectrum, lowering the fraction of energy in the visible range.

Problem 7.52. (Power radiated by the human body.)

- a) Taking $T = 310 \text{ K}$, $A = 2 \text{ m}^2$, and $e = 1$, I obtain for the power radiated by my body

$$\text{Power} = \sigma e A T^4 = (5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \text{ K}^4))(2 \text{ m}^2)(310 \text{ K})^4 = 1050 \text{ W} \approx 1 \text{ kW.}$$

This is the rate at which I would lose energy if I were naked in empty space.

- b) At this rate, the energy that I would lose in one day would be

$$(1050 \text{ W})(24 \text{ hr})\left(\frac{3600 \text{ s}}{1 \text{ hr}}\right) = 9.0 \times 10^7 \text{ J}\left(\frac{1 \text{ kcal}}{4186 \text{ J}}\right) = 20,000 \text{ kcal.}$$

That's ten times the number of calories that an average person consumes in a day (about 2000). The discrepancy is due to the fact that I am *not* naked in empty space: Most of the energy that I radiate is replaced by energy radiated (or conducted) back to me by my clothes and other surroundings.

- c) On a per-kilogram basis, my radiation rate is

$$\frac{1000 \text{ W}}{75 \text{ kg}} = 14 \text{ W/kg},$$

whereas the sun's is

$$\frac{3.9 \times 10^{26} \text{ W}}{2 \times 10^{30} \text{ kg}} = 0.0002 \text{ W/kg},$$

about 70,000 times less (and 7000 times less than my rate of fuel consumption). How is this possible? Although the sun is bright, it is also very massive. And although it generates energy by nuclear fusion, the reactions in its core actually proceed extremely slowly—giving it a ten-billion-year lifetime. I, on the other hand, have to replenish my (chemical) fuel supply on a daily basis.

Problem 7.53. (Hawking radiation from black holes.)

- a) We calculated in Problem 3.7 that the temperature of a one-solar-mass black hole is 6×10^{-8} K. For a blackbody at this temperature, the peak in the radiation spectrum (plotted as a function of photon energy) would be at $\epsilon = (2.82)kT = 1.5 \times 10^{-11}$ eV. This corresponds to a wavelength of $\lambda = hc/\epsilon = 84$ km. More generally, the peak would be at a wavelength of

$$\lambda = \frac{hc}{(2.82)kT} = \frac{hc}{2.82} \cdot \frac{16\pi^2 GM}{hc^3} = (28.0) \frac{2GM}{c^2}.$$

The quantity $2GM/c^2$ is just the “radius” of the black hole, that is, the quantity that you could plug into the formula $4\pi r^2$ to obtain the surface area. Thus, for any black hole, the typical wavelength emitted is about 28 times the “radius,” or 14 times the “diameter.”

- b) The total power radiated should be given by Stefan’s law:

$$\text{power} = \sigma AT^4 = \left(\frac{2\pi^5 k^4}{15h^3 c^2}\right) \left(\frac{16\pi G^2 M^2}{c^4}\right) \left(\frac{hc^3}{16\pi^2 kGM}\right)^4 = \frac{hc^6}{(30,720)\pi^2 G^2 M^2}.$$

For the sun’s mass (2×10^{30} kg), this expression evaluates to 9×10^{-29} watts, or 6×10^{-10} eV/s. Since the typical photon radiated has an energy of 1.5×10^{-11} eV, this means that such a black hole would emit about 40 (very feeble) photons per second.

- c) The power radiated is the same as the rate at which the black hole’s energy (Mc^2) decreases, so the rate of decrease is given by the differential equation

$$\frac{d(Mc^2)}{dt} = \sigma AT^4 = \frac{hc^6}{(30,720)\pi^2 G^2 M^2}.$$

That is,

$$\frac{dM}{dt} = -\frac{H}{M^2}, \quad \text{where} \quad H = \frac{hc^4}{(30,720)\pi^2 G^2} = 4.0 \times 10^{15} \text{ kg}^3/\text{s}.$$

(We could refer to H as Hawking's constant.) This is a separable differential equation, which we can integrate to obtain the lifetime τ of the black hole:

$$\int_{M_i}^0 M^2 dM = -H \int_0^\tau dt \quad \Rightarrow \quad \frac{M_i^3}{3} = -H\tau,$$

that is, $\tau = M_i^3 / 3H$.

- d) For $M_i = 2 \times 10^{30}$ kg, the lifetime should be

$$\tau = \frac{(2 \times 10^{30} \text{ kg})^3}{3(4.0 \times 10^{15} \text{ kg}^3/\text{s})} = 7 \times 10^{74} \text{ s.}$$

That's 2×10^{67} years, or more than 10^{57} times the age of the known universe. Black holes that form by stellar collapse should have initial masses at least this large, so there's no hope of observing such black holes disappearing any time soon.

- e) The age of the known universe is about 14 billion years or 4×10^{17} seconds. The initial mass of a black hole with this lifetime would be

$$M_i = (3H\tau)^{1/3} = [3(4 \times 10^{15} \text{ kg}^3/\text{s})(4 \times 10^{17} \text{ s})]^{1/3} = 1.7 \times 10^{11} \text{ kg},$$

smaller than the sun's mass by a factor of about 10^{19} . The "radius" of such a black hole would be

$$\frac{2GM}{c^2} = 2.6 \times 10^{-16} \text{ m,}$$

and therefore the radiation it emits (initially) would peak at a wavelength of about 28 times this, or 7 femtometers. That's comparable to the size of an atomic nucleus. A photon with this wavelength has an energy of $\epsilon = hc/\lambda = 170$ MeV. That's a very hard gamma ray, a hundred times more energetic than gamma rays emitted in nuclear reactions, though not as energetic as those produced at today's particle accelerators. As the black hole evaporates and loses mass, its temperature increases and the gamma rays emitted become even more energetic. However, a black hole that can emit MeV gamma rays can probably also emit electron-positron pairs and perhaps other species of massive particles. This would increase its rate of evaporation and decrease its lifetime. Therefore, to have lasted the age of the universe, a black hole probably would have needed an initial mass somewhat greater than I've calculated.

Problem 7.54. (Stellar surface temperatures and sizes.) Stefan's law, in conventional units, reads $L = \sigma AT^4 = 4\pi\sigma R^2T^4$, where L is the star's luminosity and R is its radius. For convenience, though, we could measure L , R , and T in units of the sun's values. In these units, the constant $4\pi\sigma$ must be equal to 1, because the sun's temperature and radius (both 1) must yield the sun's luminosity (1). Solving the equation for R then gives simply $R = \sqrt{L/T^4}$. Note also that the energy at which a blackbody spectrum peaks is directly proportional to the temperature ($\epsilon = (2.82)kT$), so the ratio of a star's temperature to that of the sun is the same as the ratio of the peak photon energies. As calculated on page 305, the sun's spectrum peaks at a photon energy of 1.41 eV.

- a) The surface temperature of Sirius A is $(2.4 \text{ eV})/(1.41 \text{ eV}) = 1.70$, in units of the sun's temperature. Therefore the radius of Sirius A should be

$$R = \sqrt{\frac{L}{T^4}} = \sqrt{\frac{24}{(1.70)^4}} = 1.69,$$

in units of the sun's radius. So even though Sirius A is somewhat hotter than the sun, it still has to be bigger in order to be 24 times as luminous.

- b) The surface temperature of Sirius B is $(7 \text{ eV})/(1.41 \text{ eV}) = 4.96$, nearly five times the sun's temperature. Therefore the radius of Sirius B should be

$$R = \sqrt{\frac{L}{T^4}} = \sqrt{\frac{0.03}{(4.96)^4}} = 0.007,$$

less than 1% of the sun's radius, and just slightly smaller than the earth's radius. This result is in rough agreement with that of Problem 7.23(d), where we calculated that a one-solar-mass white dwarf should have a radius just slightly larger than earth's. (From the orbital motion of Sirius A and B, astronomers have determined that the mass of Sirius B is almost exactly equal to that of our sun.)

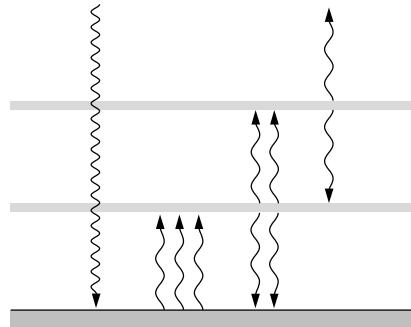
- c) The surface temperature of Betelgeuse is $(0.8 \text{ eV})/(1.41 \text{ eV}) = 0.57$, in units of the sun's temperature. Therefore the radius of Betelgeuse should be

$$R = \sqrt{\frac{L}{T^4}} = \sqrt{\frac{10,000}{(0.57)^4}} = 310.$$

That's larger than the radius of earth's *orbit*, and nearly as large as the orbit of Mars. "Supergiant" is certainly an appropriate term. As for "red," the spectrum of Betelgeuse is certainly redder than the sun's, due to its lower temperature of 3300 K which makes its spectrum peak well into the infrared and fall off considerably at the blue end of the visible range. But this temperature is still slightly hotter than the filament of an incandescent bulb, so the color of Betelgeuse shouldn't be any redder than that of incandescent light; "pale orange" would be a more accurate description.

Problem 7.55. The situation with two "blankets" is shown in the illustration at right. Because the whole earth (including the atmosphere) must be in equilibrium, the upper blanket must send one unit of (infrared) energy upward for each unit of energy absorbed from the sun. The temperature of the upper blanket is therefore

$$T_0 = \left(\frac{(0.7)(1370 \text{ W/m}^2)}{4 \cdot 5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4} \right)^{1/4} = 255 \text{ K},$$



assuming that 30% of the sun's light is reflected. But the upper blanket must send as much energy downward as it sends upward, so its *total* emission (for each unit of sunlight) is two

units. Equilibrium therefore requires that it also absorb two units of (infrared) radiation, and these two units must come from the lower blanket. Since the lower blanket is radiating twice as much energy upward as the upper blanket, its temperature must be greater by a factor of $2^{1/4}$, i.e., 303 K. Furthermore, the lower blanket must also send as much energy down as it sends up—in this case, two units. Since it emits a total of four units of energy, it must also absorb four units, of which one comes from the upper blanket. The other three must come from the ground; as a check, note that the ground is absorbing two units from the lower blanket and one from the sun, so it must emit three units. In order for the ground to emit three times as much energy upward as the upper blanket, its temperature must be greater by a factor of $3^{1/4}$:

$$T_{\text{ground}} = 3^{1/4} \quad T_0 = 3^{1/4}(255 \text{ K}) = 336 \text{ K} = 62^\circ\text{C}.$$

This would indeed be a catastrophe for life as we know it.

Problem 7.56. (Greenhouse effect on Venus.)

- a) If you're twice as close to a light source, you absorb *four* times as much energy (per square meter), because the light spreads out in *two* directions as it travels. More generally, the brightness of a source viewed from a distance r is proportional to $1/r^2$. The solar constant on Venus is therefore greater than on earth by a factor of $1/(0.7)^2 = 2.04$. Multiplying by 1370 W/m^2 gives 2800 W/m^2 for the solar constant on Venus. Repeating the calculation in equation 7.102 for this value, we obtain an equilibrium temperature of

$$T_0 = \left(\frac{2800 \text{ W/m}^2}{4 \cdot 5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}} \right)^{1/4} = 333 \text{ K},$$

assuming that none of the sunlight is reflected and that there is no greenhouse effect.

- b) If the clouds reflect 77% of incoming sunlight, then only 23% is absorbed, so we should multiply the solar constant by 0.23 in the preceding calculation. With this modification, the result is 231 K. Brrrr!
- c) Consider a time period in which one unit of sunlight is absorbed. The planet as a whole (including the atmosphere) must also emit one unit of energy, and it must be emitted by the uppermost atmospheric blanket. This implies that the uppermost blanket is at 231 K, as calculated in part (b). But the blanket also sends a unit of energy down to the next blanket. Since it emits two units total, it must also absorb two units, and these must come from the next blanket down. The second blanket therefore sends twice as much energy upward as the first, so it must be hotter by a factor of $2^{1/4}$. Meanwhile, the second blanket also sends two units of energy downward to the third. Since the second blanket is emitting four units total, and receiving one unit from the first blanket, it must receive three more from the third blanket. The third blanket must therefore send three units of energy upward, which implies that it is hotter than the first blanket by a factor of $3^{1/4}$. Continuing downward, we might guess that the fourth blanket is hotter than the first by a factor of $4^{1/4}$. To check this, note that the third blanket sends three units of energy downward, so it emits six units total, but it receives two units from the second blanket, so it must receive four more units from the

fourth blanket. We could prove by induction that the n th blanket must emit n units of energy upward and therefore must be hotter than the first by a factor of $n^{1/4}$; I'll skip the proof and take the theorem as established by the first four cases. Thus, the 70th blanket is hotter than the first by a factor of $(70)^{1/4}$, and the ground (nally) is hotter by a factor of $(71)^{1/4} = 2.90$. Multiplying by 231 K, we therefore predict that the ground temperature should be about 670 K. Ouch!

Problem 7.57. When we change variables from n to x in equation 7.109, the combination $n^3 dn$ becomes $(2LkT/hc_s)^4 x^3 dx$:

$$\begin{aligned} U &= \frac{3\pi}{2} \int_0^{n_{\max}} \frac{hc_s}{2L} \frac{n^3}{e^{hc_s n / 2LkT} - 1} dn = \frac{3\pi}{2} \int_0^{x_{\max}} \frac{hc_s}{2L} \left(\frac{2LkT}{hc_s} \right)^4 \frac{x^3}{e^x - 1} dx \\ &= \frac{3\pi}{2} \left(\frac{2L}{hc_s} \right)^3 (kT)^4 \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx. \end{aligned} \quad (1)$$

Here x_{\max} is as defined in equation 7.111, so it can be written T_D/T , where

$$T_D = \frac{hc_s}{2Lk} \left(\frac{6N}{\pi} \right)^{1/3}.$$

If we cube both sides of this relation, we obtain

$$T_D^3 = \frac{1}{k^3} \left(\frac{hc_s}{2L} \right)^3 \frac{6N}{\pi}, \quad \text{or} \quad \left(\frac{2L}{hc_s} \right)^3 = \frac{6N}{\pi} \frac{1}{k^3 T_D^3}. \quad (2)$$

Making this substitution into equation 1 gives

$$U = \frac{3\pi}{2} \frac{6N}{\pi} \frac{1}{k^3 T_D^3} (kT)^4 \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx = \frac{9NkT^4}{T_D^3} \int_0^{x_{\max}} \frac{x^3}{e^x - 1} dx,$$

which is equation 7.112.

To compute the heat capacity, go back to equation 7.109 and differentiate with respect to T :

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} = \frac{3\pi}{2} \int_0^{n_{\max}} \frac{hc_s}{2L} \frac{d}{dT} \left(\frac{n^3}{e^{hc_s n / 2LkT} - 1} \right) dn \\ &= \frac{3\pi}{2} \int_0^{n_{\max}} \frac{hc_s}{2L} \frac{(hc_s n / 2LkT^2) e^{hc_s n / 2LkT} n^3}{(e^{hc_s n / 2LkT} - 1)^2} dn \\ &= \frac{3\pi}{2} \left(\frac{hc_s}{2L} \right)^2 \frac{1}{kT^2} \int_0^{n_{\max}} \frac{n^4 e^{hc_s n / 2LkT}}{(e^{hc_s n / 2LkT} - 1)^2} dn. \end{aligned}$$

Changing variables to $x = hc_s n / 2LkT$, this expression becomes

$$C_V = \frac{3\pi}{2} \left(\frac{hc_s}{2L} \right)^2 \frac{1}{kT^2} \left(\frac{2LkT}{hc_s} \right)^5 \int_0^{x_{\max}} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{3\pi}{2} \left(\frac{2L}{hc_s} \right)^3 k^4 T^3 \int_0^{x_{\max}} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

Finally, we can again use equation 2 to write this in terms of T_D :

$$C_V = \frac{3\pi}{2} \frac{6N}{\pi} \frac{1}{k^3 T_D^3} k^4 T^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx = 9Nk \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

Problem 7.58. The density of copper (which I looked up in an introductory physics textbook) is 8.93 g/cm^3 , and the atomic mass (which I got off a periodic table) is 63.5 g/mol . Let's consider a chunk of copper containing one mole of atoms. Then the mass is 63.5 g , and the volume is

$$V = \frac{\text{mass}}{\text{density}} = \frac{63.5 \text{ g}}{8.93 \text{ g/cm}^3} = 7.11 \times 10^{-6} \text{ m}^3.$$

The theoretical Debye temperature is therefore

$$T_D = \frac{hc_s}{2k} \left(\frac{6N}{\pi V} \right)^{1/3} = \frac{(6.63 \times 10^{-34} \text{ J s})(3560 \text{ m/s})}{2(1.38 \times 10^{-23} \text{ J/K})} \left(\frac{6(6.02 \times 10^{23})}{\pi(7.11 \times 10^{-6} \text{ m}^3)} \right)^{1/3} = 466 \text{ K}.$$

Meanwhile, the slope of the line for copper in Figure 7.28 is roughly

$$\text{slope} = \frac{0.9 \text{ mJ/K}^2}{18 \text{ K}^2} = 5 \times 10^{-5} \text{ J/K}^4.$$

According to equation 7.116, this slope should be equal to $12\pi^4 Nk/5T_D^3$. Solving for T_D then gives us

$$T_D = \left(\frac{12\pi^4 Nk}{5(\text{slope})} \right)^{1/3} = \left(\frac{12\pi^4 (8.315 \text{ J/K})}{5(5 \times 10^{-5} \text{ J/K}^4)} \right)^{1/3} = 340 \text{ K}.$$

So the theoretical prediction is too large by nearly 40%. I suspect that the value used here for the speed of sound applies only to longitudinal waves, with transverse waves traveling considerably slower and therefore lowering the effective average Debye temperature.

Problem 7.59. The intercepts on the three graphs are determined only by the electronic contribution to the heat capacity. As we saw in Section 7.3, this contribution depends only on the number of conduction electrons (per mole in this case) and the Fermi energy. Copper, silver, and gold each have one conduction electron per mole, while the Fermi energy, which depends only on N/V , should also be about the same for each, since the atoms are all about the same size. The slopes of the graphs, however, are inversely proportional to T_D^3 , or equivalently, to c_s^3 . The speed of sound in a material increases with stiffness (elastic modulus) and decreases with density. Of the three metals, copper is the most stiff and the least dense, so we would expect it to have the largest value of c_s and hence the smallest slope, as indeed it does. Gold, which is quite dense but not so stiff, is at the other extreme, while silver is in between.

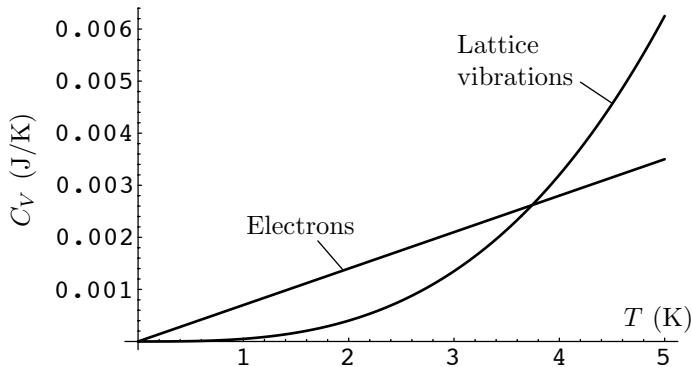
Problem 7.60. At low temperatures, the electronic contribution to the heat capacity is linear in temperature while the contribution of lattice vibrations is cubic. To draw them correctly on the same graph, it's easiest to first solve for the temperature at which they are equal. From equation 7.116, this is where

$$\gamma T = T^3, \quad \text{or} \quad T = \sqrt[3]{\gamma},$$

where γ is an abbreviation for $12\pi^4 Nk/5T_D^3$, the slope of the graph plotted in Figure 7.28. From the data for copper plotted in the figure, this slope appears to be roughly $(0.9 \text{ mJ/K}^2)/(18 \text{ K}^2) = 5 \times 10^{-5} \text{ J/K}^4$, while γ , the intercept, appears to be roughly 0.7 mJ/K^2 . Therefore the temperature at which the two contributions are equal should be

$$T = \sqrt{\frac{7 \times 10^{-4} \text{ J/K}^2}{5 \times 10^{-5} \text{ J/K}^4}} = \sqrt{14 \text{ K}^2} = 3.7 \text{ K}.$$

At this temperature, each of the contributions to the heat capacity is equal to $\gamma T = (7 \times 10^{-4} \text{ J/K}^2)(3.7 \text{ K}) = 0.0026 \text{ J/K}$. Here, then, is a plot of the two contributions separately:



Problem 7.61. If we repeat the derivation on pages 308 through 311 for the case of a liquid, the only thing that changes is the number of polarization states for each triplet (n_x, n_y, n_z) : now there is only one polarization rather than three. This change has no effect on the volume of n -space that is summed over, and therefore has no effect on the formula $n_{\max} = (6N/\pi)^{1/3}$ or on equation 7.111 for the Debye temperature:

$$T_D = \frac{hc_s}{2k} \left(\frac{6N}{\pi V} \right)^{1/3}.$$

To evaluate this expression we need to know the ratio N/V . Let's take N to be Avogadro's number, so that the mass of the sample is 4 g. At a density of 0.145 g/cm^3 , this value implies a volume of 27.6 cm^3 or $2.76 \times 10^{-5} \text{ m}^3$. The predicted Debye temperature is therefore

$$T_D = \frac{(6.63 \times 10^{-32} \text{ J s})(238 \text{ m/s})}{2(1.38 \times 10^{-23} \text{ J/K})} \left(\frac{6(6.02 \times 10^{23})}{\pi(2.76 \times 10^{-5} \text{ m}^3)} \right)^{1/3} = 19.8 \text{ K}.$$

What does change in the derivation in the text is the numerical factor multiplying the energy (and the heat capacity): The factor of 3 in equation 7.106 disappears, so each expression for U or C_V from there on should be divided by 3 for the case of a liquid. The heat capacity in the low-temperature limit is therefore $1/3$ times the formula in equation 7.115:

$$\frac{C_V}{Nk} = \frac{4\pi^4}{5} \left(\frac{T}{T_D} \right)^3.$$

The cube root of $5/4\pi^4$ is 0.234, so this is the same as

$$\frac{C_V}{Nk} = \left(\frac{T}{(0.234)T_D} \right)^3 = \left(\frac{T}{4.64 \text{ K}} \right)^3,$$

in almost perfect agreement with the measured behavior.

Problem 7.62. When $T \gg T_D$, the x values integrated over in equation 7.112 are all much less than 1, so we can expand the exponential in a power series:

$$\begin{aligned} \frac{x^3}{e^x - 1} &\approx \frac{x^3}{(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3) - 1} = \frac{x^3}{x + \frac{1}{2}x^2 + \frac{1}{6}x^3} = x^2(1 + \frac{1}{2}x + \frac{1}{6}x^2)^{-1} \\ &\approx x^2 \left[1 - (\frac{1}{2}x + \frac{1}{6}x^2) + \frac{1}{2}(-1)(-2)(\frac{1}{2}x + \frac{1}{6}x^2)^2 \right] \\ &\approx x^2 \left[1 - \frac{1}{2}x - \frac{1}{6}x^2 + \frac{1}{4}x^2 \right] = x^2 - \frac{1}{2}x^3 + \frac{1}{12}x^4. \end{aligned}$$

Integrating this expression from 0 to T_D/T , we obtain

$$\begin{aligned} U &\approx \frac{9NkT^4}{T_D^3} \left[\frac{1}{3} \left(\frac{T_D}{T} \right)^3 - \frac{1}{8} \left(\frac{T_D}{T} \right)^4 + \frac{1}{60} \left(\frac{T_D}{T} \right)^5 \right] \\ &= 9NkT_D \left[\frac{1}{3} \left(\frac{T}{T_D} \right)^3 - \frac{1}{8} + \frac{1}{60} \left(\frac{T}{T_D} \right)^5 \right]. \end{aligned}$$

To obtain the heat capacity, differentiate:

$$C_V = \frac{\partial U}{\partial T} = 9NkT_D \left[\frac{1}{3T_D} - 0 - \frac{T_D}{60T^2} \right] = 3Nk \left[1 - \frac{1}{20} \left(\frac{T_D}{T} \right)^2 \right].$$

Assuming that this formula is reasonably accurate down to $T = T_D$, it predicts that the heat capacity is 5% below its asymptotic value at $T = T_D$, and 1.25% below its asymptotic value at $T = 2T_D$.

Problem 7.63. For a two-dimensional material, the average energy in each wave mode will still be given by the Planck distribution, but to compute the total thermal energy we carry out only a double sum over modes:

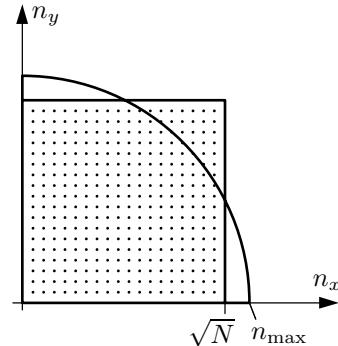
$$U = \sum_{n_x} \sum_{n_y} \frac{\epsilon}{e^{\epsilon/kT} - 1},$$

where $\epsilon = hf = hc_s/\lambda = hc_s n/2L = (hc_s/2L)\sqrt{n_x^2 + n_y^2}$. The numerical factor in front of the sum is 1, assuming that each mode has only one possible polarization (compare equation 7.106). If the material is in the shape of a square and there are N atoms, then each sum goes from 1 to \sqrt{N} , the number of modes along each direction. In other words, the sum is over a square region in n -space with area N (see the illustration on the following page). Assuming that N is large, we can replace the sum by a double integral over the same region:

$$U = \int_0^{\sqrt{N}} dn_x \int_0^{\sqrt{N}} dn_y \frac{\epsilon}{e^{\epsilon/kT} - 1}.$$

The analogue of Debye's approximation in two dimensions is to replace this square region with a quarter-circle with the same area. To find the radius n_{\max} of the circle, note that the area is $\frac{1}{4}\pi n_{\max}^2$. Setting this equal to N gives $n_{\max} = \sqrt{4N/\pi}$. We can now easily convert the integral to polar coordinates (where the measure is $(dn)(n d\theta)$):

$$U = \int_0^{n_{\max}} dn \int_0^{\pi/2} n d\theta \frac{\epsilon}{e^{\epsilon/kT} - 1} = \frac{\pi}{2} \int_0^{n_{\max}} \frac{n \epsilon}{e^{\epsilon/kT} - 1} dn.$$



To make the remaining integral more explicit, we now change variables to $x = \epsilon/kT = hc_s n / 2LkT$. The upper limit on the integral is then

$$x_{\max} = \frac{hc_s n_{\max}}{2LkT} = \frac{hc_s}{2LkT} \sqrt{\frac{4N}{\pi}} \equiv \frac{T_D}{T},$$

where the last equality defines the two-dimensional version of the Debye temperature T_D , and the energy integral itself becomes

$$\begin{aligned} U &= \frac{\pi}{2} \left(\frac{2L}{hc_s} \right)^2 (kT)^3 \int_0^{T_D/T} \frac{x^2}{e^x - 1} dx = \frac{\pi}{2} \left(\frac{\sqrt{4N/\pi}}{kT_D} \right)^2 (kT)^3 \int_0^{T_D/T} \frac{x^2}{e^x - 1} dx \\ &= \frac{2NkT^3}{T_D^2} \int_0^{T_D/T} \frac{x^2}{e^x - 1} dx. \end{aligned}$$

This is the desired expression for the thermal energy.

When $T \ll T_D$, we can replace the upper limit on the integral by ∞ (since the exponential kills off the integrand at large x anyway). In this case the integral over x cannot be expressed in terms of π —see Appendix B—but it can be evaluated numerically to give 2.404. So the energy at low temperature is

$$U \approx \frac{2NkT^3}{T_D^2} (2.404), \quad (T \ll T_D)$$

which implies that the heat capacity is

$$C_A = \frac{\partial U}{\partial T} = \frac{6NkT^2}{T_D^2} (2.404). \quad (T \ll T_D)$$

In this case the low-temperature heat capacity is proportional to T^2 , as opposed to T^3 for a three-dimensional solid. Meanwhile, in the high-temperature limit, the x in the integrand is always very small so we can expand $e^x \approx 1 + x$ to obtain

$$U \approx \frac{2NkT^3}{T_D^2} \int_0^{T_D/T} \frac{x^2}{1 + x - 1} dx = \frac{2NkT^3}{T_D^2} \cdot \frac{1}{2} \left(\frac{T_D}{T} \right)^2 = NkT, \quad (T \gg T_D)$$

in agreement with the equipartition theorem. The heat capacity in this limit is simply Nk .

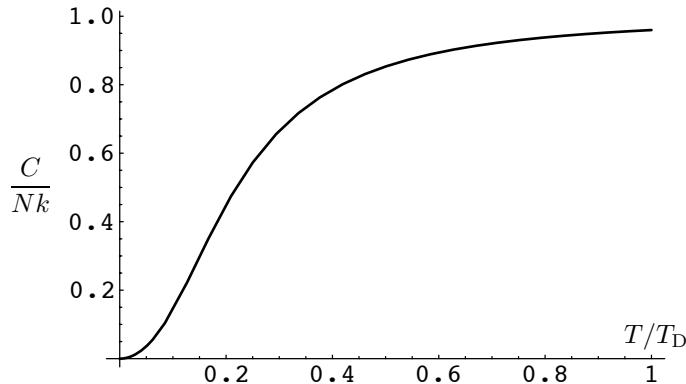
To obtain the heat capacity at intermediate temperatures, it's easiest to differentiate the energy integral before changing variables to x :

$$\begin{aligned} C_A &= \frac{\partial U}{\partial T} = \frac{\pi}{2} \int_0^{n_{\max}} \frac{\partial}{\partial T} \left(\frac{n \epsilon}{e^{\epsilon/kT} - 1} \right) dn = \frac{\pi}{2} \int_0^{n_{\max}} \frac{n \epsilon (\epsilon/kT^2) e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} dn \\ &= \frac{\pi}{2} k \left(\frac{2LkT}{hc_s} \right)^2 \int_0^{x_{\max}} \frac{x^3 e^x}{(e^x - 1)^2} dx = \frac{\pi}{2} k \frac{4N}{\pi} \left(\frac{T}{T_D} \right)^2 \int_0^{x_{\max}} \frac{x^3 e^x}{(e^x - 1)^2} dx \\ &= \frac{2NkT^2}{T_D^2} \int_0^{x_{\max}} \frac{x^3 e^x}{(e^x - 1)^2} dx. \end{aligned}$$

To plot C/Nk vs. T/T_D , I gave Mathematica the instruction

```
Plot[2*t^2*NIntegrate[x^3*Exp[x]/(Exp[x]-1)^2,{x,0,1/t}],{t,0,1}]
```

and it produced the following graph:



Although this graph looks similar to that for a three-dimensional solid (Figure 7.29), here the low-temperature behavior is quadratic (rising more suddenly) instead of cubic.

Problem 7.64. (Spin waves in a ferromagnet.)

- a) The total number of magnons at temperature T should be given by the Planck distribution, summed over all modes:

$$N_m = \sum_{n_x, n_y, n_z} \frac{1}{e^{\epsilon/kT} - 1},$$

where $\epsilon = p^2/2m^*$, $p = h/\lambda = hn/2L$, and $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$. If we convert the sum to an integral in spherical coordinates, the angular integrals give a factor of $\pi/2$ (as always), leaving us with

$$N_m = \frac{\pi}{2} \int_0^\infty \frac{n^2}{e^{\epsilon/kT} - 1} dn,$$

where I've used ∞ as the upper limit because this whole picture applies only at relatively low temperatures. Now change variables to $x = \epsilon/kT$:

$$x = \frac{p^2}{2m^*kT} = \frac{h^2 n^2}{8m^* L^2 kT}, \quad n = \sqrt{\frac{8m^* L^2 kT x}{h^2}}, \quad dn = \sqrt{\frac{2m^* L^2 kT}{h^2}} \frac{1}{\sqrt{x}} dx.$$

This variable change puts the expression for N_m into the form

$$N_m = \frac{\pi}{2} \left(\frac{8m^*L^2kT}{h^2} \right) \sqrt{\frac{2m^*L^2kT}{h^2}} \int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx = 2\pi V \left(\frac{2m^*kT}{h^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx.$$

According to *Mathematica*, the integral is equal to 2.315.

- b) If the total magnetization at $T = 0$ is $2_{\text{B}}N$, and each magnon reduces this value by 2_{B} , then the fractional reduction in magnetization is

$$\frac{2_{\text{B}}N_m}{2_{\text{B}}N} = \frac{N_m}{N} = 2\pi(2.315) \frac{V}{N} \left(\frac{2m^*kT}{h^2} \right)^{3/2} = \left(\frac{T}{T_0} \right)^{3/2},$$

where

$$T_0 = \frac{h^2}{2m^*k} \left(\frac{N}{V} \right)^{2/3} \frac{1}{(2\pi 2.315)^{2/3}} = \frac{(0.0839)h^2}{m^*k} \left(\frac{N}{V} \right)^{2/3}.$$

For iron, we're given $m^* = 1.24 \times 10^{-29}$ kg. The ratio N/V can be calculated from the density and the atomic mass, or we can look up V/N_A on page 404. So for iron, we can predict

$$T_0 = \frac{(0.0839)(6.63 \times 10^{-34} \text{ J s})^2}{(1.24 \times 10^{-29} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} \left(\frac{6.02 \times 10^{23}}{7.11 \times 10^{-6} \text{ m}^3} \right)^{2/3} = 4150 \text{ K.}$$

So the temperature has to be pretty high before the magnetization decreases by a substantial fraction.

- c) To calculate the heat capacity, we should first calculate the energy:

$$U = \sum_{n_x, n_y, n_z} \frac{\epsilon}{e^{\epsilon/kT} - 1} = \frac{\pi}{2} \int_0^\infty \frac{\epsilon n^2}{e^{\epsilon/kT} - 1} dn = 2\pi V \left(\frac{2m^*kT}{h^2} \right)^{3/2} (kT) \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx.$$

Mathematica says that this integral equals 1.783, so

$$U = 2\pi(1.783)Vk \left(\frac{2m^*k}{h^2} \right)^{3/2} T^{5/2} = (31.69)Vk \left(\frac{m^*k}{h^2} \right)^{3/2} T^{5/2}.$$

Differentiating with respect to T gives the heat capacity:

$$\frac{C_V}{Nk} = \frac{1}{Nk} \frac{\partial U}{\partial T} = (31.69) \frac{5}{2} \frac{V}{N} \left(\frac{m^*kT}{h^2} \right)^{3/2} = \left(\frac{T}{T_1} \right)^{3/2},$$

where

$$T_1 = \frac{h^2}{m^*k} \left(\frac{N}{V} \right)^{2/3} \left(\frac{2}{5(31.69)} \right)^{2/3} = \left(\frac{0.0542}{0.0839} \right) T_0 = (0.646)T_0.$$

For iron, therefore, $T_1 = 2680$ K, which implies that the magnon contribution to the heat capacity is quite small (compared to Nk) at room temperature and below. However, at sufficiently low temperatures, the magnon contribution will be greater

than the phonon contribution, which is proportional to T^3 (see equation 7.115). The temperature at which these two contributions are equal is given by

$$\left(\frac{T}{T_1}\right)^{3/2} = \frac{12\pi^4}{5} \left(\frac{T}{T_D}\right)^3, \quad \text{or} \quad T = \left(\frac{5}{12\pi^4}\right)^{2/3} \frac{T_D^2}{T_1} = (0.0264) \frac{(470 \text{ K})^2}{2680 \text{ K}} = 2.17 \text{ K}.$$

Thus, at temperatures of a few kelvin, the magnon contribution to the heat capacity should be measurable.

- d) For a similar system in two dimensions, the number of magnons at temperature T should be

$$N_m = \sum_{n_x, n_y} \frac{1}{e^{\epsilon/kT} - 1} = \frac{\pi}{2} \int_0^\infty \frac{n}{e^{\epsilon/kT} - 1} dn,$$

where I've converted the sum into an integral in polar coordinates and carried out the angular integral (over a quarter-circle). But now, changing variables to x (which is proportional to n^2) gives the integral

$$N_m \propto \int_0^\infty \frac{1}{e^x - 1} dx.$$

Near $x = 0$, we can expand $e^x \approx 1 + x + \dots$ and cancel the 1 to see that the integrand is proportional to $1/x$. Therefore, the integral diverges at its lower limit; this implies that the number of long-wavelength magnons is infinite. The only obvious way out of this contradiction is to suppose that the material doesn't magnetize in the first place, and this turns out to be true.

Problem 7.65. To evaluate the integral I used the *Mathematica* instruction

```
NIntegrate[Sqrt[x]/(Exp[x]-1),{x,0,Infinity}]
```

and it returned 2.31516, confirming the value quoted in the text.

Problem 7.66. (Bose-Einstein condensation of rubidium-87.)

- a) For a rubidium-87 atom in a cube-shaped box of width 10^{-5} m, the ground-state energy is

$$\begin{aligned} \epsilon_0 &= \frac{h^2}{8mL^2}(1^2 + 1^2 + 1^2) = \frac{3}{8} \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(87)(1.66 \times 10^{-27} \text{ kg})(10^{-5} \text{ m})^2} \\ &= 1.14 \times 10^{-32} \text{ J} = 7.1 \times 10^{-14} \text{ eV}. \end{aligned}$$

This is a tiny energy indeed.

- b) According to equation 7.126, the condensation temperature is

$$kT_c = (0.527) \left(\frac{h^2}{2\pi m L^2}\right) N^{2/3} = (0.224) N^{2/3} \epsilon_0,$$

where the coefficient 0.224 comes from comparing this expression to the previous one. If there are 10,000 atoms in our box, then the kT_c is greater than ϵ_0 by a factor of $(0.224)(10,000)^{2/3} = 104 \approx 100$, that is, $kT_c = 7.4 \times 10^{-12}$ eV or $T_c = 8.6 \times 10^{-8}$ K. This is in rough agreement with the value 10^{-7} K quoted on page 319.

- c) At $T = 0.9T_c$, the number of atoms in the ground state is

$$N_0 = \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right] N = [1 - (0.9)^{3/2}] N = (0.146)N.$$

For $N = 10,000$, this is 1460. Therefore, by equation 7.120,

$$\epsilon_0 = \frac{kT}{N_0} = \frac{(0.9)(7.4 \times 10^{-12} \text{ eV})}{1460} = 4.6 \times 10^{-15} \text{ eV.}$$

That is, the chemical potential lies below the ground-state energy by about $(0.065)\epsilon_0$. The energy of the first excited states is

$$\epsilon_1 = \frac{\hbar^2}{8mL^2}(2^2 + 1^2 + 1^2) = \frac{6\hbar^2}{8mL^2} = 2\epsilon_0,$$

so the expected number of particles in any one of these states is

$$N_1 = \frac{1}{e^{(\epsilon_1)/kT} - 1} = \frac{1}{e^{(1.065)\epsilon_0/kT} - 1} = \frac{1}{e^{1.065/(0.9)(104)} - 1} = 87,$$

and the number of particles in all three of these states is about 260. This less than the number of particles in the ground state by a factor of 5.6—significant, but not enormous.

- d) If instead there are 10^6 atoms, then

$$kT_c = (0.224)N^{2/3}\epsilon_0 = 2240 \epsilon_0 = 1.6 \times 10^{-10} \text{ eV},$$

or $T_c = 1.85 \times 10^{-6}$ K, higher than before by a factor of $100^{2/3} = 21.5$. The fraction of atoms in the ground state at $T = 0.9T_c$ is the same as before, 14.6%, but now the absolute number is 100 times larger, 1.46×10^5 . This implies

$$\epsilon_0 = \frac{kT}{N_0} = \frac{(0.9)(1.6 \times 10^{-10} \text{ eV})}{146,000} = 9.8 \times 10^{-16} \text{ eV},$$

which is only 1.4% as large as ϵ_0 itself. Under these conditions, the expected number of particles in any one of the first excited states is

$$N_1 = \frac{1}{e^{(\epsilon_1)/kT} - 1} = \frac{1}{e^{(1.014)\epsilon_0/kT} - 1} = \frac{1}{e^{1.014/(0.9)(2240)} - 1} = 1990,$$

so the number in all three of these states is about 5960. This is less than the number in the ground state by a factor of 24.5. Apparently, the ratio N_0/N_1 grows as N increases and the ratio T/T_c is held fixed. This means that the range of temperatures (below T_c) over which $3N_1$ is reasonably close to N_0 gets narrower, relative to T_c , as N increases. If we define “close” to mean within a factor of 10, then this range includes $0.9T_c$ when $N = 10^4$, but not when $N = 10^6$.

Problem 7.67. For the numbers given, equation 7.126 predicts a condensation temperature of

$$T_c = \frac{(0.527)h^2}{2\pi mk} \left(\frac{N}{V}\right)^{2/3} = \frac{(0.527)(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(1.67 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} (1.8 \times 10^{20} \text{ m}^{-3})^{2/3}$$

$$= 5.1 \times 10^{-5} \text{ K} = 51 \text{ K},$$

almost exactly equal to the measured value.

Problem 7.68. The number density of liquid helium is

$$\frac{N}{V} = \frac{0.145 \text{ g/cm}^3}{4.00 \text{ g/mol}} = 0.036 \text{ mol/cm}^3 = 2.18 \times 10^{28} \text{ atoms/m}^3.$$

Equation 7.126 therefore predicts a condensation temperature of

$$T_c = \frac{(0.527)h^2}{2\pi mk} \left(\frac{N}{V}\right)^{2/3} = \frac{(0.527)(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(4)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} (2.18 \times 10^{28} \text{ m}^{-3})^{2/3}$$

$$= 3.13 \text{ K}.$$

That's about 44% higher than the measured superfluid transition temperature—pretty close, considering that the helium is actually a liquid, not a noninteracting gas.

Problem 7.69. (Chemical potential of a Bose gas when $T > T_c$.)

- a) With the substitutions $T = tT_c$, $\epsilon = ckT_c$, and $\epsilon = xkT_c$, the exponent $(\epsilon - c)/kT$ becomes

$$\frac{\epsilon}{kT} = \frac{xkT_c}{tkT_c} = \frac{x}{t} - \frac{c}{kT}.$$

Meanwhile,

$$g(\epsilon) d\epsilon = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{3/2} V \sqrt{xkT_c} (kT_c) dx = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi mkT_c}{h^2}\right)^{3/2} V \sqrt{x} dx$$

$$= \frac{2}{\sqrt{\pi}} \frac{N}{2.612} \sqrt{x} dx,$$

where the last step follows from the definition of T_c , equation 7.126. Therefore, equation 7.122 is equivalent to

$$N = \frac{2}{\sqrt{\pi}} \frac{N}{2.612} \int_0^\infty \frac{\sqrt{x}}{e^{(x-c)/t} - 1} dx, \quad \text{or} \quad 2.315 = \int_0^\infty \frac{\sqrt{x}}{e^{(x-c)/t} - 1} dx.$$

- b) To evaluate the integral for $t = 2$ and $c = -0.8$, I gave *Mathematica* the instruction

```
NIntegrate[Sqrt[x]/(Exp[(x+.8)/2]-1),{x,0,Infinity}]
```

which returned the answer 2.3516, too large by about 1.6%.

- c) For the integral in part (b) to yield the correct result, the value of c would have to be slightly more negative. By manual trial and error, I found that $c = -0.821$ gives the correct answer (to four significant figures). It's easier, though, to have *Mathematica* do the trial and error, using the `FindRoot` function:

```
FindRoot[2.315==NIntegrate[Sqrt[x]/(Exp[(x-c)/2]-1),
{x,0,Infinity}], {c,-.8,-.9}]
```

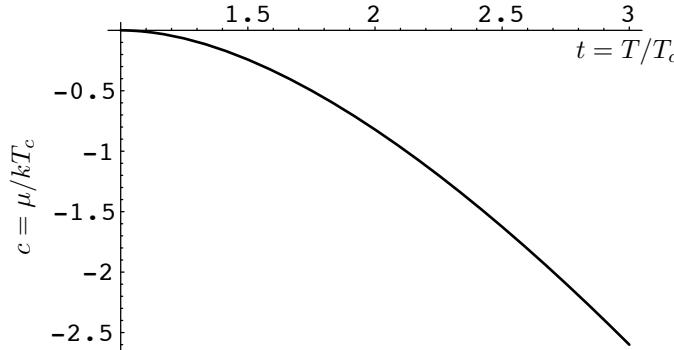
This instruction returned the value $c = -0.820792$. (The values $.8$ and $.9$ tell *Mathematica* where to begin the search.) Repeating this instruction for other values of t is now a simple matter, although for smaller t values, you get bad results unless you specify better starting points such as $.1$ and $.2$. The following instruction generates a table of all the desired c values:

```
muTable =
Table[{t,FindRoot[2.315==NIntegrate[Sqrt[x]/(Exp[(x-c)/t]-1),
{x,0,Infinity}], {c,-.1,-.2}][[1,2]]}, {t,1.2,3,.2}]
```

(The symbols `[[1,2]]` are needed to strip off the unwanted braces and “ $c \rightarrow$ ” inserted by the `FindRoot` function.) To make the plots prettier, I added on the known value at $t = 1$ with the instruction `muTable = Prepend[muTable,{1,0}]`. With or without this addition, the instruction `ListPlot[muTable]` will then generate a plot of the points calculated. But to get a smooth plot, I instead defined an “interpolating function” and plotted that:

```
muInterp = Interpolation[muTable];
Plot[muInterp[t],{t,1,3}]
```

Here is the plot:



Problem 7.70. (Heat capacity of a Bose gas.)

- a) To compute the total energy, we add up the average energies in all single-particle states, which means inserting an extra factor of ϵ into equation 7.121 or 7.122:

$$\begin{aligned} U &= \sum_{\text{all } s} \frac{\epsilon}{e^{(\epsilon_s)/kT} - 1} = \int_0^\infty \epsilon g(\epsilon) \frac{1}{e^{(\epsilon)/kT} - 1} d\epsilon \\ &= \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \int_0^\infty \frac{\epsilon^{3/2}}{e^{(\epsilon)/kT} - 1} d\epsilon. \end{aligned}$$

- b) For $T < T_c$ we can set $c = 0$, then substitute $x = \epsilon/kT$ and evaluate the integral:

$$U = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V(kT)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V(kT)^{5/2} \cdot 1.783.$$

(I did the integral with *Mathematica*.) Differentiating with respect to T gives the heat capacity,

$$C_V = \frac{\partial U}{\partial T} = \frac{5}{2} (1.783) \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V(kT)^{3/2} k = (5.031) \left(\frac{2\pi m}{h^2} \right)^{3/2} V(kT)^{3/2} k.$$

Using equation 7.126 for the condensation temperature, this result can be rewritten as

$$\frac{C_V}{Nk} = \frac{5.031}{2.612} \left(\frac{T}{T_c} \right)^{3/2} = 1.926 \left(\frac{T}{T_c} \right)^{3/2}.$$

This is a concave-up function of T , as shown in Figure 7.37. The overall constant seems to agree as well, since the figure shows that C_V/Nk is just less than 2 when $T = T_c$.

- c) In the high-temperature limit, this system should behave as an ordinary monatomic ideal gas, with three degrees of freedom per atom. So by the equipartition theorem, its heat capacity should be $\frac{3}{2}Nk$.
d) Going back to the original integral in part (a), let's change to dimensionless variables as in Problem 7.69(a):

$$U = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V(kT_c)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^{(x-c)/kT} - 1} dx = (0.432) NkT_c \int_0^\infty \frac{x^{3/2}}{e^{(x-c)/kT} - 1} dx,$$

where I've again used the definition of T_c , equation 7.126. To compute U/NkT_c I defined the following *Mathematica* function:

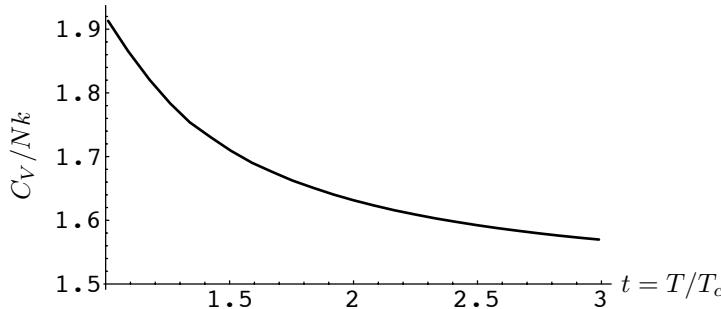
```
u[t_] := .432*NIntegrate[x^1.5/(Exp[(x-muInterp[t])/t]-1),{x,0,Infinity}]
```

Here `muInterp[t]` is the interpolating function for $c = \epsilon/kT$ defined in the Problem 7.69(c). In principle, it's now easy to differentiate this function to obtain the heat capacity. In practice, though, the numerical differentiation tends to be awkward and can compound the numerical inaccuracies that are present in the function `muInterp`. Here's a sequence of instructions that produces reasonably good results:

```
Utable = Table[{t,u[t]},{t,1.2,3,.2}]
Utable = Prepend[Utable,{1,.7703}]
Uinterp = Interpolation[Utable]
heatcap[t_] := (Uinterp[t+.01]-Uinterp[t-.01])/.02
Plot[heatcap[t],{t,1.01,2.99},PlotRange->{1.5,2}]
```

By generating a table of energy values at only the values that were calculated explicitly, I've avoided the inaccuracies in the interpolating function for c . I then added to the table the energy at $t = 1$, which is easy to calculate by setting $c = 0$.

Next, I defined a new interpolating function to compute the energy at intermediate values, and defined a heat capacity function which differentiates this energy function numerically. Since the energy function really computes U/NkT_c , differentiating with respect to $t = T/T_c$ actually gives C_V/Nk . Here's the plot produced by the final instruction:



The only significant differences between this plot and Figure 7.37 are the scale of the axes and the fact that 7.37 also shows the behavior for $T < T_c$. However, to produce Figure 7.37, I computed the “exact” values of C_V and U at intervals of $0.1(T/T_c)$, for increased accuracy.

Problem 7.71. When you know the heat capacity all the way down to $T = 0$, you can calculate the entropy of a system from equation 3.21. In our case, using the result of Problem 7.70(b),

$$S(T_f) = \int_0^{T_f} \frac{C_V}{T} dT = \frac{(1.926)Nk}{T_c^{3/2}} \int_0^{T_f} T^{1/2} dT = \frac{(1.926)Nk}{T_c^{3/2}} \cdot \frac{2}{3} T_f^{3/2}.$$

In other words, for any T below T_c ,

$$S = 1.284 \left(\frac{T}{T_c} \right)^{3/2} Nk.$$

Note also from Problem 7.70(b) that the energy (for $T < T_c$) can be written

$$U = \frac{2}{\sqrt{\pi}} \frac{1.783}{2.612} \left(\frac{T}{T_c} \right)^{3/2} NkT = (0.770) \left(\frac{T}{T_c} \right)^{3/2} NkT.$$

The Helmholtz free energy is therefore

$$F = U - TS = (0.514) \left(\frac{T}{T_c} \right)^{3/2} NkT.$$

To compute the pressure, we need to write this expression in terms of V , T , and N . Note from equation 7.126 that

$$T_c^{-3/2} = (2.612) \frac{V}{N} \left(\frac{2\pi mk}{h^2} \right)^{3/2},$$

so we have

$$F = (0.514)(2.612) \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} NkT = (1.343) \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} NkT,$$

which implies

$$P = \left(\frac{\partial F}{\partial V} \right)_{N,T} = (1.343) \left(\frac{2\pi mkT}{h^2} \right)^{3/2} kT.$$

Indeed, this expression is independent of volume (and of N). Apparently, once we are below the condensation temperature, reducing the volume (at fixed T) simply causes more atoms to join the condensate, while the pressure is due entirely to the atoms that are in excited states. (Notice from the preceding calculations that the energy and entropy, and hence the free energy and pressure, are computed entirely as integrals over the excited-state energies, completely neglecting the condensate.)

Problem 7.72. In a two-dimensional box with constant g , equation 7.122 becomes

$$N = g \int_0^\infty \frac{1}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon.$$

Suppose, now, that there is a range of temperatures at which μ is essentially equal to zero. Then the integral becomes

$$\int_0^\infty \frac{1}{e^{\epsilon/kT} - 1} d\epsilon,$$

which diverges at its lower limit. (To see this, expand the exponential in a Taylor series to obtain $1 + \epsilon/kT + \dots$. Cancel the 1's and you find that the integrand is proportional to $1/\epsilon$, which is not integrable.) In other words, if μ were zero, we would have an infinite number of particles in the low-lying excited states. With only a finite number of particles to go around, the integral must remain finite and therefore μ must be negative. This implies that, at any T that's high enough to allow converting the sum to an integral, the population of the ground state won't be much greater than the population of the low-lying excited states (because μ isn't that much closer to the former than to the latter). At very low temperatures, of course, all the particles will settle into the ground state, but this doesn't happen until kT becomes comparable to the spacing between the low-lying energy levels (when we can no longer approximate the sum as an integral). As the temperature of this system is lowered, the particles just gradually move into lower-energy states in a continuous way, with no abrupt transition. In order to get an abrupt transition, the integral for N must converge at its lower limit when $\mu = 0$; this happens only when $g(\epsilon)$ goes to zero as $\epsilon \rightarrow 0$.

Problem 7.73. (Bose-Einstein condensation in a harmonic trap.)

- a) For $n \gg 1$, the degeneracy of level n is approximately $n^2/2$. The spacing between levels is hf , so the density of states, which is the number of states per unit energy, would be $n^2/2hf = \epsilon^2/2(hf)^3$.

- b) To find the condensation temperature of this system, we just evaluate the integral (7.122) for the total number of particles, using our new density-of-states function and with ϵ set equal to zero:

$$N = \int_0^\infty g(\epsilon) \frac{1}{e^{\epsilon/kT} - 1} d\epsilon = \frac{1}{2(hf)^3} \int_0^\infty \frac{\epsilon^2}{e^{\epsilon/kT} - 1} d\epsilon = \frac{1}{2} \left(\frac{kT}{hf} \right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx.$$

The integral is the same one evaluated in Problem 7.44(a); it is approximately equal to 2.404. As in equation 7.125, this formula for N cannot possibly be true at more than one temperature. That temperature (above which ϵ becomes negative and below which the extra particles settle into the ground state) is the condensation temperature:

$$T_c = \frac{hf}{k} \left(\frac{N}{1.202} \right)^{1/3}.$$

- c) The potential energy of the “spring” is $\frac{1}{2}k_s a^2$, where k_s is the spring constant and a is the displacement from the center of the well. Since the frequency of oscillation is $f = \sqrt{k_s/m}/2\pi$, we can write $k_s = (2\pi f)^2 m$. At temperature T_c , the average particle energy is of order kT and so the amplitude of oscillation can be found by setting the spring potential energy equal to kT_c :

$$\frac{1}{2}(2\pi f)^2 m a^2 = kT_c \quad \text{or} \quad f = \frac{1}{2\pi a} \sqrt{\frac{2kT_c}{m}} \sim V^{-1/3} \sqrt{\frac{kT_c}{m}},$$

where V is the volume contained within the oscillation amplitude and I’ve dropped all small numerical factors in the last step. Using this expression to eliminate f in the formula for T_c , we obtain (again neglecting small numerical factors)

$$T_c \sim \frac{h}{k} V^{-1/3} \sqrt{\frac{kT_c}{m}} N^{1/3}, \quad \text{or} \quad (kT_c)^2 = \frac{h^2 k T_c}{m} \left(\frac{N}{V} \right)^{2/3}.$$

Canceling a factor of kT_c now gives a formula identical to equation 7.126, aside from the numerical factors.

Problem 7.74. (BEC in a harmonic trap: exact numerical treatment.)

- a) As stated in the previous problem, the degeneracy of level n is $(n+1)(n+2)/2$. Therefore equation 7.121 becomes

$$N = \sum_{n=0}^{\infty} \frac{(n+1)(n+2)}{2} \frac{1}{e^{(\epsilon - c)/kT} - 1},$$

where $\epsilon = nhf$. Substituting $\epsilon = chf$ and $T = thf$, the exponent in the denominator becomes simply $(n - c)/t$, so

$$N = \sum_{n=0}^{\infty} \frac{(n+1)(n+2)}{2} \frac{1}{e^{(n - c)/t} - 1}.$$

- b) To calculate this sum for any values of c and t , I first defined a *Mathematica* function to calculate the occupancy of any level as a function of n , c , and t . Then I defined a function to calculate the total number of particles:

```
occ[n_,c_,t_] := (1/2)(n+1)(n+2)/(Exp[(n-c)/t]-1)
theSum[c_,t_] := Sum[occ[n,c,t],{n,0,300}]
```

Notice that the sum is over all levels up to $n = 300$. To test this function for the numbers given, I gave the instruction `theSum[-10.536, 15]`, which returned the number 2000.01, close enough to the desired value of N . I tried changing the last decimal place in the value of c , and found that -10.537 gives 1999.86 while -10.535 gives 2000.15. I also checked that increasing the number of terms in the sum doesn't affect any of the digits shown in these results.

- c) To plot the occupancy as a function of n , I gave the instruction

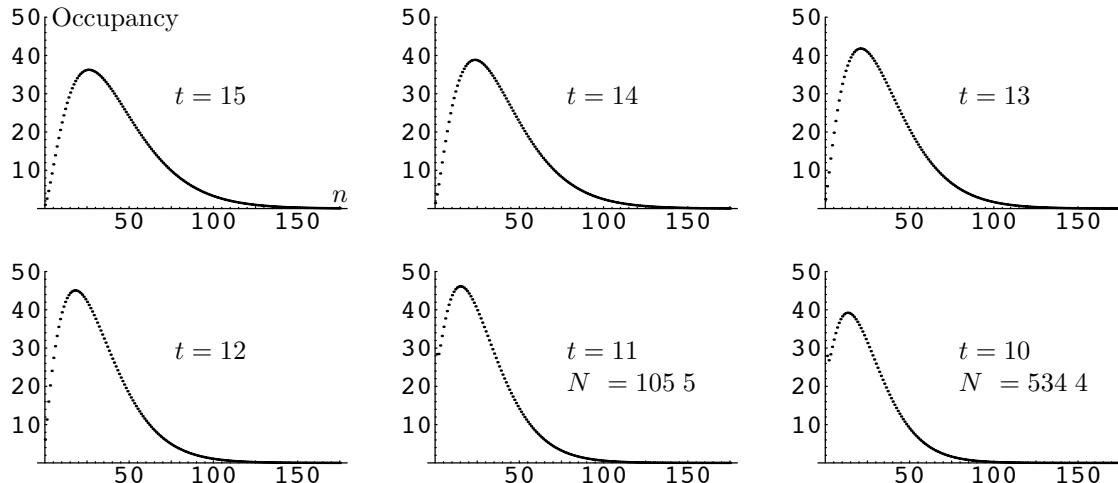
```
ListPlot[Table[{n,occ[n,-10.536,15]}, {n,0,175}]]
```

which produced the first graph shown below. Notice that the occupancy peaks at $n \approx 2t$, that is, at $\epsilon \approx 2kT$. At this temperature, the expected number of particles in the ground state is just under 1, as you can check by typing `occ[0,-10.536,15]`.

- d) As the temperature is reduced, we expect the chemical potential to increase (become less negative). It's not hard to find the correct value of c by trial and error, testing various values until `theSum` returns 2000 as desired. I did this and obtained $c = -7.3205$ at $t = 14$. Alternatively, you can let the computer do the trial-and-error by using the `FindRoot` instruction:

```
FindRoot[theSum[c,14]==2000,{c,-10,-5}]
```

This instruction returned the value $c = -7.32048$. (The numbers -10 and -5 tell the computer what values of c to try first. It's best if the actual value of c lies between these two numbers.) To plot the occupancy as a function of energy, I used another `ListPlot` command with the new values of t and c . At this temperature, the occupancy of the ground state is still quite small, slightly less than 1.5.



- e) Using the same methods as in part (d), I found the c values listed in the table below. (As the temperature drops and c approaches 0 from below, the starting values given to `FindRoot` require some fine-tuning; for example, at $t = 10$ I used -0.01 and -0.1.) At each temperature I've also listed the occupancy of the ground state. Occupancy graphs for $t = 13, 12, 11$, and 10 are shown above.

$t = kT/hf$	$c = \epsilon_0/hf$	N_0
15.0	10.536	0.98
14.0	7.3205	1.46
13.0	4.3898	2.49
12.0	1.8177	6.11
11.6	0.9328	11.9
11.4	0.5471	20.3
11.2	0.2478	44.7
11.0	0.1038	105.5
10.0	0.0187	534.4
9.0	0.0099	907.6
8.0	0.0066	1212

Down to a temperature of about 11.5, the behavior of this system is quite smooth and predictable, with the energy distribution of the particles moving gradually downward and the chemical potential moving gradually upward as t decreases. But at around $t = 11.3$, the chemical potential is close enough to zero that the population of the ground state becomes significantly larger than that of any other state; the occupancy plot acquires a “spike” at $n = 0$ which grows very rapidly as t is reduced further. At $t = 10$, more than a quarter of the particles are in the ground state, despite the fact that the rest of the particle distribution doesn’t look much different from before. At $t = 8$, more than half of the particles are in the ground state. The condensation temperature would be the temperature at which the population of the ground state becomes a significant fraction of the total number of particles. For a system of only 2000 particles, this transition temperature is not precisely defined, but if I had to pick a number, I’d put it at about $t = 11.3$. For comparison, Problem 7.73(b) predicts $kT_c/hf = (2000/1.202)^{1/3} = 11.85$. However, this formula was derived in the thermodynamic limit where N is very large. Although the transition temperature of our relatively small system is not precisely defined, the abrupt change in behavior as t is reduced from 12 to 11 is still quite dramatic, as you can see from the table and graphs.

Problem 7.75. (Corrections from quantum statistics to ideal gas behavior.)

- a) If we multiply and divide the Bose-Einstein distribution by $e^{-(\epsilon - \epsilon_0)/kT}$, we get

$$\bar{n}_{\text{BE}}(\epsilon) = \frac{e^{-(\epsilon - \epsilon_0)/kT}}{1 - e^{-(\epsilon - \epsilon_0)/kT}} = e^{-(\epsilon - \epsilon_0)/kT} [1 + e^{-(\epsilon - \epsilon_0)/kT} + \dots],$$

where in the second expression I’ve applied the binomial expansion to the denominator. In the high-temperature limit, the occupancies of all states should be much less than 1, so the exponential factor $e^{-(\epsilon - \epsilon_0)/kT}$ should be much less than 1, which implies that the expansion converges quickly.

- b) The total number of particles in all states must be N , so

$$N = \int_0^\infty g(\epsilon) \bar{n}_{\text{BE}}(\epsilon) d\epsilon \approx g_0 \int_0^\infty \sqrt{\epsilon} [e^{-(\epsilon - \mu)/kT} + e^{-2(\epsilon - \mu)/kT}] d\epsilon,$$

where g_0 is an abbreviation for the constants in equation 7.123, and I've truncated the series after the second term. The first term is

$$g_0 e^{-\mu/kT} \int_0^\infty \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon = 2g_0 e^{-\mu/kT} (kT)^{3/2} \int_0^\infty x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2} g_0 e^{-\mu/kT} (kT)^{3/2},$$

where I've changed variables to $x = \sqrt{\epsilon/kT}$ to obtain the same integral as in equations 6.49 and B.8. Similarly, the second term is

$$g_0 e^{2\mu/kT} \int_0^\infty \sqrt{\epsilon} e^{-2\epsilon/kT} d\epsilon = 2g_0 e^{2\mu/kT} (kT)^{3/2} \int_0^\infty x^2 e^{-2x^2} dx = \frac{\sqrt{\pi}}{2\sqrt{8}} g_0 e^{2\mu/kT} (kT)^{3/2}.$$

Therefore,

$$\begin{aligned} N &= \frac{\sqrt{\pi}}{2} g_0 e^{-\mu/kT} (kT)^{3/2} \left[1 + \frac{1}{\sqrt{8}} e^{-\mu/kT} \right] = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V e^{-\mu/kT} \left[1 + \frac{1}{\sqrt{8}} e^{-\mu/kT} \right] \\ &= \frac{V}{v_Q} e^{-\mu/kT} \left[1 + \frac{1}{\sqrt{8}} e^{-\mu/kT} \right], \end{aligned} \quad (1)$$

where I've substituted the constants in equation 7.123 for g_0 . Rearranging this equation gives

$$e^{-\mu/kT} = \frac{V}{N v_Q} \left[1 + \frac{1}{\sqrt{8}} e^{-\mu/kT} \right].$$

If we ignore the second term in the brackets, we obtain the “classical” result $\mu = kT \ln(V/N v_Q)$. The second term gives the first quantum correction to this result, which we assume to be small. Since it is already small, though, we can substitute the classical value of μ in this term to obtain

$$e^{-\mu/kT} = \frac{V}{N v_Q} \left[1 + \frac{1}{\sqrt{8}} \frac{N v_Q}{V} \right], \quad \text{or} \quad e^{-\mu/kT} = \frac{N v_Q}{V} \left[1 - \frac{1}{\sqrt{8}} \frac{N v_Q}{V} \right].$$

Solving for μ then gives

$$\mu = kT \ln \left[\frac{V}{N v_Q} \left(1 + \frac{N v_Q}{\sqrt{8} V} \right) \right] \approx kT \ln \left(\frac{V}{N v_Q} \right) - \frac{kT N v_Q}{\sqrt{8} V},$$

where I've expanded the logarithm of $1 + N v_Q / \sqrt{8} V$ in the last expression. Note that the first term is the familiar result for a classical ideal gas.

- c) In Problem 5.23(c) we showed that $\Phi = PV$, while in Problem 7.7 we showed that $\Phi = kT \ln Z$. Combining these results gives $P = (kT/V) \ln Z$. For a system of noninteracting particles in a box, we can treat each wave mode (or single-particle

state) as an independent subsystem and factor the grand partition function as we did for the ordinary partition function in equation 6.69:

$$\mathcal{Z}_{\text{total}} = \mathcal{Z}_1 \mathcal{Z}_2 \mathcal{Z}_3 = \prod_n \mathcal{Z}_n,$$

where n labels the various wave modes. Taking the logarithm of both sides of this equation gives

$$\ln \mathcal{Z}_{\text{total}} = \ln \mathcal{Z}_1 + \ln \mathcal{Z}_2 + \ln \mathcal{Z}_3 + \sum_n \ln \mathcal{Z}_n.$$

- d) The sum over n is really a triple sum over n_x , n_y , and n_z . Converting this triple sum into an integral in spherical coordinates over the positive octant of n -space, we obtain $\pi/2$ for the angular integrals which leaves

$$\ln \mathcal{Z} = \frac{\pi}{2} \int_0^\infty n^2 \ln \mathcal{Z}_n dn.$$

Meanwhile, using equation 7.24 for the grand partition function of a single mode,

$$\ln \mathcal{Z}_n = \ln \left(\frac{1}{1 - e^{-(\epsilon - \mu)/kT}} \right) = -\ln(1 - e^{-(\epsilon - \mu)/kT}).$$

Working again in the approximation where this exponential term is much less than 1, we can use the second-order Taylor expansion of the logarithm, $\ln(1 + x) \approx x - \frac{1}{2}x^2$, to obtain

$$\ln \mathcal{Z}_n = e^{-(\epsilon - \mu)/kT} + \frac{1}{2}e^{-2(\epsilon - \mu)/kT} + \dots$$

Therefore the logarithm of the total grand partition function is approximately

$$\begin{aligned} \ln \mathcal{Z} &= \frac{\pi}{2} \int_0^\infty n^2 \left[e^{-(\epsilon - \mu)/kT} + \frac{1}{2}e^{-2(\epsilon - \mu)/kT} \right] \\ &= \frac{\pi}{2} e^{-\mu/kT} \left[\int_0^\infty n^2 e^{-\epsilon/kT} dn + \frac{1}{2} e^{-\mu/kT} \int_0^\infty n^2 e^{-2\epsilon/kT} dn \right]. \end{aligned}$$

Now change variables again to $x = \sqrt{\epsilon/kT} = n\sqrt{h^2/8mL^2kT}$:

$$\begin{aligned} \ln \mathcal{Z} &= \frac{\pi}{2} \left(\frac{8mL^2kT}{h^2} \right)^{3/2} e^{-\mu/kT} \left[\int_0^\infty x^2 e^{-x^2} dx + \frac{1}{2} e^{-\mu/kT} \int_0^\infty x^2 e^{-2x^2} dx \right] \\ &= \frac{\pi}{2} \left(\frac{8mL^2kT}{h^2} \right)^{3/2} e^{-\mu/kT} \left[\frac{\sqrt{\pi}}{4} + \frac{1}{2} e^{-\mu/kT} \frac{\sqrt{\pi}}{4} \frac{1}{\sqrt{8}} \right] \\ &= \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V e^{-\mu/kT} \left[1 + \frac{1}{2\sqrt{8}} e^{-\mu/kT} \right] = \frac{V}{v_Q} e^{-\mu/kT} \left[1 + \frac{1}{2\sqrt{8}} e^{-\mu/kT} \right]. \end{aligned}$$

For the first factor of $e^{-\mu/kT}$, we can substitute the result of part (b). The second term in brackets, however, is already small compared to 1 so there we can just plug in the

lowest-order result, $e^{-kT} = Nv_Q/V$. Multiplying everything out and keeping only the two largest terms, we obtain

$$\ln \mathcal{Z} = \frac{V}{v_Q} \frac{Nv_Q}{V} \left[1 - \frac{1}{\sqrt{8}} \frac{Nv_Q}{V} \right] \left[1 + \frac{1}{2\sqrt{8}} \frac{Nv_Q}{V} \right] = N \left[1 - \frac{Nv_Q}{4\sqrt{2}V} \right].$$

To get the pressure, we just multiply by kT/V :

$$P = \frac{NkT}{V} \left[1 - \frac{Nv_Q}{4\sqrt{2}V} \right].$$

- e) Comparison to the second-order virial expansion,

$$PV = NkT \left(1 + \frac{B(T)}{(V/n)} \right),$$

gives for the second virial coefficient

$$B(T) = \frac{N_A v_Q}{4\sqrt{2}} = \frac{N_A}{4\sqrt{2}} \left(\frac{\hbar^2}{2\pi m k T} \right)^{3/2}.$$

For helium-4 atoms, this evaluates to

$$\begin{aligned} B(T) &= \frac{6.02 \times 10^{23} \text{ mol}^{-1}}{4\sqrt{2}} \left(\frac{(6.63 \times 10^{-34} \text{ J s})^2}{2\pi(4)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} \right)^{3/2} T^{-3/2} \\ &= (7.07 \times 10^{-5} \text{ m}^3 \text{ K}^{3/2}/\text{mol}) T^{-3/2} = (70.7 \text{ cm}^3 \text{ K}^{3/2}/\text{mol}) T^{-3/2}. \end{aligned}$$

So at $T = 1 \text{ K}$, we predict $B(T) = 70.7 \text{ cm}^3/\text{mol}$, while at 2 K , we predict $B(T) = 25.0 \text{ cm}^3/\text{mol}$. Experimental values of $B(T)$ for helium are given in Figure 8.2. The lowest-temperature point is for 2 K , with $B(T) = 174 \text{ cm}^3/\text{mol}$. Thus, quantum statistics makes a measurable contribution to $B(T)$ for helium at low temperatures, although it is not the dominant effect, as discussed in Section 8.1. A plot of the predicted contribution to $B(T)$ is shown below.

- f) For spin-1/2 fermions, we must make two modifications to the preceding calculation. First, we must change just about every minus sign to plus and vice-versa; second, we must take the two possible spin orientations into account. Starting with the distribution function in part (a), the $-$ in the denominator becomes $+$, so the relative sign between the first two terms in the expansion becomes $-$. This relative sign change carries all the way through part (b). Meanwhile, the extra factor of 2 shows up in the density of states, so equation (1) becomes

$$N = \frac{2V}{v_Q} e^{-kT} \left[1 - \frac{1}{\sqrt{8}} e^{-kT} \right].$$

The remaining equations of part (b) are similarly modified; in particular,

$$e^{-kT} = \frac{Nv_Q}{2V} \left[1 + \frac{1}{\sqrt{8}} \frac{Nv_Q}{2V} \right].$$

Part (c) is the same as before. In part (d), the sum over n picks up an extra factor of 2, which carries through to the integral for $\ln \mathcal{Z}$. Furthermore, the single-mode grand partition function is now $\mathcal{Z}_n = 1 + e^{(\epsilon)/kT}$, by equation 7.21. This change converts the relative + sign in the next several lines to a -. Eventually we obtain

$$\ln \mathcal{Z} = \frac{2V}{v_Q} e^{-\epsilon/kT} \left[1 - \frac{1}{2\sqrt{8}} e^{-\epsilon/kT} \right].$$

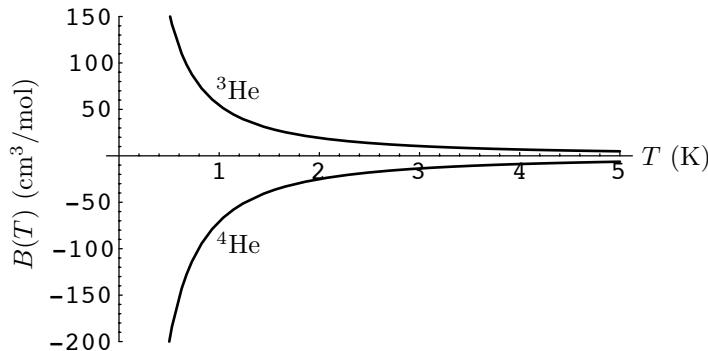
The overall factor of 2 cancels when we plug in our formula for $e^{-\epsilon/kT}$, but we still get an extra factor of 1/2 in the correction term:

$$\ln \mathcal{Z} = N \left[1 + \frac{1}{\sqrt{8}} \frac{Nv_Q}{2V} \right] \left[1 - \frac{1}{2\sqrt{8}} \frac{Nv_Q}{2V} \right] = N \left[1 + \frac{1}{2\sqrt{8}} \frac{Nv_Q}{2V} \right].$$

Thus, the correction term is only half as large as in the spin-0 case (for a given m and T), and is positive instead of negative. This also goes for the correction to the pressure, and for the second virial coefficient,

$$B(T) = +\frac{N_A v_Q}{8\sqrt{2}} = +\frac{N_A}{8\sqrt{2}} \left(\frac{\hbar^2}{2\pi m k T} \right)^{3/2}.$$

Since a helium-3 atom has 3/4 the mass of a helium-4 atom, we predict that the magnitude of the virial coefficient for helium-3 should be $(1/2)(4/3)^{3/2} = 0.77$ times that for helium-4, for instance, 54.4 cm³/mol at 1 K. The plot below shows the predictions for both isotopes as a function of temperature.



8

Systems of Interacting Particles

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Problem 8.1. The formulas for the first three diagrams are written in equations 8.17, 8.18, and 8.19, and are explained in the text. The next diagram is

$$\text{Diagram } \begin{array}{c} \bullet \\ \backslash \quad / \\ \bullet \quad \bullet \end{array} = \frac{1}{3!} \frac{N(N-1)(N-2)}{V^3} \int d^3r_1 d^3r_2 d^3r_3 f_{12}f_{23}f_{31}.$$

This diagram has a symmetry factor of $3! = 6$, which is the number of equivalent ways of numbering the three dots. This diagram comes from terms in equation 8.13 in which there are three f -functions involving only three molecules. The number of such triplets is $N(N-1)(N-2)/3!$, with the $3!$ necessary to avoid counting the same triplet more than once. The next diagram is

$$\text{Diagram } \begin{array}{c} \bullet & \bullet & \bullet \\ | & | & | \\ \bullet & & \bullet \end{array} = \frac{1}{3!} \frac{N(N-1)(N-2)(N-3)}{V^4} \int d^3r_1 d^3r_2 d^3r_3 d^3r_4 f_{12}f_{13}f_{14}.$$

Again the symmetry factor is $3!$, the number of ways of interchanging the three outer molecules with each other. Here there are again three f -functions, all with a single molecule in common. There are N ways of choosing this “central” molecule, and then $(N-1)(N-2)(N-3)/3!$ distinct ways of choosing the other three. The next diagram is

$$\text{Diagram } \begin{array}{c} \bullet & \bullet & \bullet \\ | & | & | \\ \bullet & & \bullet \end{array} = \frac{1}{2} \frac{N(N-1)(N-2)(N-3)}{V^4} \int d^3r_1 d^3r_2 d^3r_3 d^3r_4 f_{12}f_{23}f_{34}.$$

This time the symmetry factor is 2, because the order of the dots could be reversed without changing the diagram. The number of ways of choosing four molecules to interact in this way is $N(N-1)(N-2)(N-3)/2$; the factor of 2 avoids over-counting because the same sequence of molecules could be chosen in the opposite order. The next diagram is

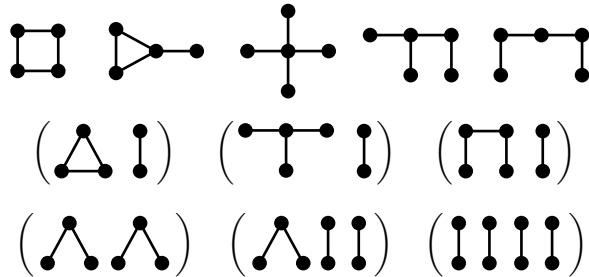
$$\text{Diagram } \left(\begin{array}{c} \bullet & \bullet \\ | & | \\ \bullet & \bullet \end{array} \right) = \frac{1}{2} \frac{1}{2} \frac{N(N-1)(N-2)(N-3)(N-4)}{V^5} \int d^3r_1 d^3r_2 d^3r_3 d^3r_4 d^3r_5 f_{12}f_{34}f_{45}.$$

This diagram has a symmetry factor of 4, simply the product of the symmetry factors of the two subdiagrams; in choosing five molecules to interact in this way, we have $N(N-1)/2$ choices for the first pair, and then $(N-2)(N-3)(N-4)/2$ remaining choices for the other three. Finally, the last diagram is

$$\text{Diagram } \left(\begin{array}{c} \bullet & \bullet & \bullet \\ | & | & | \\ \bullet & \bullet & \bullet \end{array} \right) = \frac{1}{3!} \frac{1}{2^3} \frac{N(N-1)(N-2)(N-3)(N-4)(N-5)}{V^6} \int d^3r_1 \dots d^3r_6 f_{12}f_{34}f_{56}.$$

The factor of $3!$ comes from the ways of interchanging the subdiagrams with each other, while the factor of 2^3 comes from the number of ways of reversing the individual sub-diagrams. Alternatively, we can count the number of ways of choosing six molecules to interact in disjoint pairs: $N(N - 1)/2$ for the first pair, $(N - 2)(N - 3)/2$ for the second pair, $(N - 4)(N - 5)/2$ for the third pair, and then divide by $3!$ because any of the three pairs could have been chosen first, and either of the remaining two could have been chosen second.

Problem 8.2. Here are all the diagrams corresponding to four factors of f_{ij} :



Problem 8.3. Expanding the exponential in a third-order Taylor series, we have

$$\begin{aligned} \exp\left(\frac{1}{2}\left(\frac{\bullet}{\bullet} + \frac{\bullet}{\bullet}\Delta\right)\right) &= 1 + \left(\frac{\bullet}{\bullet} + \frac{\bullet}{\bullet}\Delta\right) + \frac{1}{2}\left(\frac{\bullet}{\bullet} + \frac{\bullet}{\bullet}\Delta\right)^2 + \frac{1}{3!}\left(\frac{\bullet}{\bullet} + \frac{\bullet}{\bullet}\Delta\right)^3 \\ &= 1 + \frac{\bullet}{\bullet} + \frac{\bullet}{\bullet}\Delta + \frac{1}{2}\left(\frac{\bullet}{\bullet}\right)^2 + \left(\frac{\bullet}{\bullet}\Delta\right) + \frac{1}{2}\left(\Delta\right)^2 \\ &\quad + \frac{1}{3!}\left(\frac{\bullet}{\bullet}\right)^3 + \frac{1}{2}\left[\left(\frac{\bullet}{\bullet}\right)^2 \Delta\right] + \frac{1}{2}\left[\frac{\bullet}{\bullet} (\Delta)^2\right] + \frac{1}{3!}(\Delta)^3 \end{aligned}$$

Notice that wherever a diagram appears squared, there is an accompanying factor of $1/2$. If we approximate $N = (N - 1) = (N - 2)$, then $1/2$ times the square of a diagram is the same thing as a disconnected diagram in which the original diagram is duplicated:

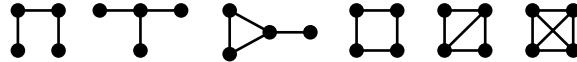
$$\frac{1}{2}\left(\frac{\bullet}{\bullet}\right)^2 \approx \left(\frac{\bullet}{\bullet} \frac{\bullet}{\bullet}\right); \quad \frac{1}{2}(\Delta)^2 \approx \left(\Delta \Delta\right).$$

In each case, the factor of $1/2$ is implicit in the symmetry factor of the disconnected diagram. Similarly,

$$\frac{1}{3!}\left(\frac{\bullet}{\bullet}\right)^3 \approx \left(\frac{\bullet}{\bullet} \frac{\bullet}{\bullet} \frac{\bullet}{\bullet}\right); \quad \frac{1}{3!}(\Delta)^3 \approx \left(\Delta \Delta \Delta\right).$$

With these approximations, therefore, the numerical factors in our formula completely disappear, leaving a simple sum of all possible diagrams, connected and disconnected, that can be constructed from up to three of the basic two-dot and triangle diagrams.

Problem 8.4. Here are all the connected diagrams with four dots:



(If you think you've found another diagram, I promise that it is equivalent to one of these six.) The first three diagrams can be disconnected by removal of a single dot, so they do not appear in equation 8.23.

Problem 8.5. If we define $\vec{r}_a = \vec{r}_2 - \vec{r}_1$ and $\vec{r}_b = \vec{r}_2 - \vec{r}_3$, then

$$\begin{aligned} \text{Diagram} &= \frac{1}{2} \frac{N^3}{V^3} \int d^3 r_1 d^3 r_2 d^3 r_3 f_{12} f_{23} = \frac{1}{2} \frac{N^3}{V^3} \int d^3 r_2 \left(\int d^3 r_a f(r_a) \right) \left(\int d^3 r_b f(r_b) \right) \\ &= \frac{1}{2} \frac{N^3}{V^2} \left(\int d^3 r f(r) \right)^2, \end{aligned}$$

where in the last line I've used $\int d^3 r_2 = V$ and renamed r_a and r_b to simply r . Similarly, if we define $\vec{r}_a = \vec{r}_2 - \vec{r}_1$, $\vec{r}_b = \vec{r}_3 - \vec{r}_1$, and $\vec{r}_c = \vec{r}_4 - \vec{r}_1$, then

$$\begin{aligned} \text{Diagram} &= \frac{1}{3!} \frac{N^4}{V^4} \int d^3 r_1 d^3 r_2 d^3 r_3 d^3 r_4 f_{12} f_{13} f_{14} \\ &= \frac{1}{3!} \frac{N^4}{V^4} \int d^3 r_1 \left(\int d^3 r_a f(r_a) \right) \left(\int d^3 r_b f(r_b) \right) \left(\int d^3 r_c f(r_c) \right) \\ &= \frac{1}{3!} \frac{N^4}{V^3} \left(\int d^3 r f(r) \right)^3. \end{aligned}$$

Finally, if we define $\vec{r}_a = \vec{r}_1 - \vec{r}_2$, $\vec{r}_b = \vec{r}_2 - \vec{r}_3$, and $\vec{r}_c = \vec{r}_3 - \vec{r}_4$, then

$$\begin{aligned} \text{Diagram} &= \frac{1}{2} \frac{N^4}{V^4} \int d^3 r_1 d^3 r_2 d^3 r_3 d^3 r_4 f_{12} f_{23} f_{34} \\ &= \frac{1}{2} \frac{N^4}{V^4} \int d^3 r_2 d^3 r_3 f_{23} \left(\int d^3 r_a f(r_a) \right) \left(\int d^3 r_c f(r_c) \right) \\ &= \frac{1}{2} \frac{N^4}{V^4} \left(\int d^3 r f(r) \right)^2 \int d^3 r_2 \left(\int d^3 r_b f(r_b) \right) \\ &= \frac{1}{2} \frac{N^4}{V^3} \left(\int d^3 r f(r) \right)^3. \end{aligned}$$

Notice that in this case I've worked my way in from each end of the diagram, integrating over the relative position of each molecule that dangles by a single line. By this method, any diagram that doesn't contain any closed loops (such as triangles or squares) can be written in terms of the same basic integral as in the two-dot diagram.

Problem 8.6. Let v represent the volume of a molecule, so that a three-dimensional integral over a product of f 's evaluates to some number of order v . Then the basic two-dot diagram has one integral that gives v and another that gives V , so we can estimate

$$\text{Diagram} \sim \frac{N^2}{V^2} v V = \frac{N^2 v}{V}.$$

Similarly, using the results of the previous problem,

$$\begin{array}{c} \text{Diagram} \\ \bullet \quad \bullet \end{array} \sim \frac{N^3 v^2}{V^2}; \quad \begin{array}{c} \text{Diagram} \\ \bullet \quad \bullet \quad \bullet \\ | \quad | \quad | \end{array} \sim \frac{N^4 v^3}{V^3}; \quad \begin{array}{c} \text{Diagram} \\ \bullet \quad \bullet \quad \bullet \\ | \quad | \quad | \end{array} \sim \frac{N^4 v^3}{V^3}.$$

The disconnected diagrams, aside from their symmetry factors, are basically products of connected diagrams, so

$$\left(\begin{array}{c} \bullet \quad \bullet \\ | \quad | \end{array} \right) \sim \frac{N^4 v^2}{V^2}; \quad \left(\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ | \quad | \quad | \end{array} \right) \sim \frac{N^5 v^3}{V^3}; \quad \left(\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ | \quad | \quad | \end{array} \right) \sim \frac{N^6 v^3}{V^3}.$$

The only remaining diagram in equation 8.20 is the triangle. If we imagine defining relative coordinates $\vec{r}_a = \vec{r}_1 - \vec{r}_2$ and $\vec{r}_b = \vec{r}_1 - \vec{r}_3$, then the arguments of the f -functions can be written as r_a , r_b , and $|\vec{r}_a - \vec{r}_b|$. A change of variables then leaves one overall integral that gives a factor of V , while the remaining two integrals, of a product of three f -functions, must evaluate to something of order v^2 . Therefore,

$$\begin{array}{c} \text{Diagram} \\ \triangle \end{array} \sim \frac{N^3 v^2}{V^2}.$$

Looking over these estimates, we should note that while V/v is greater than N in a low-density gas, it is normally greater by only a few orders of magnitude (perhaps a factor of a thousand). Thus, the basic two-dot diagram might be of order $N/1000$, which is a large number. Connected diagrams with three or more dots are suppressed by more factors of V/Nv , so at least they're smaller than the two-dot diagram. But the disconnected diagrams are much larger, since they have a greater excess of powers of N over powers of v/V . For example, the first disconnected diagram would typically be of order $(N/1000)^2$, while the third disconnected diagram would be of order $(N/1000)^3$. Because these diagrams are growing larger and larger, the series isn't going to converge until the symmetry factors also become quite large. Fortunately, exponentiating the series saves us from having to evaluate all the disconnected diagrams.

Problem 8.7. Let's carefully write out the quadratic term in the series 8.22:

$$\begin{aligned} \frac{1}{2} \left(\begin{array}{c} \bullet \\ | \end{array} \right)^2 &= \frac{1}{2} \left(\frac{1}{2} \frac{N(N-1)}{V^2} \int d^3 r_1 d^3 r_2 f_{12} \right)^2 = \frac{1}{8} \frac{N^2(N-1)^2}{V^2} \left(\int d^3 r f(r) \right)^2 \\ &= \left[\frac{1}{8} N^4 - \frac{1}{4} N^3 + \frac{1}{8} N^2 \right] \frac{v^2}{V^2}, \end{aligned}$$

where v is defined to equal $\int d^3 r f(r)$, a number that's on the order of the volume of a molecule. On the other hand, the diagrams in equations 8.18 and 8.19 are

$$\begin{aligned} \left(\begin{array}{c} \bullet \quad \bullet \\ | \quad | \end{array} \right) &= \frac{1}{8} \frac{N(N-1)(N-2)(N-3)}{V^4} \int d^3 r_1 d^3 r_2 d^3 r_3 d^3 r_4 f_{12} f_{34} \\ &= \frac{1}{8} \frac{N^4 - 6N^3 + 11N^2 - 6N}{V^2} \left(\int d^3 r f(r) \right)^2 \\ &= \left[\frac{1}{8} N^4 - \frac{3}{4} N^3 + \frac{11}{8} N^2 - \frac{3}{4} N \right] \frac{v^2}{V^2} \end{aligned}$$

and

$$\begin{aligned} \text{Diagram} &= \frac{1}{2} \frac{N(N-1)(N-2)}{V^3} \int d^3r_1 d^3r_2 d^3r_3 f_{12}f_{23} \\ &= \frac{1}{2} \frac{N^3 - 3N^2 + 2N}{V^2} \left(\int d^3r f(r) \right)^2 \\ &= \left[\frac{1}{2}N^3 - \frac{3}{2}N^2 + N \right] \frac{v^2}{V^2}, \end{aligned}$$

where I've written everything in terms of the same basic integral as in Problem 8.5. The sum of these two diagrams is therefore

$$\left(\text{Diagram} \right) + \text{Diagram} = \left[\frac{1}{8}N^4 - \frac{1}{4}N^3 - \frac{1}{8}N^2 + \frac{1}{4}N \right] \frac{v^2}{V^2}.$$

Comparing this expression to the first one above, we find that

$$\frac{1}{2} \left(\text{Diagram} \right)^2 = \left(\text{Diagram} \right) + \text{Diagram} + \left[\frac{1}{4}N^2 - \frac{1}{4}N \right] \frac{v^2}{V^2}.$$

Now recall that for a low-density gas, V/v must be greater than N by at least a couple of orders of magnitude. This implies that the terms proportional to N^4 and N^3 in the preceding expressions are large, but the leftover terms proportional to N^2 and N are actually much less than 1, when we include the factor of $(v/V)^2$. These terms therefore contribute negligibly to the partition function. Alternatively, when we take the logarithm of the partition function to get the free energy, then differentiate with respect to V to get the pressure, the leading terms will give contributions that are intensive as desired (proportional to powers of N/V), but the leftover terms will have more powers of V in the denominator than powers of N in the numerator, so they will vanish in the thermodynamic limit.

Problem 8.8. Each diagram in equation 8.23, when evaluated, will give one overall factor of V , times an integral that is of order v^{n-1} , where v is the volume of a molecule and n is the number of dots in the diagram. Thus, a diagram with n dots is of order $N^n(v/V)^{n-1}$. When such a diagram is differentiated to obtain a contribution to the pressure (see equation 8.27), it then picks up another factor of V in the denominator. To obtain the corresponding term in the virial expansion, we factor out N/V , which gives an expression of order $(Nv/V)^{n-1}$. This expression has the form of the n th term in the virial expansion (equation 8.33), since it is a density-independent quantity times $(N/V)^{n-1}$. In particular, the third virial coefficient, $C(T)$, is determined entirely by the triangle diagram:

$$\text{Diagram} = \frac{1}{3!} \frac{N^3}{V^3} \int d^3r_1 d^3r_2 d^3r_3 f_{12}f_{23}f_{31}.$$

Changing variables to $\vec{r}_a = \vec{r}_2 - \vec{r}_1$ and $\vec{r}_b = \vec{r}_2 - \vec{r}_3$, this becomes

$$\begin{aligned} \text{Diagram} &= \frac{1}{6} \frac{N^3}{V^3} \int d^3r_1 \left(\int d^3r_a d^3r_b f(r_a) f(r_b) f(|\vec{r}_a - \vec{r}_b|) \right) \\ &= \frac{1}{6} \frac{N^3}{V^2} \int d^3r_a d^3r_b f(r_a) f(r_b) f(|\vec{r}_a - \vec{r}_b|). \end{aligned}$$

To obtain the contribution of this diagram to the pressure, we differentiate with respect to V and multiply by kT :

$$\frac{1}{3} \frac{N^3 kT}{V^3} \int d^3 r_a d^3 r_b f(r_a) f(r_b) f(|\vec{r}_a - \vec{r}_b|).$$

Then, to obtain the third virial coefficient, we factor out $(NkT/V)(N/V)^2$:

$$C(T) = \frac{1}{3} \int d^3 r_a d^3 r_b f(r_a) f(r_b) f(|\vec{r}_a - \vec{r}_b|).$$

Carrying out this integral would be very hard, because the quantity $|\vec{r}_a - \vec{r}_b|$ is complicated no matter what coordinate system we use. Even for a very simple f -function (as in Problem 8.11), the integrand will be such a horrible function of the integration variables that there's no way to disentangle all the integrals and carry them out one by one. Instead, we would have to resort to a multidimensional numerical integration procedure such as Monte Carlo integration.

Problem 8.9. To find the minimum of the Lennard-Jones potential, we set its derivative equal to zero:

$$0 = \frac{d}{dr} u(r) = u_0 \left[-12r_0^{12}r^{-13} - 2(-6)r_0^6r^{-7} \right] = 12u_0 \left(\frac{r_0^6}{r^7} \right) \left[\left(\frac{r_0}{r} \right)^6 + 1 \right].$$

The solution is $r = r_0$. At this point, the value of the Lennard-Jones function is

$$u(r_0) = u_0[1 - 2] = -u_0.$$

The point where $u(r) = 0$ is at

$$\left(\frac{r_0}{r} \right)^{12} = 2 \left(\frac{r_0}{r} \right)^6, \quad \text{or} \quad \left(\frac{r_0}{r} \right)^6 = 2,$$

which implies $r = r_0/2^{1/6} \approx (0.89)r_0$.

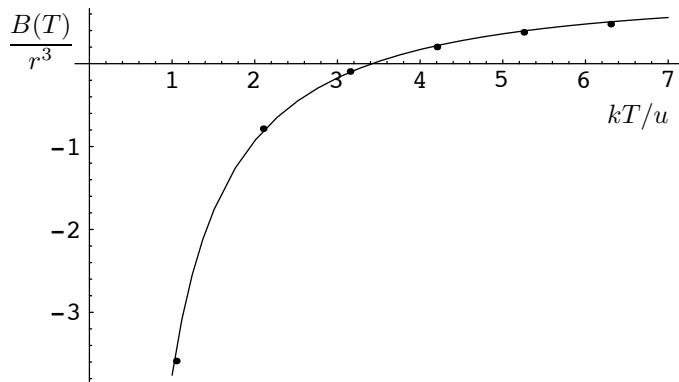
Problem 8.10. To calculate and plot the Lennard-Jones prediction for $B(T)$, I used the following *Mathematica* instructions:

```
u[r_] := (1/r)^12 - 2*(1/r)^6
b[t_] := -2*Pi*NIntegrate[r^2*(Exp[-u[r]/t]-1),{r,0,Infinity}]
LJplot = Plot[b[t],{t,1,7}]
```

The first instruction defines a function $u(r)$, where u is measured in units of u_0 and r is measured in units of r_0 . The second function then defines $B(T)$ in terms of a numerical integral; the dimensionless temperature variable t is equal to kT/u_0 . Note also that since r is measured in units of r_0 , the value of this function is actually $B(T)/r_0^3$. The last line produces the plot itself, over the desired range of temperatures. To plot the data for nitrogen, I used the following instructions:

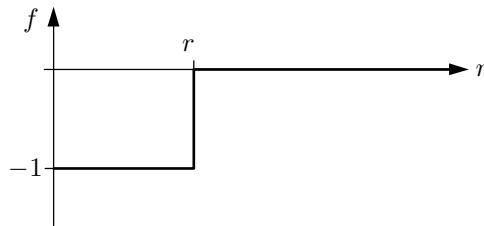
```
r0 = 4.2; u0 = 0.0082;
tList = {100,200,300,400,500,600}*(8.617*10^-5)/u0;
bList = {-160,-35,-4.2,9.0,16.9,21.3}/(6.02*10^23)/(r0*10^-8)^3;
N2plot = ListPlot[Transpose[{tList,bList}]]
```

The first line defines the constants r_0 and u_0 , in units of ångstroms and electron-volts. (I started with the values 4.0 and 0.01, then adjusted the values by trial and error to obtain a good fit to the theoretical prediction.) The second line defines a list of t values, multiplying the kelvin temperatures by k/u_0 to convert them to the dimensionless quantity t . The third line defines a list of values of B , similarly scaled by a factor of r_0^3 for comparison to the theoretical plot. Note also the factor of 10^{-8} to convert ångstroms to centimeters, and the factor of Avogadro's number to convert the virial coefficient per mole to the virial coefficient per molecule. The fourth line combines the two lists of numbers and produces a plot of the data points. Finally, to show the theoretical curve and the data on the same graph, I gave the instruction `Show[LJplot,N2plot]`, which produced the following:



Although the fit isn't perfect, it's probably within the experimental error of the data points, and it's definitely much better than the fit to the van der Waals model in Problem 1.17.

Problem 8.11. The Mayer f -function is defined as $e^{-u(r)/kT} - 1$. For a gas of hard spheres, this would be zero when $r > r_0$ (and $u(r) = 0$) and -1 when $r < r_0$ (and $u(r) = \infty$). Here is a plot:



The second virial coefficient for this gas would therefore be

$$B(T) = -2\pi \int_0^\infty r^2 f(r) dr = +2\pi \int_0^{r_0} r^2 dr = \frac{2\pi r_0^3}{3}.$$

This is just a constant, independent of temperature. Therefore, at low densities, the pressure of the gas should be greater than NkT/V by a fraction equal to $NB/V = N(2\pi r_0^3/3)/V$. Although the precise numerical factor is hard for me to interpret, this result is sensible because the fractional increase in pressure is of the same order as the fraction of the total volume occupied by the molecules themselves.

Problem 8.12. Taking $u(r)$ to be infinite for $r < r_0$, the integral (8.36) for $B(T)$ conveniently splits into two pieces:

$$B(T) = 2\pi \int_0^\infty r^2(e^{-\beta u(r)} - 1) dr = 2\pi \int_0^{r_0} r^2(e^{-\beta u(r)} - 1) dr + 2\pi \int_{r_0}^\infty r^2(e^{-\beta u(r)} - 1) dr.$$

In the first piece, $e^{-\beta u(r)} = e^{-\infty} = 0$, so the integral evaluates to $-r_0^3/3$ as in Problem 8.11. In the second piece, we are to assume that $|u(r)|$ is no greater than u_0 and that $kT \gg u_0$, so we can expand $e^{-\beta u(r)} \approx 1 - \beta u(r)$. Canceling the 1's, we obtain

$$B(T) \approx \frac{2\pi r_0^3}{3} + 2\pi \int_{r_0}^\infty r^2 \beta u(r) dr.$$

The factor of $\beta = 1/kT$ can be pulled outside the integral, so this expression has the form

$$B(T) = b - \frac{a}{kT},$$

where

$$b = \frac{2\pi r_0^3}{3} \quad \text{and} \quad a = 2\pi \int_{r_0}^\infty r^2 u(r) dr.$$

This result agrees with the prediction of the van der Waals model, Problem 1.17(c), although here we see that this form for $B(T)$ should be accurate only at relatively high temperatures, and only if the molecules have an impenetrable “hard core” where $u = \infty$. The prediction for b is of the order of the volume of a molecule as expected. The prediction for a is of order $u_0 r_0^3$, assuming that $u(r)$ becomes negligible beyond a distance of order r_0 ; this is what we would expect from the discussion on page 180.

Problem 8.13. The average energy of an interacting gas can be computed from the formula derived in Problem 6.16:

$$U = \frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \ln Z_{\text{ideal}} - \frac{\partial}{\partial \beta} \ln Z_c.$$

The first term is the same as for an ideal gas, so it evaluates to $\frac{3}{2}NkT$ as in Section 6.7. The correction term can be written in terms of diagrams using equation 8.23:

$$\Delta U = \frac{\partial}{\partial \beta} \left(\text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \dots \right).$$

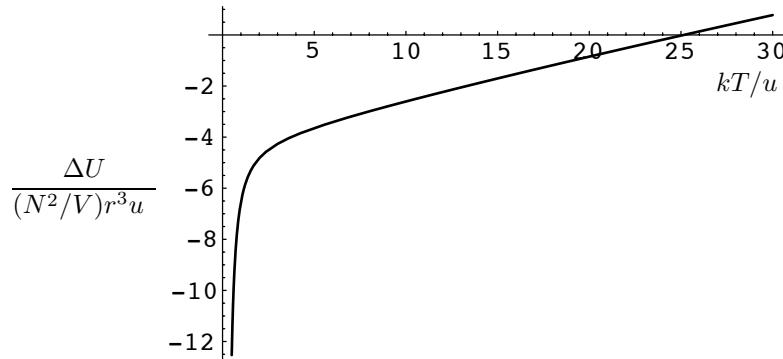
If we keep only the first diagram, and evaluate it explicitly as in equation 8.31, then

$$\begin{aligned} \Delta U &= \frac{\partial}{\partial \beta} \left(\frac{1}{2} \frac{N^2}{V} \int d^3 r f(r) \right) = \frac{1}{2} \frac{N^2}{V} (4\pi) \int_0^\infty r^2 \frac{\partial}{\partial \beta} (e^{-\beta u(r)} - 1) dr \\ &= 2\pi \frac{N^2}{V} \int_0^\infty r^2 u(r) e^{-\beta u(r)} dr. \end{aligned}$$

To plot this correction term for the case of a Lennard-Jones interaction, I used the following *Mathematica* instructions:

```
u[r_] := (1/r)^12 - 2*(1/r)^6
deltaU[t_] := 2*Pi*NIntegrate[r^2*u[r]*Exp[-u[r]/t], {r, 0, Infinity}]
Plot[deltaU[t], {t, .5, 30}]
```

Here I'm using dimensionless variables: $r = r/r_0$ and $u = u/u_0$. The function `deltaU` is actually $\Delta U/(N^2/V)r_0^3u_0$, and t is actually kT/u_0 . Here's the plot produced:



The correction to the energy is generally negative, due to the attractive interaction between molecules. However, at very high temperatures, the correction becomes positive because of the large positive interaction energy during hard collisions. The correction to the heat capacity (at constant volume) is proportional to the slope of this graph, so it is always positive: extra energy is now needed to raise the temperature of the gas by any given amount. For argon at room temperature, $u_0 = 0.0105$ eV (from Figure 8.2), so $kT/u_0 = 2.46$. At this point, the slope of the graph is roughly 0.55. This slope is actually

$$\text{slope} = \frac{d}{dt} \left(\frac{\Delta U}{(N^2/V)r_0^3u_0} \right) = \frac{1}{Nkr_0^3(N/V)} \frac{d(\Delta U)}{dT},$$

so the correction to C_V/Nk is

$$(0.55)r_0^3 \frac{N}{V} \approx (0.55)r_0^3 \frac{P}{kT} = \frac{(0.55)(3.86 \times 10^{-10} \text{ m})^3 (10^5 \text{ N/m}^2)}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 7.7 \times 10^{-4}.$$

That's about 0.05% of the ideal gas value of $3/2$. In other words, molecular interactions increase the heat capacity by about one part in 2000. According to the graph, the correction should be somewhat less at higher temperatures, and considerably greater at lower temperatures.

Problem 8.14. (Grand canonical treatment of a weakly interacting gas.)

- a) The grand partition function involves a sum over all states of the system, which includes all possible particle numbers N , and for each N , all possible states for this many particles:

$$\mathcal{Z} = \sum_{\text{all } s} e^{-\beta(U_s - N_s)} = \sum_{N=1}^{\infty} \sum_{\substack{\text{states for} \\ N \text{ particles}}} e^{-\beta U} e^{\beta N} = \sum_N Z(N) e^{\beta N}.$$

In the last step I've used the definition of the ordinary partition function of a system of N particles as the sum of $e^{-\beta U}$ over all states for this fixed number of particles.

- b) The ordinary partition function $Z(N)$ is the product of $Z_{N,\text{ideal}}$ times the configuration integral, which in turn can be written as a sum of diagrams according to equation 8.20. Therefore,

$$\begin{aligned} Z &= \sum_N Z_{N,\text{ideal}} Z_{Nc} e^{\beta N} \\ &= \sum_N \frac{1}{N!} \left(\frac{V}{v_Q} \right)^N e^{\beta N} \left[1 + \underset{\bullet}{\text{I}} + \underset{\bullet}{\text{A}} + (\underset{\bullet}{\text{II}} \underset{\bullet}{\text{II}}) + \underset{\bullet}{\text{III}} + \dots \right]. \end{aligned}$$

Now consider just a single term in this sum over diagrams, containing a diagram with n dots. This term has the form

$$\begin{aligned} &\sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{Ve^{\beta}}{v_Q} \right)^N \frac{N(N-1)}{\text{symmetry factor}} \frac{(N-n+1)}{V^n} \frac{1}{\int(\)} \\ &= \sum_{N=n}^{\infty} \frac{1}{(N-n)!} \left(\frac{Ve^{\beta}}{v_Q} \right)^{N-n} \left[\left(\frac{e^{\beta}}{v_Q} \right)^n \frac{1}{\text{symm. fact.}} \int(\) \right]. \end{aligned}$$

The quantity in square brackets is independent of N , so we can factor it out of the sum. From now on, I'll represent this quantity by a new diagram, which looks the same as the previous diagram but is translated using a new rule 1:

1. For each dot, write down a factor of $(\lambda/v_Q) \int d^3 r_i$, where $\lambda = e^{\beta}$.

(Rules 2 and 3, for the f -functions and the symmetry factor, are the same as on page 331.) Meanwhile, notice how the factors of $N(N-1)$ in the numerator have canceled the first n terms of the sum. The remaining sum now starts with $N=n$, but if we rewrite it in terms of $\tilde{N} \equiv N-n$, we can carry it out explicitly:

$$\sum_{N=n}^{\infty} \frac{1}{(N-n)!} \left(\frac{\lambda V}{v_Q} \right)^{N-n} = \sum_{\tilde{N}=0}^{\infty} \frac{1}{\tilde{N}!} \left(\frac{\lambda V}{v_Q} \right)^{\tilde{N}} = \exp \left(\frac{\lambda V}{v_Q} \right).$$

These simplifications can be made for every term in the grand partition function, so we now have

$$Z = \exp \left(\frac{\lambda V}{v_Q} \right) \left[1 + \underset{\bullet}{\text{I}} + \underset{\bullet}{\text{A}} + (\underset{\bullet}{\text{II}} \underset{\bullet}{\text{II}}) + \underset{\bullet}{\text{III}} + \dots \right],$$

where the diagrams are now to be evaluated using the new rule 1. But since the diagrams no longer include the awkward factors of $N(N-1)$, the exponentiation of the disconnected diagrams is now much simpler than before. For example, the relation

$$1 + \underset{\bullet}{\text{I}} + (\underset{\bullet}{\text{II}} \underset{\bullet}{\text{II}}) + (\underset{\bullet}{\text{II}} \underset{\bullet}{\text{II}} \underset{\bullet}{\text{II}}) + \dots = \exp \left(\underset{\bullet}{\text{I}} \right)$$

holds exactly, and when the more complicated diagrams are included in the sum, they also exponentiate exactly (as partially demonstrated in Problem 8.3). Therefore,

$$\begin{aligned}\mathcal{Z} &= \exp\left(\frac{\lambda V}{v_Q}\right) \exp\left(\text{dot diagram} + \text{triangle diagram} + \text{square diagram} + \dots\right) \\ &= \exp\left(\frac{\lambda V}{v_Q} + \text{dot diagram} + \text{triangle diagram} + \text{square diagram} + \dots\right).\end{aligned}$$

- c) As shown in Problem 7.7, the grand free energy can be expressed as $\Phi = -kT \ln \mathcal{Z}$. In our case,

$$\Phi = -kT \left(\frac{e^\beta V}{v_Q} + \text{dot diagram} + \text{triangle diagram} + \text{square diagram} + \dots \right).$$

Given Φ , we can calculate P and N using the results of Problem 5.23:

$$\begin{aligned}P &= \frac{\Phi}{V} = \frac{kT\lambda}{v_Q} + \frac{kT}{V} \left(\text{dot diagram} + \text{triangle diagram} + \text{square diagram} + \dots \right); \\ \overline{N} &= \left(\frac{\partial \Phi}{\partial \lambda} \right)_{T,V} = kT \frac{\partial}{\partial \lambda} \left(\frac{e^\beta V}{v_Q} + \text{dot diagram} + \text{triangle diagram} + \text{square diagram} + \dots \right) \\ &= \frac{\lambda V}{v_Q} + 2 \text{dot diagram} + 3 \text{triangle diagram} + 4 \text{square diagram} + \dots.\end{aligned}$$

In the last step I've used the fact that each n -dot diagram depends on λ only through the factor $\lambda^n = e^{n\beta}$. The derivative with respect to λ therefore brings down a factor of $n\beta$, and the β is canceled by the overall factor of kT .

- d) If we keep only the first diagram in each sum, then

$$\overline{N} = \frac{\lambda V}{v_Q} + 2 \cdot \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^2 I_2, \quad \text{where } I_2 \equiv \int d^3 r_1 d^3 r_2 f_{12}.$$

This expression implicitly determines λ in terms of \overline{N} . To lowest order, we have $\lambda/v_Q = \overline{N}/V$. This lowest-order relation is good enough for the correction term, so we can write

$$\overline{N} = \frac{\lambda V}{v_Q} + \left(\frac{\overline{N}}{V} \right)^2 I_2, \quad \text{or} \quad \frac{\lambda}{v_Q} = \frac{\overline{N}}{V} \quad \left(\frac{\overline{N}}{V} \right)^2 \frac{I_2}{V}.$$

Meanwhile, the pressure is

$$P = \frac{kT\lambda}{v_Q} + \frac{kT}{V} \cdot \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^2 I_2$$

In the first term we can substitute the previous relation for λ/v_Q , while in the correction term we can just use the lowest-order relation $\lambda/v_Q = \overline{N}/V$:

$$\begin{aligned}P &= kT \left[\frac{\overline{N}}{V} + \left(\frac{\overline{N}}{V} \right)^2 \frac{I_2}{V} \right] + \frac{1}{2} \frac{kT}{V} \left(\frac{\overline{N}}{V} \right)^2 I_2 = \frac{\overline{N} k T}{V} - \frac{1}{2} \frac{\overline{N}^2 k T I_2}{V^3} \\ &= \frac{\overline{N} k T}{V} \left(1 - \frac{1}{2} \frac{\overline{N}}{V^2} \int d^3 r_1 d^3 r_2 f_{12} \right).\end{aligned}$$

If we change integration variables as in equation 8.29, one of the integrals will just give a factor of V , while the other one, over the relative coordinate, will become $\int d^3r f(r)$. Thus, this result is the same as the one derived in the text, equation 8.32.

- e) Before trying to calculate the next corrections to \bar{N} and P , let's write the Λ -shaped diagram in terms of I_2 . Changing variables as in Problem 8.5, and carrying out the integral over \vec{r}_2 , we have

$$\text{Diagram} = \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^3 \int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{23} = \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^3 V \left(\int d^3r f(r) \right)^2 = \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^3 \frac{1}{V} I_2^2.$$

Let me also write the triangle diagram as

$$\text{Diagram} = \frac{1}{6} \left(\frac{\lambda}{v_Q} \right)^3 I_3, \quad \text{where } I_3 \equiv \int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{23} f_{31}.$$

Then according to the results of part (c),

$$\begin{aligned} \bar{N} &= \frac{\lambda V}{v_Q} + 2 \text{Diagram} + 3 \text{Diagram} + 3 \text{Diagram} = \frac{\lambda V}{v_Q} + \left(\frac{\lambda}{v_Q} \right)^2 I_2 + \frac{3}{2} \left(\frac{\lambda}{v_Q} \right)^3 \frac{1}{V} I_2^2 + \frac{3}{6} \left(\frac{\lambda}{v_Q} \right)^3 I_3 \\ &= \frac{\lambda V}{v_Q} + \left(\frac{\bar{N}}{V} - \frac{\bar{N}^2}{V^2} I_2 \right)^2 I_2 + \frac{3}{2} \frac{\bar{N}^3}{V^4} I_2^2 + \frac{1}{2} \frac{\bar{N}^3}{V^3} I_3. \end{aligned}$$

In the second line I've inserted the lower-order results of part (d), keeping only terms through order I_2^2 and I_3 and dropping smaller terms. Solving for λ/v_Q gives

$$\frac{\lambda}{v_Q} = \frac{\bar{N}}{V} - \frac{\bar{N}^2}{V^3} I_2 + \frac{1}{2} \frac{\bar{N}^3}{V^5} I_2^2 - \frac{1}{2} \frac{\bar{N}^3}{V^4} I_3,$$

where I've again dropped a term of order I_2^3 . We're now ready to calculate the pressure:

$$\begin{aligned} \frac{P}{kT} &= \frac{\lambda}{v_Q} + \frac{1}{V} \left(\text{Diagram} + \text{Diagram} + \text{Diagram} \right) = \frac{\lambda}{v_Q} + \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^2 \frac{I_2}{V} + \frac{1}{2} \left(\frac{\lambda}{v_Q} \right)^3 \frac{I_2^2}{V^2} + \frac{1}{6} \left(\frac{\lambda}{v_Q} \right)^3 \frac{I_3}{V} \\ &= \frac{\bar{N}}{V} - \frac{\bar{N}^2}{V^3} I_2 + \frac{1}{2} \frac{\bar{N}^3}{V^5} I_2^2 - \frac{1}{2} \frac{\bar{N}^3}{V^4} I_3 + \frac{1}{2} \left(\frac{\bar{N}}{V} - \frac{\bar{N}^2}{V^3} I_2 \right)^2 \frac{I_2}{V} + \frac{1}{2} \frac{\bar{N}^3}{V^3} \frac{I_2^2}{V^2} + \frac{1}{6} \frac{\bar{N}^3}{V^3} \frac{I_3}{V} \\ &= \frac{\bar{N}}{V} - \frac{1}{2} \frac{\bar{N}^2}{V^3} I_2 - \frac{1}{3} \frac{\bar{N}^3}{V^4} I_3 = \frac{\bar{N}}{V} \left(1 - \frac{1}{2} \frac{\bar{N} I_2}{V} - \frac{1}{3} \frac{\bar{N}^2 I_3}{V^2} \right). \end{aligned}$$

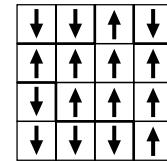
Here I've again dropped terms of order I_2^3 and smaller. The terms proportional to I_2^2 , however, have canceled, leaving only the I_3 term, which comes from the triangle diagram, to contribute to the third virial coefficient. In fact, we can simply read off

$$B(T) = -\frac{1}{2} \frac{I_2}{V}, \quad C(T) = -\frac{1}{3} \frac{I_3}{V},$$

in agreement with equation 8.34 and Problem 8.8.

Problem 8.15. This 4×4 lattice has 24 “bonds” joining neighboring dipoles, of which 10 (highlighted in the illustration at right) are between antiparallel dipoles and the other 14 are between parallel dipoles. Therefore the total energy is

$$U = 10\epsilon + 14(-\epsilon) = -4\epsilon.$$



Problem 8.16. A system of 100 two-state dipoles has 2^{100} , or 1.27×10^{30} , possible microstates. That’s the total number of terms in the partition function, so if we could calculate a billion terms per second, it would take us

$$\frac{1.27 \times 10^{30}}{10^9} \text{ seconds} = 1.27 \times 10^{21} \text{ seconds} = 4.0 \times 10^{13} \text{ years}$$

to calculate all the terms. The age of the known universe is approximately 15 billion years, so this is about 2700 times the age of the known universe.

Problem 8.17. For an Ising model of just two elementary dipoles, the energy is just ϵ if the dipoles are parallel and $-\epsilon$ if the dipoles are antiparallel. The states of the system and their Boltzmann factors are:

$$\uparrow\uparrow: e^{\epsilon/kT}; \quad \uparrow\downarrow: e^{-\epsilon/kT}; \quad \downarrow\uparrow: e^{-\epsilon/kT}; \quad \downarrow\downarrow: e^{\epsilon/kT}.$$

The partition function is therefore

$$Z = 2e^{\epsilon/kT} + 2e^{-\epsilon/kT} = 4 \cosh(\epsilon/kT).$$

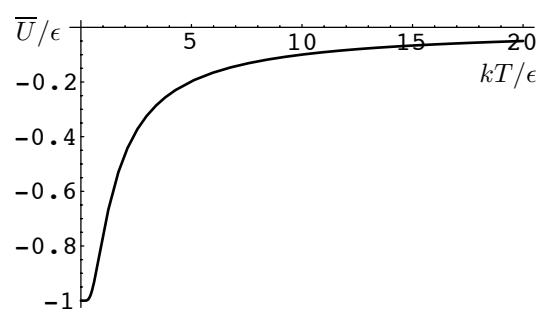
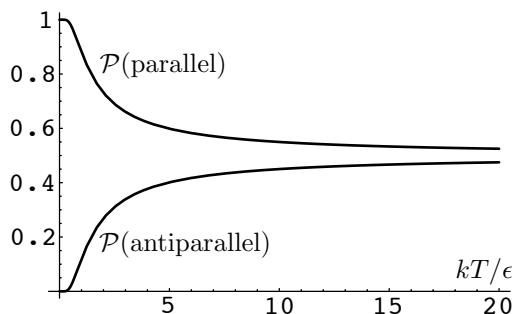
The probability of the two dipoles being parallel is

$$\mathcal{P}(\text{parallel}) = \frac{2e^{\epsilon/kT}}{2e^{\epsilon/kT} + 2e^{-\epsilon/kT}} = \frac{1}{1 + e^{-2\epsilon/kT}},$$

while the probability of them being antiparallel is

$$\mathcal{P}(\text{antiparallel}) = \frac{2e^{-\epsilon/kT}}{2e^{\epsilon/kT} + 2e^{-\epsilon/kT}} = \frac{1}{1 + e^{2\epsilon/kT}}.$$

These formulas are plotted in the figure below (left).



In the high-temperature limit, the probabilities of all four states become equal, while in the low-temperature limit, the probabilities of the antiparallel states go to zero. When the antiparallel states have a (combined) probability of 1/3, then each parallel state is as probable as both antiparallel states put together; this happens when

$$\frac{1}{3} = \frac{1}{1 + e^{2\epsilon/kT}} \quad \text{or} \quad \frac{2\epsilon}{kT} = \ln 2 \quad \text{or} \quad \frac{kT}{\epsilon} = \frac{2}{\ln 2} = 2.89.$$

At lower temperatures, each parallel state is *more* probable than both antiparallel states put together. Finally, the average energy of the system is

$$\bar{U} = \frac{2(-\epsilon)e^{\epsilon/kT} + 2(\epsilon)e^{-\epsilon/kT}}{2e^{\epsilon/kT} + 2e^{-\epsilon/kT}} = \epsilon \tanh \frac{\epsilon}{kT}.$$

This function is plotted above (right). The average energy goes to zero in the high-temperature limit and to $-\epsilon$ in the low-temperature limit, as we would expect.

Problem 8.18. Starting from equation 8.43 for the partition function, the average energy of a one-dimensional Ising model is

$$\begin{aligned} \bar{U} &= \frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \ln(2 \cosh \beta \epsilon)^N = N \frac{\partial}{\partial \beta} \ln(2 \cosh \beta \epsilon) \\ &= \frac{N}{2 \cosh \beta \epsilon} \frac{\partial}{\partial \beta} (2 \cosh \beta \epsilon) = \frac{N \epsilon \sinh \beta \epsilon}{\cosh \beta \epsilon} = N \epsilon \tanh \beta \epsilon. \end{aligned}$$

Problem 8.19. According to equation 8.51, the dipole-dipole interaction energy ϵ for iron should be roughly

$$\epsilon = \frac{kT_c}{n} = \frac{(8.62 \times 10^{-5} \text{ eV/K})(1043 \text{ K})}{10} = 0.009 \text{ eV} \approx 0.01 \text{ eV},$$

where I've taken $n = 10$ to get an order-of-magnitude estimate. This is comparable to the intermolecular interaction energies determined in Figure 8.2, although the nature of the interaction is quite different here.

Problem 8.20. For a two-dimensional square lattice, $n = 4$ so equation 8.50 becomes

$$\bar{s} = \tanh \frac{4\bar{s}}{t}, \quad \text{where } t = kT/\epsilon.$$

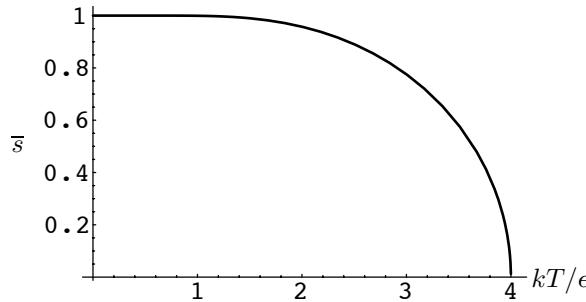
This equation should have a nontrivial solution, between 0 and 1, for any value of t below the critical temperature (which is at $t = 4$). The *Mathematica* instruction

```
FindRoot[s==Tanh[4s/t],{s,.5}]
```

will find the solution for any t value; the starting point 0.5 is sufficient to ensure that it finds the desired positive solution, rather than one of the other two. To plot the solution as a function of t , I embedded this instruction inside a *Plot* function:

```
Plot[FindRoot[s==Tanh[4s/t],{s,.5}][[1,2]],{t,0,4},PlotRange->All]
```

The appendage `[[1,2]]` strips off the unwanted baggage from the expression returned by `FindRoot`, while the `PlotRange` option overrides *Mathematica*'s idiosyncratic desire to show only part of the resulting graph. Here is the full graph of the predicted magnetization as a function of temperature:



Problem 8.21. To solve equation 8.50 when $\beta\epsilon n \ll 1$ and $\bar{s} \approx 1$, we need an expansion of $\tanh x$ when x is large. Starting from the definition,

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{1 - e^{-2x}}{1 + e^{-2x}} \approx 1 - 2e^{-2x},$$

where in the last step I've expanded the denominator using the binomial approximation, and dropped terms of order e^{-4x} and smaller. With this approximation, equation 8.50 becomes

$$\bar{s} = 1 - 2e^{-2\beta\epsilon\bar{s}} \approx 1 - 2e^{-2\beta\epsilon}.$$

In other words, \bar{s} is less than 1 by an amount

$$\Delta\bar{s} = 2e^{-2n\epsilon/kT}.$$

This expression goes to zero exponentially as $T \rightarrow 0$. In Problem 7.64, however, we saw that the magnetization of a real ferromagnet at low temperature differs from its saturated value by an amount proportional to $T^{3/2}$ (due to the excitation of long-wavelength magnons). In the Ising model, an excitation away from the ground state must have an energy of at least $2n\epsilon$ over the ground state energy; therefore such excitations are exponentially suppressed when $kT < 2n\epsilon$. The difference between the Ising model and the spin-wave model of Problem 7.64 is analogous to the difference between the Einstein model of lattice vibrations (in which all energy units are of the same size ϵ , and therefore the heat capacity is exponentially suppressed when $kT < \epsilon$) and the Debye model (in which long-wavelength excitations can have arbitrarily low energies, giving the heat capacity a weaker power-law dependence at low temperatures).

Problem 8.22. In the presence of an external field B , the energy of a typical dipole (due to its interaction with both its neighbors and the external field) is either

$$E_{\uparrow} = \epsilon n \bar{s} - B_B \quad \text{or} \quad E_{\downarrow} = +\epsilon n \bar{s} + B_B,$$

where \bar{s} is the average alignment of the dipole's n neighbors, as in equations 8.46 and 8.47. The partition function for this dipole is therefore

$$Z_i = e^{\beta E_{\uparrow}} + e^{\beta E_{\downarrow}} = e^{\beta\epsilon n \bar{s} + \beta B_B} + e^{\beta\epsilon n \bar{s} - \beta B_B} = 2 \cosh(\beta\epsilon n \bar{s} + \beta B_B),$$

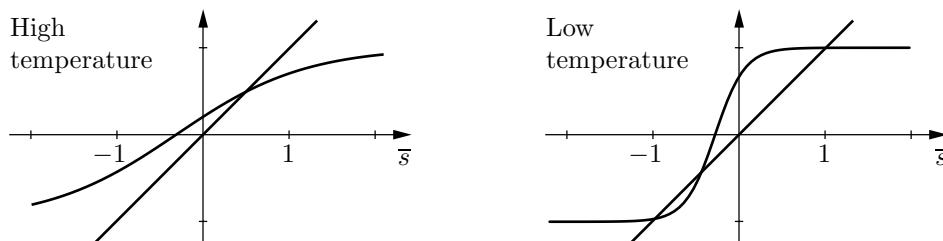
and the average expected value of its spin alignment is

$$\begin{aligned}\bar{s}_i &= \frac{1}{Z_i} \left[(1)e^{\beta n\bar{s} + \beta_B B} + (-1)e^{-\beta n\bar{s} - \beta_B B} \right] \\ &= \frac{2 \sinh(\beta n\bar{s} + \beta_B B)}{2 \cosh(\beta n\bar{s} + \beta_B B)} = \tanh(\beta n\bar{s} + \beta_B B).\end{aligned}$$

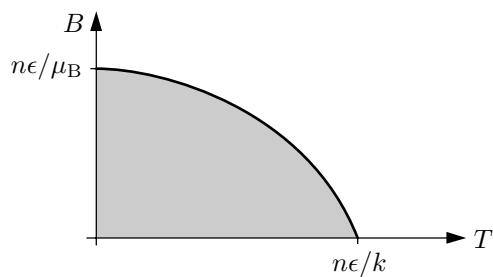
If we now make the mean field approximation $\bar{s}_i = \bar{s}$ (that is, the thermal average alignment of the i th dipole is the same as the instantaneous average alignment of its neighbors), then \bar{s} is determined by the equation

$$\bar{s} = \tanh(\beta n\bar{s} + \beta_B B).$$

This is the same as equation 8.50, except that the argument of the tanh function is shifted by $\beta_B B$. Graphically, this shifts the tanh curve to the left: It now intersects the horizontal axis at $\bar{s} = -B/n\epsilon$. Two examples of the graphical solution of this modified equation are shown below. At relatively high temperatures there is only a single solution for \bar{s} , but now this solution is shifted to a positive value instead of zero, the solution in the absence of a magnetic field. However, if the temperature is sufficiently low and the field strength is not too great, the equation has three solutions. The middle solution is unstable, while the most-negative solution is metastable, with most of the dipoles pointing against the external field but parallel to each other.



At what values of T and B does the metastable solution exist? Even at zero external field, there is a negative- \bar{s} solution only when $kT < n\epsilon$. Increasing the field strength shifts the tanh curve to the left, which requires it to be steeper near the origin (i.e., lower temperature) to intersect the straight line \bar{s} . But even at zero temperature, when the tanh function becomes an infinitely steep step function, it doesn't intersect the straight line unless it crosses the origin to the right of $\bar{s} = -1$, that is, unless $B/n\epsilon < 1$. The conditions under which the metastable solution exists are indicated (roughly) by the shaded region of the B - T graph below.



Problem 8.23. (Lattice gas.)

- a) Let m_i represent the state of the i th site, with $m_i = 0$ for unoccupied sites and $m_i = 1$ for occupied sites. Then the number of molecules and the total energy of the system can be written

$$N = \sum_i m_i; \quad U = u_0 \sum_{\substack{\text{neighboring} \\ \text{pairs } i,j}} m_i m_j.$$

In terms of these sums, the grand partition function is

$$\mathcal{Z}_{\text{lattice}} = \sum_{\{m_i\}} e^{-\beta(U - N)},$$

where the sum runs over all possible sets of states for the sites.

- b) Now define $s_i = 2m_i - 1$, so $s_i = -1$ for unoccupied sites and $s_i = 1$ for occupied sites. Solving this relation for m_i gives $m_i = \frac{1}{2}(s_i + 1)$. The quantity $U - N$ in the exponent of \mathcal{Z} is then

$$\begin{aligned} U - N &= u_0 \sum_{\text{pairs}} \frac{1}{4}(s_i + 1)(s_j + 1) - \sum_i \frac{1}{2}(s_i + 1) \\ &= \frac{u_0}{4} \sum_{\text{pairs}} s_i s_j - \frac{u_0}{4} \sum_{\text{pairs}} (s_i + s_j) - \frac{1}{2} \sum_i s_i + (\text{constant}), \end{aligned}$$

where the constant is independent of the state of the system (though it does depend on u_0 and ϵ). In the second term of the second line, each site gets counted once for each of its neighbors, so this sum is equal to n times the sum over sites of s_i . Combining this term with the next one then gives

$$U - N = \frac{u_0}{4} \sum_{\text{pairs}} s_i s_j - \left(\frac{n u_0}{4} + \frac{1}{2} \right) \sum_i s_i + (\text{constant}).$$

In the ordinary partition function for an Ising ferromagnet in the presence of a magnetic field, on the other hand, the exponent instead contains the quantity

$$U_{\text{magnet}} = \epsilon \sum_{\text{pairs}} s_i s_j - \mu_B B \sum_i s_i.$$

Thus, if we ignore the constant, then $\mathcal{Z}_{\text{lattice}} = Z_{\text{magnet}}$, provided that we associate

$$\frac{u_0}{4} \leftrightarrow \epsilon \quad \text{and} \quad \frac{n u_0}{4} + \frac{1}{2} \leftrightarrow \mu_B B.$$

In other words, we can convert $\mathcal{Z}_{\text{lattice}}$ into Z_{magnet} by substituting $u_0 \rightarrow 4\epsilon$ and $n u_0 \rightarrow 2 \mu_B B - 2n\epsilon$. (The constant term leads to an extra factor in the partition function that depends on T and B (or for the lattice gas, T and μ) but is independent of the state of the system. It therefore has no effect on the relative probabilities of the system states under a given set of external conditions.)

- c) With the association $s_i = 2m_i - 1$, the low-density states of the lattice gas, with most m_i 's equal to zero, correspond to states of the magnet in which most of the dipoles point down. The high-density states of the lattice gas (when we would call it a liquid) correspond to states of the magnet in which most of the dipoles point up. For the magnet, the boundary between the up and down phases lies at $B = 0$, and extends from $T = 0$ up to the critical point at $kT = n\epsilon$. Therefore, the lattice gas should have a first-order phase transition at $= nu_0/2$, ending at a critical point at $kT = nu_0/4$. To locate the predicted phase boundary in the P - T plane, we would have to calculate the predicted pressure as a function of $$. This is possible in principle (using the relation $PV = \Phi = kT \ln Z$, but not easy. Qualitatively, however, we would expect some relation that isn't too different from that of a real-world ideal gas. For a monatomic ideal gas, for instance, equation 3.63 or 6.93 implies

$$= kT \ln \left(\frac{kT}{Pv_Q} \right), \quad \text{or} \quad P = \frac{kT}{v_Q} e^{-kT}.$$

The lattice gas model predicts a phase transition $= nu_0/2$, which corresponds to a pressure given by some power of T times an exponential of the form $e^{-nu_0/2kT}$. This is the same type of exponential function predicted in Problem 5.35, and it agrees reasonably well with experiments over limited ranges of temperature and pressure.

Problem 8.24. (Critical exponents of the Ising model in the mean field approximation.)

- a) To derive the approximation for $\tanh x$, write it in terms of exponentials and expand each of them in a Taylor series to third order:

$$\begin{aligned} \tanh x &= \frac{e^x - e^{-x}}{e^x + e^{-x}} \approx \frac{(1 + x + \frac{x^2}{2} + \frac{x^3}{6}) - (1 - x + \frac{x^2}{2} - \frac{x^3}{6})}{(1 + x + \frac{x^2}{2} + \frac{x^3}{6}) + (1 - x + \frac{x^2}{2} - \frac{x^3}{6})} = \frac{2(x + \frac{x^3}{6})}{2(1 + \frac{x^2}{2})} \\ &\approx \left(x + \frac{x^3}{6} \right) \left(1 - \frac{x^2}{2} \right) \approx x - \frac{x^3}{2} + \frac{x^3}{6} = x - \frac{x^3}{3}. \end{aligned}$$

(In the second line I've used the binomial expansion and dropped terms containing powers of x higher than 3.)

- b) Close to the critical temperature, the solution to equation 8.50 is at $\bar{s} \ll 1$. Since $\beta\epsilon n$ is very close to 1, the argument of the tangent is small so we can expand it to obtain

$$\bar{s} = (\beta\epsilon n \bar{s}) - \frac{1}{3}(\beta\epsilon n \bar{s})^3.$$

The solution $\bar{s} = 0$ is not the one we want, so we can divide through by $\beta\epsilon n \bar{s}$ to obtain

$$\frac{1}{\beta\epsilon n} = 1 - \frac{1}{3}(\beta\epsilon n \bar{s})^2, \quad \text{or} \quad \bar{s} = \frac{1}{\beta\epsilon n} \sqrt{3 \left(1 - \frac{1}{\beta\epsilon n} \right)}.$$

But $\beta\epsilon n$ is just T_c/T , so we have

$$\bar{s} = \frac{T}{T_c} \sqrt{3 \left(1 - \frac{T}{T_c} \right)} = \frac{\sqrt{3} T}{T_c^{3/2}} \sqrt{T_c - T} \approx \sqrt{\frac{3}{T_c}} (T_c - T)^{1/2},$$

where the last approximation is valid when T is very close to T_c . The total magnetization of the system is just \bar{s} times the magnetic moment per dipole times the

number of dipoles, so this result tells us that as $T \rightarrow T_c$, the magnetization goes to zero in proportion to $(T_c - T)^{1/2}$. The exponent 1/2 is the mean-field prediction for the critical exponent β .

- c) As shown in Problem 8.22, the mean-field condition in the presence of an external magnetic field B is

$$\bar{s} = \tanh(\beta\epsilon n \bar{s} + \beta_B B),$$

where β_B is the magnetic moment per dipole. Near the critical point, we can expand the hyperbolic tangent function:

$$\bar{s} = (\beta\epsilon n \bar{s} + \beta_B B) - \frac{1}{3}(\beta\epsilon n \bar{s} + \beta_B B)^3. \quad (1)$$

When T is slightly above T_c , this equation only has one solution, so the first term in the expansion is sufficient. We can then differentiate with respect to B to obtain

$$\frac{\partial \bar{s}}{\partial B} = \beta\epsilon n \frac{\partial \bar{s}}{\partial B} + \beta_B, \quad \text{or} \quad \frac{\partial \bar{s}}{\partial B} = \frac{\beta_B}{1 - \beta\epsilon n} = \frac{\beta_B}{k}(T - T_c)^{-1}.$$

The magnetization is $M = N_B \bar{s}$, so the susceptibility is simply

$$\chi = \frac{\partial M}{\partial B} = N_B \frac{\partial \bar{s}}{\partial B} = \frac{N_B^2}{k}(T - T_c)^{-1},$$

indicating that the critical exponent γ is equal to 1.

Calculating the susceptibility when T is slightly *below* T_c is somewhat trickier. Equation 1 now has three solutions for \bar{s} , and we must be careful to choose the one found in part (b). Differentiating equation 1 with respect to B gives

$$\frac{\partial \bar{s}}{\partial B} = \beta\epsilon n \frac{\partial \bar{s}}{\partial B} + \beta_B - (\beta\epsilon n \bar{s} + \beta_B B)^2 \left(\beta\epsilon n \frac{\partial \bar{s}}{\partial B} + \beta_B \right).$$

Having taken this derivative, we can now set $B = 0$ to obtain the susceptibility in the limit of zero external field. Substituting the result of part (b) for \bar{s} , we have

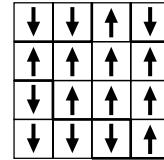
$$\begin{aligned} \frac{\partial \bar{s}}{\partial B} &= \beta\epsilon n \frac{\partial \bar{s}}{\partial B} + \beta_B - 3 \left(1 - \frac{1}{\beta\epsilon n} \right) \left(\beta\epsilon n \frac{\partial \bar{s}}{\partial B} + \beta_B \right) \\ &\approx \beta\epsilon n \frac{\partial \bar{s}}{\partial B} + \beta_B - 3 \beta\epsilon n (1) \frac{\partial \bar{s}}{\partial B}, \end{aligned}$$

where I've dropped the final β_B term because it is much smaller than the other β_B term, suppressed by a factor that is very small when T is close to T_c . Combining similar terms and solving for $\partial \bar{s}/\partial B$ now gives

$$\frac{\partial \bar{s}}{\partial B} = \frac{\beta_B}{2(\beta\epsilon n - 1)} = \frac{\beta_B/kT}{2(T_c/T - 1)} = \frac{\beta_B}{2k}(T_c - T)^{-1}.$$

To get the susceptibility we again multiply by N_B . The result is the same as for $T > T_c$, except that T and T_c are reversed and there is now an extra factor of 1/2. Thus the critical exponent γ is again equal to 1. (You may recall from Problem 5.55(f) that the compressibility of a van der Waals fluid has exactly the same dependence on $T - T_c$.)

Problem 8.25. With periodic boundary conditions, the lattice now has an additional 8 “bonds” along what used to be the edges. Of these, four (highlighted along the right and bottom edges) are between antiparallel dipoles and four are between parallel dipoles. So the total energy is now $U = 14\epsilon + 18(-\epsilon) = -4\epsilon$, coincidentally the same as before.



Problem 8.26. I implemented the `ising` program in True BASIC, a language that is very easy to use but that runs rather slowly. Here is my code:

```

program ising
dim s(50,50)                      declare array of dipoles
input prompt "Size of lattice (max 50): ": size      set size, T at run time
input prompt "Temperature (units of epsilon/k): ": T
randomize                           different random numbers for each run
set window 0,(size+2)*1.55,(size+2)*1.1,0       coordinates for graphics
call initialize(s,size)
for iteration = 1 to 100*size^2
    let i = int(rnd*size+1)           choose a random row number
    let j = int(rnd*size+1)           and a random column number
    call deltaU(s,i,j,size,Ediff)    compute hypothetical delta-E of flip
    if Ediff <= 0 then              if flipping reduces the energy...
        let s(i,j) = -s(i,j)         then flip it
        call colorsquare(i,j,s(i,j))
    else
        if rnd < exp(-Ediff/T) then
            let s(i,j) = -s(i,j)
            call colorsquare(i,j,s(i,j))
        end if
    end if
    next iteration
end

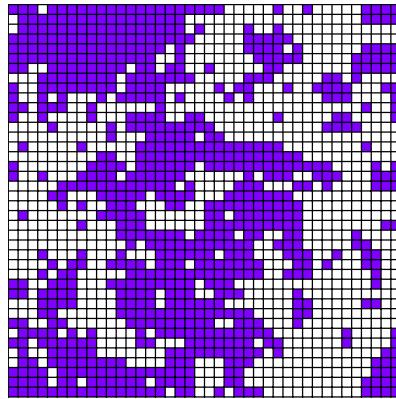
sub deltaU(s(),i,j,size,Ediff)      compute delta-U of flipping a dipole
    if i=1 then let top = s(size,j) else let top = s(i-1,j)
    if i=size then let bottom = s(1,j) else let bottom = s(i+1,j)
    if j=1 then let left = s(i,size) else let left = s(i,j-1)
    if j=size then let right = s(i,1) else let right = s(i,j+1)
    let Ediff = 2*s(i,j)*(top+bottom+left+right)
end sub                                (note periodic boundary conditions)

sub initialize(s(),size)             initialize to a random array
    for i = 1 to size
        for j = 1 to size
            if rnd < .5 then let s(i,j) = 1 else let s(i,j) = -1
            call colorsquare(i,j,s(i,j))
        next j
    next i
end sub

sub colorsquare(i,j,s)               color square i,j according to s
    if s = 1 then set color "blue" else set color "yellow"
    box area j,j+1,i,i+1
end sub

```

- a) My results from running this program on a 20×20 lattice for 40,000 iterations are shown in Figure 8.9 of the text. By squinting and drawing circles around the largest “clusters” that are all one color, I estimate the maximum cluster diameters to be roughly 3 squares at $T = 10$, 4 squares at $T = 5$, 5 squares at $T = 4$, 6 squares at $T = 3$, and 9 squares (though it’s hard to tell with so few clusters) at $T = 2.5$.
- b) With a 40×40 lattice, the largest cluster diameters were roughly 4 squares at $T = 10$, 4.5 squares at $T = 5$, 5 squares at $T = 4$, and 7 squares at $T = 3$. These sizes tend to be slightly larger than I found with a 20×20 lattice, but I suspect that this is merely because I had a larger region to search; after multiple runs with the smaller lattice I probably would have found similar results. The illustration at right shows the result of a run with $T = 2.5$. Here the clusters are significantly larger than I found with the 20×20 lattice—up to about 14 squares in diameter. Although I did sometimes obtain clusters this large with the smaller lattice, it was hard to be sure that they weren’t artifacts of the small lattice size (with periodic boundary conditions).
- c) My results for $T = 2$ and $T = 1.5$ are shown in Figure 8.9. At $T = 2$ I count 20 black squares, which leaves 380 white squares. The blacks cancel 20 of the whites, leaving a net magnetization of 360 units in the white direction, or 90% of the maximum possible value. At $T = 1.5$ there are two white squares and 398 black, so the net magnetization is 396 units in the black direction, or 99% of saturation. When I ran the simulation at $T = 1$ and it didn’t get stuck in a metastable state with two domains (as shown in Figure 8.9), the magnetization was almost always complete, with dipoles flipping to the opposite orientation only occasionally. In a total of 20 runs, the simulation ended in a two-domain state 7 times, in a totally magnetized state 12 times, and in a magnetized state with a single dipole flipped oppositely just one time. Excluding the runs that ended with two domains, there was just one unit of the opposite alignment for 5199 units of the dominant alignment, or a net magnetization of 5198 units out of 5200, that is, 99.96%.
- d) With a 10×10 lattice at $T = 2.5$, the simulation spends most of its time in states with a significant excess of one color over the other, but the dominant color spontaneously reverses pretty often. This effect is even more pronounced at somewhat lower temperatures, although you need to wait longer for the reversals, so it helps to have a faster computer. I don’t think this behavior has any particularly deep implications—it’s really an artifact of the small lattice size—but it certainly is fun to watch.
- e) Figure 8.10 shows the result of a run with a 400×400 lattice at $T = 2.27$. (To speed up this simulation, I ported the program to Pascal and used a compiler intended for professional software development. It ran for 10 hours on a 1996-vintage computer.) As you can see, the largest clusters are more than half the size of the lattice. So it is certainly plausible that, with a sufficiently large lattice and sufficiently long running time, we can obtain arbitrarily large clusters at $T = 2.27$.



Problem 8.27. Here is a version of the `ising` program in True BASIC for calculating the average energy and the heat capacity:

```

program isingE

dim s(50,50)
input prompt "Lattice size (max 50)": size
input prompt "Number of iterations per dipole": iMax
randomize
call initialize(s,size,energy)
open #1: name "isingE.out", create newold, org text
erase #1
print #1: "Lattice size = "; size
print #1: "Number of iterations per dipole = "; iMax
print "Temperature      Average U      Average U^2      Heat Cap."
print #1: "Temperature      Average U      Average U^2      Heat Cap."
for T = 4 to .99 step -.1
    let cumulativeU = 0
    let cumulativeU2 = 0
    for iteration = 1 to iMax*size^2
        let i = int(rnd*size+1)
        let j = int(rnd*size+1)
        call deltaU(s,i,j,size,Ediff)
        if Ediff <= 0 then
            let s(i,j) = -s(i,j)
            let energy = energy + Ediff          a flip changes the energy
        else
            if rnd < exp(-Ediff/T) then
                let s(i,j) = -s(i,j)
                let energy = energy + Ediff        here too
            end if
        end if
        let cumulativeU = cumulativeU + energy      sum energy over iterations
        let cumulativeU2 = cumulativeU2 + energy^2     and squared energies
    next iteration
    let averageU = cumulativeU / (iMax*size^2)      compute averages
    let averageU2 = cumulativeU2 / (iMax*size^2)
    let heatcap = (averageU2 - averageU^2) / T^2      and heat capacity
    print T, averageU, averageU2, heatcap
    print #1: T, averageU, averageU2, heatcap
next T
close #1
end

```

Although the Monte Carlo algorithm is the same as in the `ising` program in the text, this time I've dispensed with the graphics (for speed) and added code to update the `energy` variable each time a dipole is flipped. After each iteration the current energy is added to `cumulativeU`, which is eventually divided by the number of iterations to give the average energy. Although the straightforward way to get the heat capacity is to numerically

differentiate the energy with respect to temperature, a more elegant (and more accurate) method is to use the result of Problem 6.18, which implies

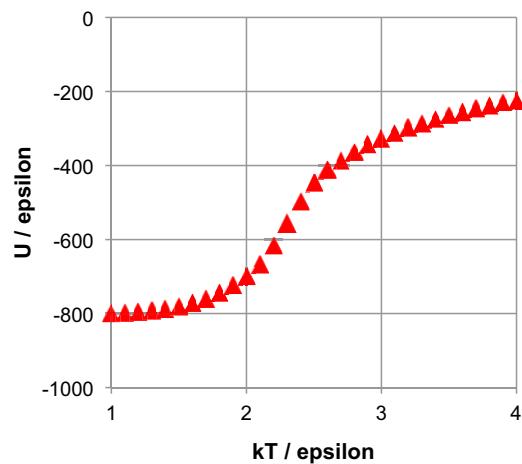
$$\frac{C}{k} = \frac{\overline{U^2} - \overline{U}^2}{(kT)^2}.$$

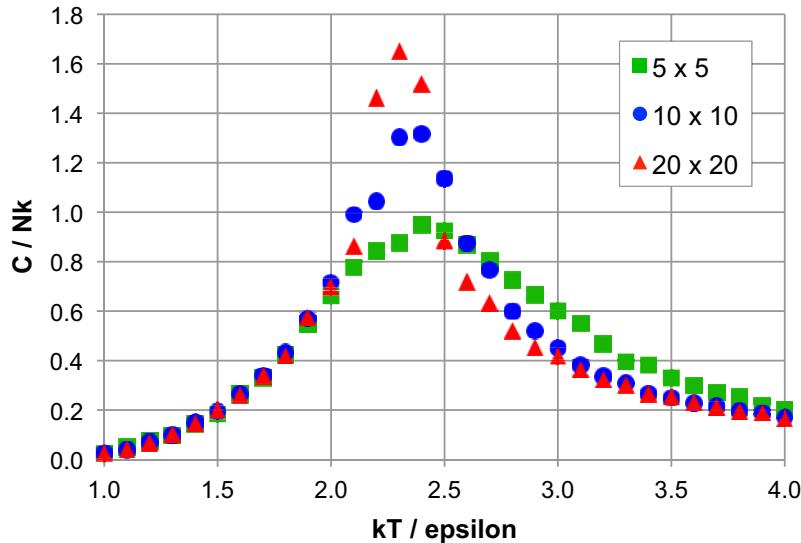
I've therefore summed the squared energy over iterations as well, averaged this quantity at the end, and used it in the preceding formula to get the heat capacity. Finally, I've looped over temperatures and printed out the results (both to the screen and to a file on disk) for each temperature. The only other trick is to get the `initialize` routine to return the initial energy. Here is the modified routine:

```
sub initialize(s(,),size,energy)
  for i = 1 to size
    for j = 1 to size
      if rnd < .5 then let s(i,j) = 1 else let s(i,j) = -1
    next j
  next i
  let energy = 0                                now compute the initial energy...
  for i = 1 to size-1
    for j = 1 to size-1
      let energy = energy - s(i,j)*s(i,j+1) - s(i,j)*s(i+1,j)
    next j
    let energy = energy - s(i,size)*s(i,1) - s(i,size)*s(i+1,size)
  next i
  for j = 1 to size-1
    let energy = energy - s(size,j)*s(size,j+1) - s(size,j)*s(1,j)
  next j
  let energy = energy - s(size,size)*s(size,1) - s(size,size)*s(1,size)
end sub
```

Notice that the last row and last column get special treatment, according to the periodic boundary conditions. The `deltaU` subroutine is exactly the same as in the previous problem.

Although you can get pretty good results with shorter runs, I ran this program for 10,000 iterations per dipole, with lattice sizes of 5, 10, and 20. I then copied the output into a spreadsheet for plotting. Plotted at right is the energy as a function of temperature for the 20×20 lattice. At low temperatures the energy goes to the lowest possible value—in this case, 800 units—while at high temperatures the energy approaches zero from below. The energy rises most steeply near the critical temperature, as might be expected. The behavior near the critical temperature is less dramatic for smaller lattices, as shown in the heat capacity graph on the next page.





Away from the critical point, the calculated heat capacity is relatively independent of the lattice size. Near the critical point, however, the peak in the heat capacity is much more pronounced for larger lattices. In the limit of an infinitely large lattice, the heat capacity goes to infinity at the critical temperature, according to Onsager's exact solution; see Gould and Tobochnik (1996) for a plot of the heat capacity in the infinite-lattice limit.

Problem 8.28. Here's a version of the `ising` program in True BASIC that keeps track of the magnetization values:

```

program isingM

dim s(20,20)
dim mhist(-400 to 400)
input prompt "Lattice size (max 20): ": size
let sizesq = size^2
input prompt "Temperature (units of epsilon/k): ": T
randomize
call initialize(s,size,mag)
for i = -sizesq to sizesq
    let mhist(i) = 0                      initialize magnetization histogram
next i
do
    for iteration = 1 to 10000
        let i = int(rnd*size+1)
        let j = int(rnd*size+1)
        let mag = mag - s(i,j)                subtract this s value from mag
        call deltaU(s,i,j,size,Ediff)
        if Ediff <= 0 then
            let s(i,j) = -s(i,j)
        else

```

```

        if rnd < exp(-Ediff/T) then
            let s(i,j) = -s(i,j)
        end if
    end if
    let mag = mag + s(i,j)           add new s value to mag
    let mhist(mag) = mhist(mag) + 1   increment slot in histogram
next iteration
call drawhistogram(mhist,sizesq)
get mouse x,y,mousestate
loop until mousestate = 1
open #1: name "isingM.out", create newold, org text
erase #1
print #1: "Temperature = "; T
for i = -sizesq to sizesq step 2      write final results to a file
    print #1: i, mhist(i)
next i
close #1
end

```

The current value of the total magnetization (the sum of all the `s` values) is stored in the variable `mag`. The tally of how often each `mag` value occurs is kept in the array `mhist`. After every 10,000 iterations, the program plots the current values of `mhist` and then checks the mouse button to decide whether to keep running. When the mouse button is pressed, the final values are written to a file and execution stops. The subroutine `deltaU` is exactly the same as in Problem 8.26. The `initialize` subroutine is modified slightly to compute the initial magnetization:

```

sub initialize(s(),size,mag)
    let mag = 0
    for i = 1 to size
        for j = 1 to size
            if rnd < .5 then let s(i,j) = 1 else let s(i,j) = -1
            let mag = mag + s(i,j)
        next j
    next i
end sub

```

There's also a new subroutine `drawhistogram`:

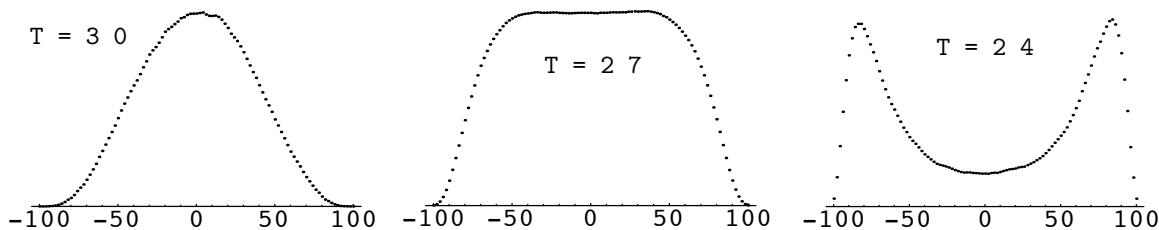
```

sub drawhistogram(mhist(),sizesq)           draw bar graph of magnetizations
    let histmax = 0
    for i = -sizesq to sizesq step 2
        let histmax = max(histmax,mhist(i))   find largest value to set scale
    next i
    clear
    set window -sizesq-1,sizesq+2,-.1,1.1
    set color "green"
    for i = -sizesq to sizesq step 2
        box area i,i+1,0,mhist(i)/histmax
    next i
end sub

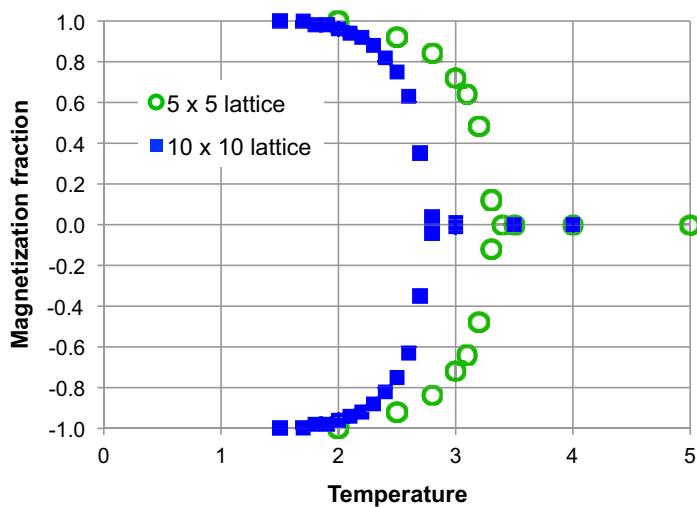
```

Note that since `mag` changes by ± 2 each time a dipole flips, only every other entry in the `mhist` array is used.

I ran this program at a variety of temperatures for both 5×5 and 10×10 lattices. At high temperatures, the magnetization was sharply peaked around zero. The peak grew broader with decreasing temperature, until it became flat and then split into two peaks. For the 5×5 lattice, this splitting occurred at around $T = 3.2$, while for the 10×10 lattice, it occurred at around $T = 2.7$. Here are some representative plots of the magnetization distribution for the 10×10 lattice:



The temperature at which the peak splits into two is essentially that at which the typical cluster size reaches the size of the lattice. At still lower temperatures, the two peaks move toward the ends of the graph and the valley between them becomes very deep, indicating that the system will hardly ever reverse its magnetization spontaneously. In the figure below, I've plotted the mostly likely magnetization value(s) as a function of temperature, for both the 5×5 lattice (circles) and the 10×10 lattice (squares). Presumably, in the limit of an infinitely large lattice, the split from zero magnetization into positive and negative nonzero values would occur at the critical temperature, $T = 2.27$.



Problem 8.29. Here's the final version of the code that I wrote, in True BASIC, to compute correlation functions for the Ising model:

```

program isingC
dim s(100,100)
dim cc(0 to 50)           array of cumulative correlation functions
input prompt "Lattice size (max 100): ": size
input prompt "Temperature (units of epsilon/k): ": T
set window -1,int(size/2)+2,-1.1,1.3    coordinates for c(r) bar graph
randomize
call initialize(s,size)
for r = 0 to int(size/2)
  let cc(r) = 0
next r
let pass = 0
do
  let pass = pass + 1
  for iteration = 1 to 5*size^2
    let i = int(rnd*size+1)
    let j = int(rnd*size+1)
    call deltaU(s,i,j,size,Ediff)
    if Ediff <= 0 then
      let s(i,j) = -s(i,j)
    else
      if rnd < exp(-Ediff/T) then
        let s(i,j) = -s(i,j)
      end if
    end if
  next iteration
  if pass > 40 then call computecorr(s,size,cc,pass-40)
  get mouse x,y,mousestate
loop until mousestate = 1
call saveresults(size,T,pass-40,cc)
end

```

The array `cc(r)`, which stores the cumulative correlation function over many passes, is not needed in parts (a) and (b); nor is the `pass` variable or the call to `saveresults`. The `deltaU` subroutine is the same as in Problem 8.26, as is the `initialize` routine, except that I deleted the call to `colorsquare` from it. The major enhancement to this version of the program is the `computecorr` subroutine:

```

sub computecorr(s(),size,cc(),pass)
  let ssum = 0
  for i = 1 to size
    for j = 1 to size
      let ssum = ssum + s(i,j)      first add up s's to get average
    next j
  next i
  let svsquared = (ssum/(size^2))^2
  let cc(0) = cc(0) + (1 - svsquared)

```

```

call plotbar(0,cc(0)/pass,1-savsquared)      first plot c(0)
let rmax = int(size/2)                      r goes up to half the lattice size
for r = 1 to rmax
  let csum = 0
  for i = 1 to size
    for j = 1 to size
      let right = j + r
      if right > size then let right = right - size
      let down = i + r
      if down > size then let down = down - size
      let csum = csum + s(i,j)*(s(i,right) + s(down,j))
    next j
  next i
  let cofr = csum/(2*size^2) - savsquared
  let cc(r) = cc(r) + cofr
  call plotbar(r,cc(r)/pass,cofr)
next r
end sub

```

Finally, we need routines to plot the correlation function and to save the final results in a file:

```

sub plotbar(r,bar1,bar2)      plot two bars, side by side
  set color "white"
  box area r,r+1,-1,1        erase old bars
  set color "cyan"
  box area r,r+.5,0,bar1     time-average c(r) in one color
  set color "magenta"
  box area r+.5,r+1,0,bar2   instantaneous c(r) in another
end sub

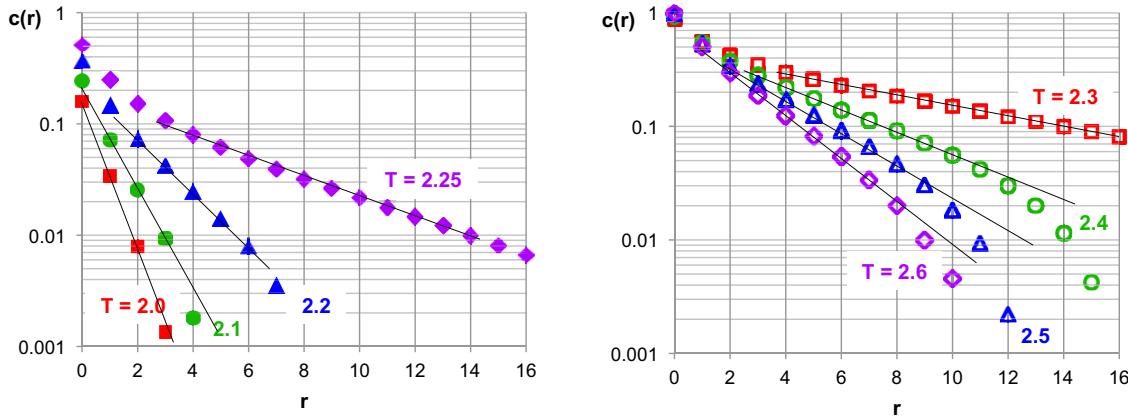
sub saveresults(size,T,pass,cc())
  open #1: name "isingC.out", create newold, org text
  erase #1
  print #1: "Lattice size = "; size
  print #1: "Temperature = "; T
  print #1: "Number of passes after equilibration = "; pass
  print #1: " r           c(r)"
  for r = 0 to int(size/2)
    print #1: r, cc(r)/pass
  next r
end sub

```

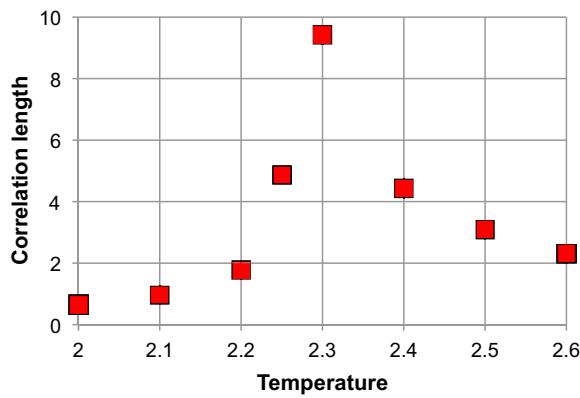
- a) See the code listed above. As already noted, the array `cc(r)` and the `pass` variable are not needed in parts (a) and (b).
- b) At temperatures well above the critical temperature $T = 2.27$, the correlation function falls off quite rapidly, and goes to zero at a relatively small value of r (for example, around $r = 3$ when $T = 5$). As the temperature is reduced, the correlation function falls off less rapidly, until the critical temperature is reached, where the correlation

function remains nonzero well past $r = 20$. Below the critical temperature, the correlation function becomes very small even at $r = 0$, because the whole lattice becomes magnetized. Again, though, the correlation function falls off more gradually with distance when T is close to the critical temperature.

- c) To compute the average correlation function over many passes, I added the array $cc(r)$ to the code as shown above. Notice that on average, each dipole will have five chances to be flipped during each “pass.” The program waits for 40 passes, to allow the system to equilibrate, before it begins to compute the average correlation function. However, just below the critical temperature, 40 passes wasn’t enough when starting from a random initial state. Therefore, at $T = 2.25$, I changed the `initialize` routine to give the system an initial magnetization; I did this by comparing the random number to 0.2 instead of 0.5 in deciding each initial alignment. I used a lattice size of 20 when well away from the critical temperature, but increased the lattice size near the critical temperature, to a maximum size of 100 at $T = 2.25$ and 2.3. I then copied the final output into a spreadsheet program and plotted the correlation functions on a logarithmic scale. Here are the results for temperatures near the critical temperature:



To extract the correlation length, I drew a straight line through the flattest part of each of these graphs, measured the distance over which it fell by a factor of 10, and divided by $\ln 10$ to obtain the distance to fall off by a factor of e . Here is a plot of the correlation length vs. temperature:



Problem 8.30. To simulate a one-dimensional Ising model, about all you need to do is remove all references to the second index j from the two-dimensional `ising` program. Here is a one-dimensional version of the program from Problem 8.26, which simply draws the system as a row of colored strips across the screen:

```

program ising1D
dim s(500)
input prompt "Size of lattice (max 500): ": size
input prompt "Temperature (units of epsilon/k): ": T
randomize
set window 0,size+2,0,10
call initialize(s,size)
do
  for iteration = 1 to 100
    let i = int(rnd*size+1)
    call deltaU(s,i,size,Ediff)
    if Ediff <= 0 then
      let s(i) = -s(i)
      call colorsquare(i,s(i))
    else
      if rnd < exp(-Ediff/T) then
        let s(i) = -s(i)
        call colorsquare(i,s(i))
      end if
    end if
  next iteration
  get mouse x,y,mousestate
loop until mousestate = 1
end

sub deltaU(s(),i,size,Ediff)
  if i = 1 then let left = s(size) else let left = s(i-1)
  if i = size then let right = s(1) else let right = s(i+1)
  let Ediff = 2*s(i)*(left+right)
end sub

sub initialize(s(),size)
  for i = 1 to size
    if rnd < .5 then let s(i) = 1 else let s(i) = -1
    call colorsquare(i,s(i))
  next i
end sub

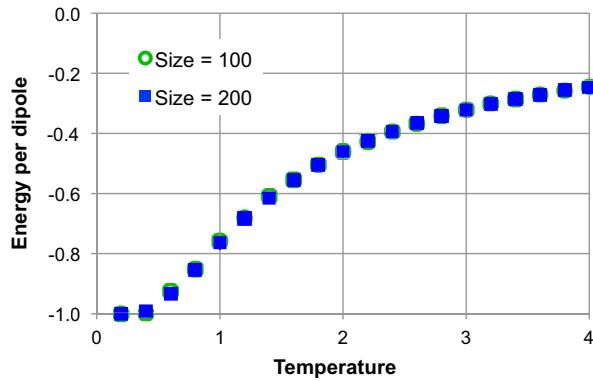
sub colorsquare(i,s)
  if s = 1 then set color "blue" else set color "magenta"
  box area i,i+1,5,6
end sub

```

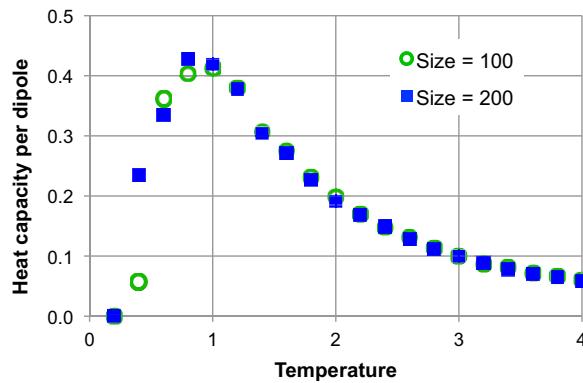
- a) Since the system is now just a one-dimensional row of dipoles, counting the number of clusters or domains is a simple matter of counting how many times the color changes as you cross the screen. After waiting a while for the system to equilibrate, I found

(in a lattice of 100 dipoles) 42 domains at $T = 5$, 40 at $T = 4$, 34 at $T = 3$, 28 at $T = 2$, and 16 at $T = 1$. At $T = 0.5$, the system spent quite a bit of its time with just a single domain; fluctuations would create new domains only occasionally, so there were rarely more than four domains, and I never saw more than six (after equilibration). Increasing the lattice size to 500, I found an average domain size of about 60 at $T = 0.5$. Neglecting the spontaneous creation of new domains, each domain boundary simply does a random walk, so any domain with a width of at least 2 is as likely to grow as to shrink in the next iteration. Thus, it is not surprising that this system has no strong tendency to magnetize except as T goes to zero. The simulation confirms that there is no abrupt phase transformation above $T = 0.5$, and suggests that, with sufficiently large lattices, we would find no abrupt transition at any positive temperature.

- b) To calculate the average energy and the heat capacity, I modified the `isingE` program from Problem 8.27 to simulate a one-dimensional system. (The modifications are quite straightforward, so I won't bother to reprint the code here.) I then ran the simulation for a lattice of 100 sites, with 5000 iterations per dipole at each temperature. Here is a graph of the average energy:



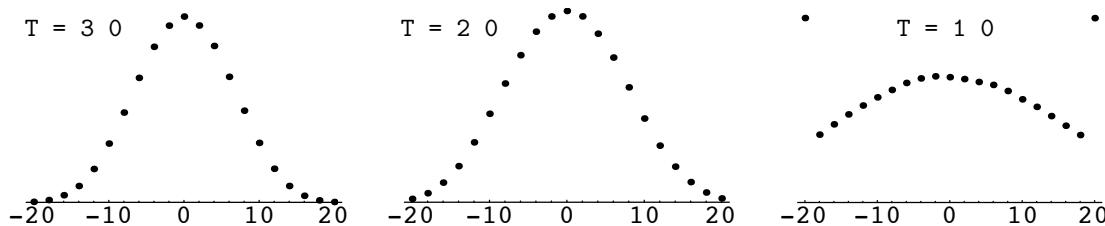
To check for finite-size effects, I also ran the simulation for a lattice size of 200. These results are also plotted in the graph above, but the points lie right on top of those for the 100-site lattice. I also plotted the heat capacity for both lattice sizes:



Here there's enough noise in the data to separate some of the plotted points. Note, however, that the lattice size does not significantly affect the height of the peak in the

heat capacity. This peak does not become infinitely sharp in the limit of an infinite lattice, so there is no discontinuous behavior in this system as the temperature is varied. In fact, these graphs are essentially identical to those predicted by the analytic solution, equation 8.44. The heat capacity graph is also the same as that plotted in Figure 3.10 (with B replaced by ϵ).

- c) To calculate the magnetization distribution, I modified the program from Problem 8.28 for the one-dimensional case. Again, the modifications were straightforward enough that I won't bother listing the code. I ran the simulation for a 20-site lattice at various temperatures and obtained the following results:



As the temperature decreases, the central peak becomes broader. Eventually, at about $T = 1.3$, two new peaks developed at the extreme magnetization values (total saturation). However, these peaks are an artifact of the small lattice size: they diminished and eventually vanished when I repeated the simulation using a larger lattice (for instance, at $T = 1$ they vanished when the lattice size was increased to 50). These peaks arise because a fully magnetized state is made artificially stable in a small lattice with periodic boundary conditions. Meanwhile, the central peak in the magnetization distribution remains present; it never splits into two peaks as in the two-dimensional case (Problem 8.28). So here again, we see that there is no phase transition like that of the two-dimensional Ising model.

Problem 8.31. First I created a 3D version of the original `ising` program, which simply shows the simulation as a lattice of colored squares on the screen. However, rather than trying to show the whole lattice, the `colorsquare` routine draws only the frontmost “panel”:

```
program ising3D
dim s(20,20,20)
input prompt "Lattice size (max 20): ": size
input prompt "Temperature (units of epsilon/k): ": T
set window 0,(size*1.5)+2,size+2,0
randomize
call initialize(s,size)
do
  for iteration = 1 to 100
    let i = int(rnd*size+1)
    let j = int(rnd*size+1)
    let k = int(rnd*size+1)
    call deltaU(s,i,j,k,size,Ediff)
    if Ediff <= 0 then
      let s(i,j,k) = -s(i,j,k)
      call colorsquare(s(i,j,k),i,j,k)
```

```

    else
        if rnd < exp(-Ediff/T) then
            let s(i,j,k) = -s(i,j,k)
            call colorsquare(s(i,j,k),i,j,k)
        end if
    end if
next iteration
get mouse x,y,mousestate
loop until mousestate = 1
end

sub deltaU(s,,,i,j,k,size,Ediff)
    if i = 1 then let top = s(size,j,k) else let top = s(i-1,j,k)
    if i = size then let bottom = s(1,j,k) else let bottom = s(i+1,j,k)
    if j = 1 then let left = s(i,size,k) else let left = s(i,j-1,k)
    if j = size then let right = s(i,1,k) else let right = s(i,j+1,k)
    if k = 1 then let front = s(i,j,size) else let front = s(i,j,k-1)
    if k = size then let back = s(i,j,1) else let back = s(i,j,k+1)
    let Ediff = 2*s(i,j,k)*(top+bottom+left+right+front+back)
end sub

sub initialize(s,,,size)
    for i = 1 to size
        for j = 1 to size
            for k = 1 to size
                if rnd < .5 then let s(i,j,k) = 1 else let s(i,j,k) = -1
                call colorsquare(s(i,j,k),i,j,k)
            next k
        next j
    next i
end sub

sub colorsquare(s,i,j,k)
    if k <> 1 then exit sub      draw only front panel of array
    if s = 1 then set color "red" else set color "yellow"
    box area j,j+1,i,i+1
end sub

```

I ran this program with a lattice size of 20 at various temperatures, and observed behavior very similar to the two-dimensional case, except that a single cluster took over the whole lattice at temperatures of 4.3 and below. This behavior seems to indicate a phase transition at around $T = 4.3$. At $T = 4.4$, single clusters would grow to span the lattice, but would then quickly evaporate. At higher temperatures, the clusters remained smaller, while at lower temperatures, the overall magnetization became more and more complete. At $T = 3.0$, for example, oppositely aligned clusters rarely grew past a width of 2.

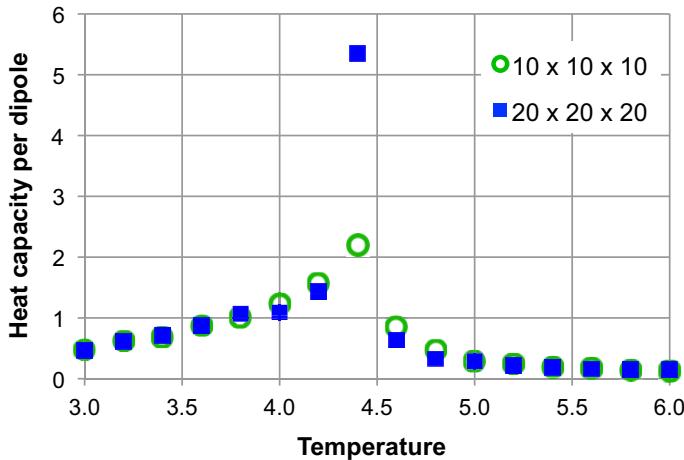
I also modified the `isingE` program from Problem 8.27 to simulate a three-dimensional lattice. Most of this modification was straightforward, so I won't show all the code. The only tricky part was generalizing the code used to compute the initial energy. The basic method used in Problem 8.27 got too confusing for me, so I eventually settled on a more brute-force approach:

```

let energy = 0
for i = 1 to size
    for j = 1 to size
        for k = 1 to size
            if i = size then let bottom = s(1,j,k) else let bottom = s(i+1,j,k)
            if j = size then let right = s(i,1,k) else let right = s(i,j+1,k)
            if k = size then let back = s(i,j,1) else let back = s(i,j,k+1)
            let energy = energy - s(i,j,k)*(bottom+right+back)
        next k
    next j
next i

```

I ran this program for lattice sizes of 10 (with 5000 iterations per dipole at each temperature) and 20 (with 1000 iterations per dipole at each temperature). Here is a plot of the calculated heat capacities:



The heat capacity peaks at $T = 4.4$ (plus or minus 0.1 or so), and the peak grows much sharper as the lattice size is increased. There are some intriguing differences between the shapes of the peaks for two- and three-dimensional systems, which might merit further investigation. The existence of the phase transition at around $T = 4.4$, however, seems well established by the data plotted here.

Problem 8.32. (Block spin transformations.)

- a) I started with the True BASIC version of the `ising` program from Problem 8.26, and added the following routine to perform the block spin transformation:

```

sub bst(s(),size)           do the block spin transformation
    for i = 2 to size-1 step 3
        for j = 2 to size-1 step 3
            let block = s(i-1,j-1) + s(i-1,j) + s(i-1,j+1) + s(i,j-1) + s(i,j)
            let block = block + s(i,j+1) + s(i+1,j-1) + s(i+1,j) + s(i+1,j+1)
            call colorsquare((i+1)/3,size+1+(j+1)/3,sgn(block))
        next j
    next i
end sub

```

For each block of nine dipoles, we add the `s` values in the variable `block`. The `sgn()` function returns 1 if `block` is positive and -1 if `block` is negative. Note also that the arguments of `colorsquare` are adjusted to draw the transformed lattice to the right of the original one. The main program that calls the `bst` routine is modified very little from Problem 8.26; here are the modified portions, with the Metropolis algorithm omitted:

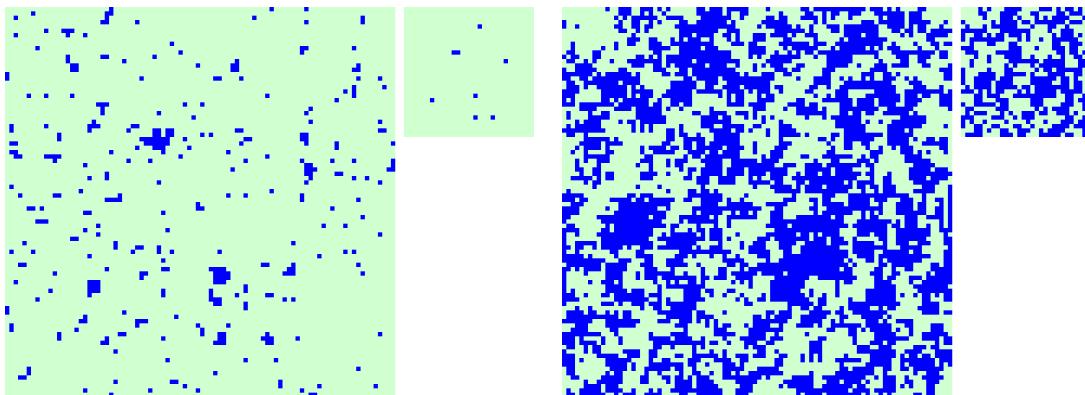
```

program isingBST
dim s(120,120)
input prompt "Lattice size (max 120): ": size
let size = size - mod(size,3)
input prompt "Temperature (units of epsilon/k): ": T
set window 0,(size*1.5)+2,size+2,0
clear
randomize
call initialize(s,size)
do
  for iteration = 1 to 10000
    [Metropolis algorithm, as in Problem 8.26]
    next iteration
    call bst(s,size)
    get mouse x,y,mousestate
  loop until mousestate = 1
end

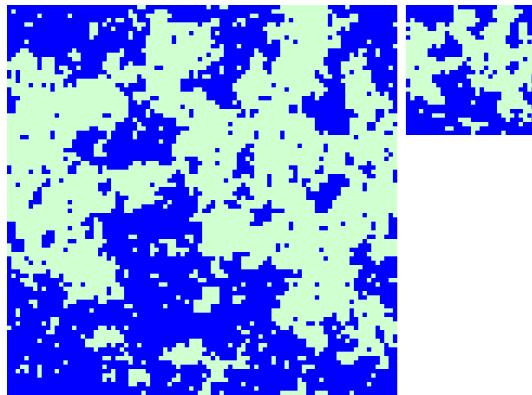
```

Notice that the lattice size is forced to be a multiple of 3. The `deltaU`, `initialize`, and `colorsquare` routines in this program are exactly the same as in Problem 8.26, except that I changed the `initialize` routine to generate a 60%/40% mix instead of 50/50, in order to speed up the equilibration at low temperatures.

- b) Here are some typical snapshots of the equilibrated system, with the transformed lattice shown to the right of the original lattice. On the left is a run with $T = 2$ (below the critical temperature), while on the right is a run with $T = 3$ (above the critical temperature).



Notice that, at $T = 2$, the transformed lattice is *more* strongly magnetized than the original lattice, with oppositely aligned clusters limited to a smaller size. In this case, the transformed temperature is therefore *less* than the original temperature. Similarly, at $T = 3$, the clusters in the transformed lattice are limited to a smaller size than in the original lattice. Here, however, both lattices are unmagnetized, and the smaller cluster size corresponds to a *higher* effective temperature. I found similar results at other temperatures: Below the critical temperature, the transformed temperature was always less than the original, while above the critical temperature, the transformed temperature was always greater than the original. *At* the critical temperature, the transformed temperature appeared to be essentially *equal* to the original temperature. Here is a snapshot from a run at $T = 2.3$:



Notice in this case that the transformed lattice looks pretty much like a typical slice cut from the original lattice—its effective temperature is essentially the same.

- c) Starting anywhere below the critical temperature, a block spin transformation reduces the effective temperature, so repeated block spin transformations should eventually take the temperature to zero. Similarly, starting anywhere above the critical temperature, a block spin transformation increases the effective temperature, so repeated block spin transformations should eventually take the temperature to infinity. Besides zero and infinity, the only other fixed point would be the critical temperature itself, and the only initial temperature that would “flow” to this fixed point would be the critical temperature. As it says in the text, since a system at its critical point is essentially unchanged when we average over short distances, we might expect many aspects of the critical behavior to be independent of the detailed nature of the microscopic interactions between particles.

A Elements of Quantum Mechanics

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Problem A.1. (Photon fundamentals.)

- a) Starting from the values listed inside the front cover,

$$hc = (4.136 \times 10^{-15} \text{ eV s})(2.998 \times 10^8 \text{ m/s}) = 12.40 \times 10^{-7} \text{ eV m} = 1240 \text{ eV nm.}$$

- b) For a 650-nm photon,

$$E = hf = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{650 \text{ nm}} = 1.91 \text{ eV.}$$

For a 450-nm photon,

$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{450 \text{ nm}} = 2.76 \text{ eV.}$$

For a 0.1-nm photon,

$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{0.1 \text{ nm}} = 12,400 \text{ eV} = 12.4 \text{ keV.}$$

And for a 1-mm photon,

$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{10^6 \text{ nm}} = 0.00124 \text{ eV.}$$

- c) In one second, a 1-milliwatt light source would emit one millijoule of energy, or 10^{-3} J . Each 633-nm photon has an energy of

$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{633 \text{ nm}} = 1.96 \text{ eV,}$$

so the total number of photons emitted in one second would be

$$N = \frac{10^{-3} \text{ J}}{1.96 \text{ eV}} \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) = 3.18 \times 10^{15},$$

or about three quadrillion.

Problem A.2. (Photoelectric effect.)

- a) A voltage reading of 0.8 V implies a maximum electron kinetic energy of 0.8 eV. On the other hand, a 400-nm photon has an energy of

$$E_{\text{photon}} = hf = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{400 \text{ nm}} = 3.1 \text{ eV}.$$

So of the total of 3.1 eV of energy absorbed by each electron, at most 0.8 eV remains when the electron has escaped from the metal. The remaining energy, 2.3 eV, must have gone into getting the electron out of the metal in the first place; this is the “work function.”

- b) A 300-nm photon has an energy in eV of $1240/300 = 4.13$. Subtract off the work function of 2.3 eV, and the electron should still have a kinetic energy of 1.83 eV upon leaving the cathode. Therefore the voltage can now build up to 1.83 V before the electrons can no longer cross to the anode. With 500-nm photons, on the other hand, the energy per photon in eV is $1240/500 = 2.48$; subtract 2.3 eV and we obtain only 0.18 eV for the maximum electron kinetic energy, so the voltage can now build up to only 0.18 V. Finally, since the energy of a 600-nm photon in eV is only $1240/600 = 2.07$, and this is less than the work function, an electron that absorbs such a photon cannot escape from the cathode at all. Therefore there is no flow of electrons to the anode and the voltage will remain at zero.

Problem A.3. For a photon,

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda},$$

where the first equality comes from the ultra-relativistic energy-momentum relation, the second equality follows from the Einstein relation, and the third equality is simply a consequence of the relation between frequency and wavelength (wave speed = wavelength/period = λf).

Problem A.4. The relativistic definitions of energy and momentum are usually written as

$$E = \frac{mc^2}{\sqrt{1 - (v/c)^2}}; \quad \vec{p} = \frac{mv\vec{v}}{\sqrt{1 - (v/c)^2}}.$$

Dividing the magnitude of the momentum by the energy, we therefore have

$$\frac{|\vec{p}|}{E} = \frac{m|\vec{v}|}{mc^2} = \frac{|\vec{v}|}{c^2}$$

for any particle. But for a particle traveling at the speed of light, $|\vec{v}| = c$, so

$$\frac{|\vec{p}|}{E} = \frac{c}{c^2} = \frac{1}{c}, \quad \text{or} \quad E = |\vec{p}|c.$$

Problem A.5. 10,000 eV is much less than the electron's rest energy (mc^2) of 511,000 eV, so we can use the nonrelativistic formula for kinetic energy, $K = \frac{1}{2}mv^2 = p^2/2m$. Therefore the momentum is

$$p = \sqrt{2mK} = \sqrt{2(9.11 \times 10^{-31} \text{ kg})(10^4 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})} = 5.4 \times 10^{-23} \text{ kg m/s.}$$

The wavelength of these electrons is therefore

$$\lambda = \frac{h}{p} = \frac{6.63 \times 10^{-34} \text{ J s}}{5.4 \times 10^{-23} \text{ kg m/s}} = 1.23 \times 10^{-11} \text{ m} = 0.0123 \text{ nm,}$$

roughly ten times smaller than an atom.

Problem A.6. As with light waves, the bright bands in a two-slit electron interference pattern occur where

$$d \sin \theta = n\lambda,$$

where d is the slit spacing, θ is the angle measured from straight ahead, and n is any integer. In this experiment, the angles are very small, so $\sin \theta \approx \tan \theta$. Setting $n = 1$, we then have

$$\lambda = d \tan \theta = (6 \times 10^{-6} \text{ m}) \frac{100 \text{ nm}}{16 \text{ cm}} = 0.00375 \text{ nm.}$$

The electrons' kinetic energy was therefore

$$K = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{(hc)^2}{2(mc^2)\lambda^2} = \frac{(1240 \text{ eV nm})^2}{2(511,000 \text{ eV})(0.00375 \text{ nm})^2} = 107,000 \text{ eV,}$$

or in round numbers, 100 keV. The voltage used to accelerate the electrons was therefore about 100 kilovolts. (Notice that I've used the trick of multiplying and dividing by c^2 , which allows me to work entirely in terms of eV's and nanometers. This trick is handy whenever you already know the rest energy, mc^2 , in eV.)

Problem A.7. (Wavelengths of other particles.)

- a) For a 1-eV neutron,

$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{h}{\sqrt{2mK}} = \frac{6.63 \times 10^{-34} \text{ J s}}{\sqrt{2(1.67 \times 10^{-27} \text{ kg})(1 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})}} \\ &= 2.9 \times 10^{-11} \text{ m} = 0.029 \text{ nm,} \end{aligned}$$

somewhat smaller than the diameter of an atom.

- b) Let's say the baseball has a mass of 0.25 kg and a speed of 40 m/s. Then its de Broglie wavelength would be

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{(0.25 \text{ kg})(40 \text{ m/s})} = 6.63 \times 10^{-35} \text{ m} \approx 7 \times 10^{-20} \text{ fm.}$$

That's more than a billion billion times smaller than an atomic nucleus. To observe diffraction effects, however, we normally need to make waves pass through or around objects whose sizes are comparable to the wavelength (or measure small angles that are of the order of the ratio of the wavelength to the object size). Baseball bats are enormously larger than baseball wavelengths, and for that matter, the physical size of the ball is also enormously larger than its wavelength, so diffraction effects are going to be utterly unmeasurable.

Problem A.8. (Mathematical properties of definite-momentum wavefunctions.)

- a) A sine or cosine function of kx goes through one complete oscillation when $kx = 2\pi$. A complete oscillation is one wavelength, so at this point, $x = \lambda$ and therefore $k = 2\pi/\lambda$. But $\lambda = h/p$, so finally, $k = 2\pi p/h$.
- b) The probability of finding the particle at any x value is proportional to

$$|\Psi(x)|^2 = (\text{Re } \Psi)^2 + (\text{Im } \Psi)^2 = (A \cos kx)^2 + (A \sin kx)^2 = A^2[\cos^2 kx + \sin^2 kx] = A^2,$$

which is a constant, independent of x .

- c) The total probability of finding the particle *somewhere* must be 100%, or 1. But the total area under the graph of $|\Psi|^2$ is A^2 times the width of the range of x values over which the formula holds. If this width is infinite, then A^2 must be infinitesimal in order for the area to be finite.

- d) Just calculate the derivative:

$$\frac{d\Psi}{dx} = A \frac{d}{dx}(\cos kx + i \sin kx) = A(-k \sin kx + ik \cos kx) = Aik(\cos kx + i \sin kx) = ik\Psi,$$

where I've used the fact that $i^2 = -1$ in the second-to-last step.

- e) According to the usual rules for differentiation,

$$\frac{d}{dx}(Ae^{ikx}) = A \frac{d}{dx}(e^{ikx}) = Aike^{ikx} = ik(Ae^{ikx}),$$

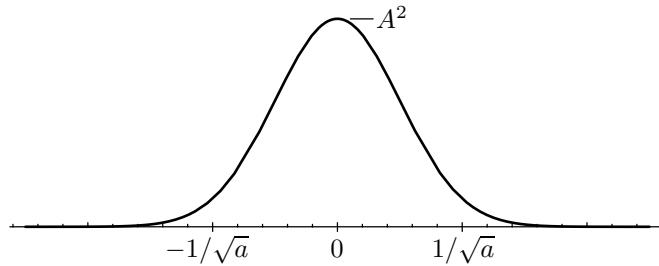
so the function Ae^{ikx} obeys the same differential equation as in part (d).

Problem A.9. (A Gaussian wavepacket.)

- a) The square modulus of $\Psi(x)$ is

$$\begin{aligned} (\text{Re } \Psi)^2 + (\text{Im } \Psi)^2 &= [A(\cos k_0 x)e^{-ax^2}]^2 + [A(\sin k_0 x)e^{-ax^2}]^2 \\ &= A^2 e^{-2ax^2} (\cos^2 k_0 x + \sin^2 k_0 x) = A^2 e^{-2ax^2}. \end{aligned}$$

This is a simple Gaussian function:



- b) The total probability of finding the particle at some x must equal 1. Therefore,

$$1 = \int_{-\infty}^{\infty} |\Psi(x)|^2 dx = A^2 \int_{-\infty}^{\infty} e^{-2ax^2} dx = A^2 \sqrt{\frac{\pi}{2a}},$$

according to equation B.6. Solving for A gives

$$A^2 = \sqrt{\frac{2a}{\pi}}, \quad \text{or} \quad A = \left(\frac{2a}{\pi}\right)^{1/4}.$$

(Technically, A could be negative or even complex, but such generality is not necessary in this problem.)

- c) The average value of x^2 is

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2 |\Psi|^2 dx = A^2 \int_{-\infty}^{\infty} x^2 e^{-2ax^2} dx = A^2 \cdot \frac{1}{2} \sqrt{\frac{\pi}{(2a)^3}} = \frac{1}{2} \sqrt{\frac{2a}{\pi}} \sqrt{\frac{\pi}{(2a)^3}} = \frac{1}{4a},$$

where I've used equation B.8 to evaluate the integral. Meanwhile, because $|\Psi(x)|^2$ is centered on $x = 0$ and symmetrical, $\overline{x} = 0$. Therefore the standard deviation is

$$\Delta x = \sqrt{\overline{x^2} - (\overline{x})^2} = \sqrt{\overline{x^2}} = \sqrt{\frac{1}{4a}} = \frac{1}{2\sqrt{a}}.$$

- d) For our wavepacket,

$$\tilde{\Psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{ikx} A e^{ik_0 x} e^{-ax^2} dx = \frac{A}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2 - i(k - k_0)x} dx.$$

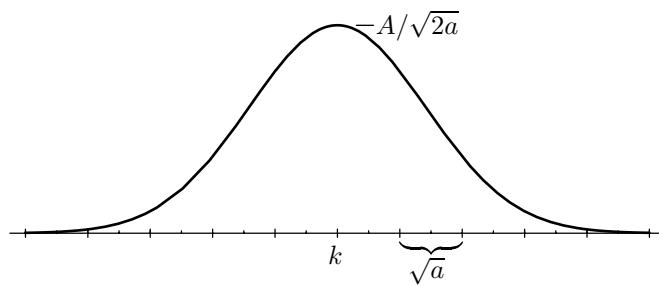
To evaluate this integral, we can complete the square in the exponent:

$$\begin{aligned} ax^2 - i(k - k_0)x &= a \left[x^2 + \frac{i(k - k_0)}{a} x + \left(\frac{i(k - k_0)}{2a} \right)^2 \right] + a \left(\frac{i(k - k_0)}{2a} \right)^2 \\ &= a \left[x + \frac{i(k - k_0)}{2a} \right]^2 - \frac{(k - k_0)^2}{4a}. \end{aligned}$$

Changing variables to $y = x + i(k - k_0)/2a$, we then have

$$\tilde{\Psi}(k) = \frac{A}{\sqrt{2\pi}} e^{-(k - k_0)^2/4a} \int_{-\infty}^{\infty} e^{-ay^2} dy = \frac{A}{\sqrt{2\pi}} e^{-(k - k_0)^2/4a} \sqrt{\frac{\pi}{a}} = \frac{A}{\sqrt{2a}} e^{-(k - k_0)^2/4a}.$$

This is also a Gaussian function, centered on $k = k_0$:



- e) From the graph of $\tilde{\Psi}(k)$, you can see that the “width” of this function depends on a but not on k_0 ; therefore we can set $k_0 = 0$ to simplify the calculation of Δk . The average value of k^2 is then

$$\begin{aligned}\bar{k^2} &= \int_{-\infty}^{\infty} k^2 |\tilde{\Psi}(k)|^2 dk = \frac{A^2}{2a} \int_{-\infty}^{\infty} k^2 e^{-k^2/2a} dk = \frac{A^2}{2a} \cdot \frac{1}{2} \sqrt{\pi(2a)^3} = \frac{A^2}{2} \sqrt{2\pi a} \\ &= \frac{1}{2} \sqrt{\frac{2a}{\pi}} \sqrt{2\pi a} = a,\end{aligned}$$

where I've again used equation B.8 to evaluate the integral. With $k_0 = 0$, the average value of k is zero, so we have simply

$$\Delta k = \sqrt{\bar{k^2} - \bar{k}^2} = \sqrt{a - 0} = \sqrt{a}.$$

- f) Any wavenumber k corresponds to a momentum $p_x = \hbar k / 2\pi$, as shown in Problem A.8(a). The uncertainty in momentum is therefore

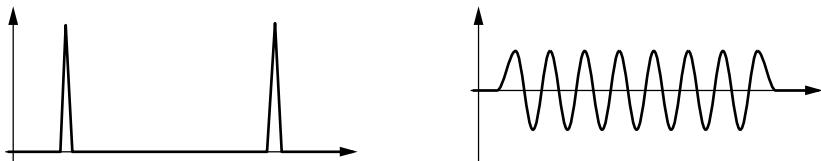
$$\Delta p_x = \frac{\hbar}{2\pi} \Delta k = \frac{\hbar}{2\pi} \sqrt{a}.$$

Multiplying by the result of part (c), we then have

$$(\Delta x)(\Delta p_x) = \frac{1}{2\sqrt{a}} \cdot \frac{h\sqrt{a}}{2\pi} = \frac{h}{4\pi},$$

which is the smallest possible value for this product, according to the uncertainty principle (equation A.7).

Problem A.10. There are many wavefunctions for which the product $(\Delta x)(\Delta p_x)$ is much greater than $h/4\pi$. Here are two examples:

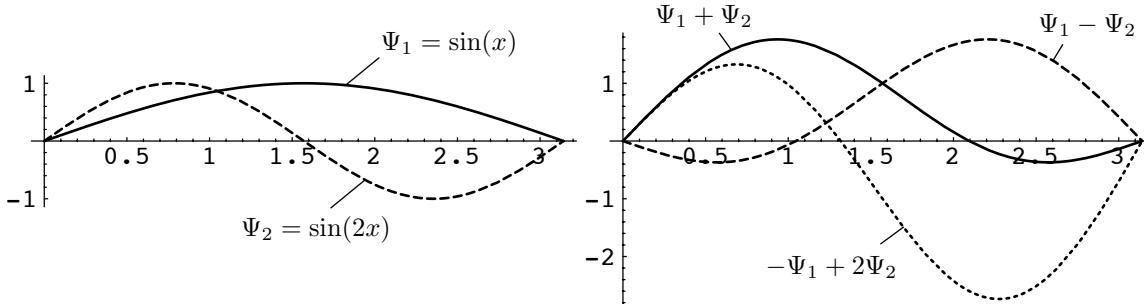


In the first example, Δx is of the order of the separation distance between the spikes. Meanwhile, since a spike is not a periodic function, its Fourier transform must contain contributions from k values up to the order of 1 over the width of the spike. The same is true for a pair of spikes, so Δp_x is of order \hbar over the spike width. The product $(\Delta x)(\Delta p_x)$ is therefore of order \hbar times the ratio of the separation distance to the spike width, and this ratio can be as large as we like. In the second example, we have an approximately sinusoidal function over a width of several wavelengths. Here, Δx is roughly the full width of the function. If this function had a corresponding imaginary part, a quarter-cycle out of phase with the real part, then Δp_x would be quite small. But if there is no imaginary part, then $|p_x|$ is fairly well defined, but p_x could be positive or negative, and this makes Δp_x quite large, of order $p_x = \hbar/\lambda$. The product $(\Delta x)(\Delta p_x)$ is therefore of order \hbar times the number of waves, and this number can be as large as we like.

Problem A.11. Some nontrivial linear combinations of Ψ_1 and Ψ_2 would be

$$\sin x + \sin 2x, \quad \sin x - \sin 2x, \quad \sin x + 2 \sin 2x.$$

Here are the graphs of these functions:



Problem A.12. For a one-dimensional box of length L , the minimum energy is $E_1 = h^2/8mL^2$. Setting $L = 10^{-15}$ m and m equal to the proton's mass, we obtain

$$E_1 = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8(1.67 \times 10^{-27} \text{ kg})(10^{-15} \text{ m})^2} = 3.3 \times 10^{-11} \text{ J} = 200 \text{ MeV}.$$

For a three-dimensional cube-shaped box, the energy would be three times this, or about 600 MeV. This is almost comparable to the rest energy of the proton, so we can barely get away with using the nonrelativistic formula $E = p^2/2m$. However, the diameter of an atomic nucleus is actually somewhat larger than this, so typical kinetic energies of nucleons inside nuclei are actually somewhat less. Furthermore, this kinetic energy is compensated by a large negative potential energy, due to the strong nuclear force. The net binding energy per nucleon in most nuclei is only about 8 MeV.

Problem A.13. (Ultrarelativistic particles in boxes.)

- a) As in the nonrelativistic case, an integer number of half-wavelengths must equal the length of the box: $n\lambda/2 = L$, where n is any positive integer. Solving for λ gives $\lambda = 2L/n$, which implies $p = h/\lambda = hn/2L$, the same as for a nonrelativistic particle. The only difference in the ultrarelativistic case is that $E = pc$, so we now have simply $E = hc n/2L$.
- b) For an electron in a one-dimensional box of width 10^{-15} m, the lowest possible energy ($n = 1$) would be

$$E_1 = \frac{hc}{2L} = \frac{1240 \text{ eV nm}}{2(10^{-6} \text{ nm})} = 6 \times 10^8 \text{ eV} = 600 \text{ MeV}.$$

(Here I've used the numerical value of hc derived in Problem A.1(a).) This is more than 1000 times greater than an electron's rest energy, so the ultrarelativistic formula $E = pc$ is quite appropriate. Furthermore, this energy is about three times larger than the energy of a proton confined to the same volume (as calculated in the previous problem). In order for electrons to reside inside nuclei but not contribute significantly

to the masses of nuclei, this zero-point energy would have to be compensated, to very high accuracy, by some kind of negative potential energy. While such a precise cancelation isn't impossible, it seems highly unlikely.

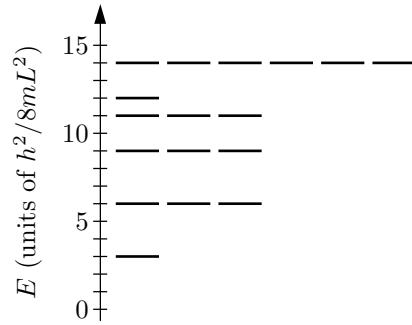
- c) As computed in part (b), a massless particle confined inside a one-dimensional box of width 10^{-15} m has a zero-point energy of 600 MeV. Three such particles (all in the same spatial wavefunction) would have a total energy of 1800 MeV or 1.8×10^9 eV. In joules, that's 2.9×10^{-10} J. The corresponding mass is therefore

$$m = \frac{E}{c^2} = \frac{2.9 \times 10^{-10} \text{ J}}{(3 \times 10^8 \text{ m/s})^2} = 3.2 \times 10^{-27} \text{ kg.}$$

This is of the same order of magnitude as the measured mass of the proton and neutron, so this model is quite plausible. However, it's only an order-of-magnitude estimate; I've neglected the three-dimensional nature of the "box" as well as the negative potential energy that holds the quarks together.

Problem A.14. The allowed energies, in units of $\hbar^2/8mL^2$, are $n_x^2 + n_y^2 + n_z^2$, where each of the three n 's is a positive integer. To obtain energies of less than 15 units, we need to list all combinations of three positive integers whose squares add up to less than 15. The table below shows all these combinations and a few more, just to check that we've found them all. Those that add up to less than 15 energy units are plotted in the graph at right.

n 's	$\sum n^2$	Degeneracy
1,1,1	3	1
1,1,2	6	3
1,1,3	11	3
1,1,4	18	3
1,2,2	9	3
1,2,3	14	6
1,3,3	19	3
2,2,2	12	1
2,2,3	17	3



If you squint at the graph a bit, you can see that the average density of states is increasing as you go upward. This trend continues at higher energies, where the average number of states per unit energy goes as the square root of the energy, as shown in Section 7.3.

Problem A.15. (Vibrational states of CO.)

- a) For this vibrational frequency, the spacing between the energy levels is

$$\hbar f = (4.14 \times 10^{-15} \text{ eV s})(6.4 \times 10^{13} \text{ s}^{-1}) = 0.265 \text{ eV.}$$

So if we take the ground state to have energy zero, the next four states would have energies 0.26 eV, 0.53 eV, 0.79 eV, and 1.06 eV. If we also include the zero-point energy, then all five levels get shifted up by 0.13 eV.

- b) To excite a CO molecule from the ground state to the next-lowest vibrational state, we need an energy of 0.265 eV. A photon with this energy would have a wavelength of

$$\lambda = \frac{c}{f} = \frac{hc}{\hbar f} = \frac{1240 \text{ eV nm}}{0.265 \text{ eV}} = 4700 \text{ nm} = 4.7 \text{ m,}$$

in the infrared.

Problem A.16. (Vibrational spectrum of N₂.)

- a) The transition between the lowest vibrational states of the two electronic states emits light with a wavelength of about 337 nm. The difference in energy between these states is therefore the energy of a photon with this wavelength,

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{337 \text{ nm}} = 3.68 \text{ eV.}$$

This ΔE does include the difference in the zero-point energies, $\frac{1}{2}h\Delta f$, between the two states, but it doesn't include any other vibrational energy.

- b) Consider the 0 → 1 transition, at a wavelength of 357 nm. The energy of this transition is

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{357 \text{ nm}} = 3.47 \text{ eV,}$$

which is 0.21 eV less than the 0 → 0 transition. Therefore, the first excited vibrational state of the lower electronic level must lie above the ground state by 0.21 eV. Similarly, for the 1 → 0 transition at 316 nm,

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{316 \text{ nm}} = 3.92 \text{ eV,}$$

which is 0.24 eV greater than the 0 → 0 transition. Therefore, the first excited vibrational state of the upper electronic level must lie above the (upper) ground state by 0.24 eV. Apparently, the units of vibrational energy are slightly larger for the upper electronic level than for the lower; this implies that the upper level vibrates at a higher frequency, due to a “stiffer spring” holding the atoms together.

- c) For the 2 → 0 transition at 298 nm,

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{298 \text{ nm}} = 4.17 \text{ eV,}$$

while for the 2 → 1 transition at 313 nm,

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{313 \text{ nm}} = 3.96 \text{ eV.}$$

The difference between these energies again represents the difference between the two lowest levels of the lower electronic state, and again this difference is 0.21 eV. Similarly, for the 0 → 3 transition at 406 nm,

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{406 \text{ nm}} = 3.05 \text{ eV,}$$

while for the 1 → 3 transition at 376 nm,

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{376 \text{ nm}} = 3.30 \text{ eV.}$$

The difference between these energies, which is the spacing between the two lowest levels of the upper electronic state, is again 0.24 eV.

- d) The splitting within each group of lines occurs because the vibrational levels of one electronic state are farther apart than those of the other. If the level spacing were perfectly uniform within each electronic level, however, the splitting between adjacent lines would be exactly the same in all cases. (Here I'm referring to the splitting in energy, not wavelength. However, a uniform energy spacing would lead to an approximately uniform wavelength spacing over narrow ranges of wavelengths.) As a numerical example, let's take the $3 \rightarrow 5$ transition at 367 nm, which has an energy of

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{367 \text{ nm}} = 3.38 \text{ eV},$$

and the $3 \rightarrow 6$ transition at 389 nm, with

$$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{389 \text{ nm}} = 3.19 \text{ eV}.$$

The difference between these two energies is only 0.19 eV, so levels 5 and 6 must be somewhat closer in energy than levels 1 and 2 (which are separated by 0.21 eV).

- e) The frequency of oscillation of the lower electronic state is roughly

$$f = \frac{E}{h} = \frac{0.21 \text{ eV}}{4.14 \times 10^{-15} \text{ eV s}} = 5.1 \times 10^{13} \text{ Hz}.$$

If we had a single nitrogen atom attached by a spring to a fixed point, then the frequency would be related to the spring constant by $f = (1/2\pi)\sqrt{k_s/m}$, so this frequency would imply

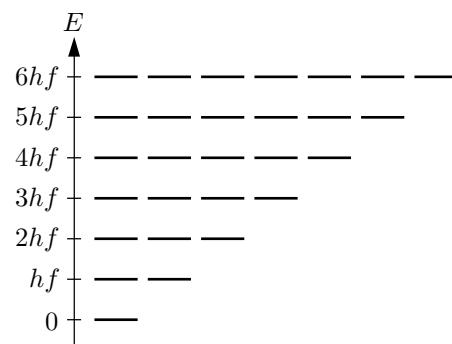
$$k_s = m(2\pi f)^2 = (14 \cdot 1.66 \times 10^{-27} \text{ kg})(2\pi \cdot 5.1 \times 10^{13} \text{ s}^{-1})^2 = 2400 \text{ N/m}.$$

However, in this case the fixed point is actually the midpoint between the two molecules, which we can think of as the midpoint of the spring. Because the two molecules are moving symmetrically, the *full* spring must stretch twice as far for a given force. Therefore its spring constant (force per unit stretch) is only half as much, 1200 N/m.

Problem A.17. Neglecting the zero-point energies of both one-dimensional oscillators, the allowed energies would simply be

$$E = hfq_x + hfq_y = hf(q_x + q_y) = hfq,$$

where q_x and q_y are nonnegative integers, and therefore q is any nonnegative integer. (Including the zero-point energies would shift all the levels up by another hf .) The degeneracy of level q is just the number of ways of writing q as the sum of two non-negative integers, that is, the number of ways of allocating q units of energy among two oscillators. Since we can put anywhere from zero to q units into the x oscillator, and the rest go into y , the number of different allocations is simply $q + 1$. The energy level diagram is shown at right.



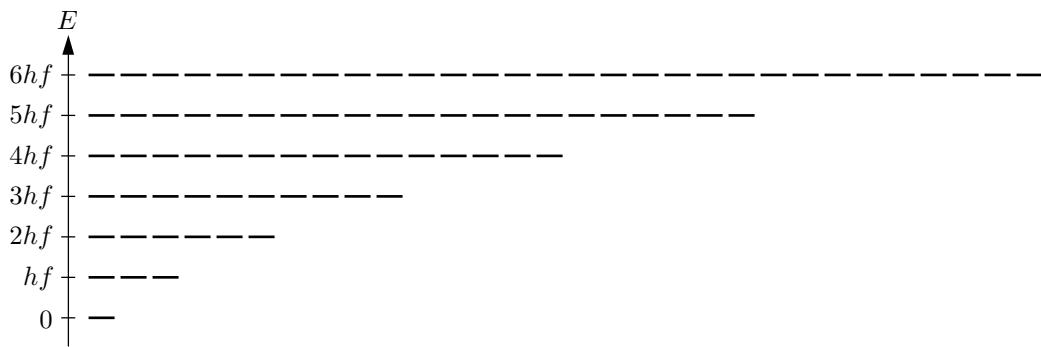
Problem A.18. For an isotropic three-dimensional oscillator, the allowed energies would be

$$E = hfq_x + hfq_y + hfq_z = hfq,$$

where the q 's are all nonnegative integers. (Again I am neglecting the zero-point energies. Adding these in would shift all the levels upward by $\frac{3}{2}hf$.) The degeneracy of level q is equal to the number of ways of allocating q units of energy among three oscillators. If we think of this system as an Einstein solid with $N = 3$, we can borrow the multiplicity formula (and its derivation) from page 55:

$$\text{degeneracy} = \binom{q+3-1}{q} = \binom{q+2}{q} = \frac{(q+2)!}{(q!)(2!)} = \frac{(q+2)(q+1)}{2}.$$

Starting with $q = 0$, the degeneracies of the first few levels are therefore 1, 3, 6, 10, 15, 21, 28, as listed in Figure 2.4. Here's the energy level diagram:



Problem A.19. For the $2 \rightarrow 1$ transition in hydrogen, the energy of the photon emitted is

$$E_{\text{ph}} = E_2 - E_1 = (-13.6 \text{ eV}) \left(\frac{1}{2^2} - \frac{1}{1^2} \right) = (13.6 \text{ eV}) \left(1 - \frac{1}{4} \right) = 10.2 \text{ eV},$$

and the wavelength is $hc/E_{\text{ph}} = (1240 \text{ eV nm})/(10.2 \text{ eV}) = 122 \text{ nm}$. Similarly, for the $3 \rightarrow 2$ transition,

$$E_{\text{ph}} = E_3 - E_2 = (-13.6 \text{ eV}) \left(\frac{1}{3^2} - \frac{1}{2^2} \right) = (13.6 \text{ eV}) \left(\frac{1}{4} - \frac{1}{9} \right) = 1.89 \text{ eV},$$

and the wavelength is $(1240/1.89) \text{ nm} = 656 \text{ nm}$. For the $4 \rightarrow 2$ transition,

$$E_{\text{ph}} = E_4 - E_2 = (-13.6 \text{ eV}) \left(\frac{1}{4^2} - \frac{1}{2^2} \right) = (13.6 \text{ eV}) \left(\frac{1}{4} - \frac{1}{16} \right) = 2.55 \text{ eV},$$

and the wavelength is $(1240/2.55) \text{ nm} = 486 \text{ nm}$. Finally, for the $5 \rightarrow 2$ transition,

$$E_{\text{ph}} = E_5 - E_2 = (-13.6 \text{ eV}) \left(\frac{1}{5^2} - \frac{1}{2^2} \right) = (13.6 \text{ eV}) \left(\frac{1}{4} - \frac{1}{25} \right) = 2.86 \text{ eV},$$

and the wavelength is $(1240/2.86) \text{ nm} = 434 \text{ nm}$. (The last three wavelengths are all in the visible range, and make up the first three lines of the “Balmer series.” The $2 \rightarrow 1$ transition, on the other hand, produces an ultraviolet photon, the first in the “Lyman series.”)

Problem A.20. To get an integer number of full wavelengths along a path of length $2\pi r$, we must have $n\lambda = 2\pi r$ for some integer n . The allowed wavelengths are then $\lambda = 2\pi r/n$, and the allowed momenta are $p = h/\lambda = hn/2\pi r$. For a circular orbit, the angular momentum is just rp , so the allowed angular momentum values would be $hn/2\pi$, that is, integer multiples of \hbar . Although this “derivation” is pretty shy, it does give the correct prediction for the values of L_z (or any other component of \vec{L}).

Problem A.21. The general rules for a hydrogen atom are that n can be any positive integer, and ℓ must be strictly less than n . Furthermore, for any system, the quantum number m can range from $-\ell$ to ℓ in integer steps. According to these rules, here are the allowed sets of quantum numbers for hydrogen wavefunctions, up to $n = 3$:

$n :$	1	2	2	2	3	3	3	3	3	3	3	3
$\ell :$	0	0	1	1	0	1	1	1	2	2	2	2
$m :$	0	0	1	0	1	0	1	0	1	0	1	2

Notice that there is one state with $n = 1$, while there are $2^2 = 4$ states with $n = 2$ and $3^2 = 9$ states with $n = 3$.

Problem A.22. (Rotation of CO molecules.)

- a) For a transition from $j = 0$ to $j = 1$, the energy required is 2ϵ and therefore the frequency should be

$$f = \frac{E_{\text{photon}}}{h} = \frac{2\epsilon}{h} = \frac{2(0.00024 \text{ eV})}{4.14 \times 10^{-15} \text{ eV s}} = 1.16 \times 10^{11} \text{ Hz},$$

or 116 GHz. A transition from $j = 1$ to $j = 2$, on the other hand, requires twice this much energy (since the $j = 2$ level has energy 6ϵ), so the frequency would have to be 232 GHz.

- b) Since $\epsilon = \hbar^2/2I$, we have

$$I = \frac{\hbar^2}{2\epsilon} = \frac{\hbar^2}{8\pi^2\epsilon} = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8\pi^2(0.00024 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})} = 1.45 \times 10^{-46} \text{ kg m}^2.$$

- c) The oxygen nucleus in the CO molecule has $4/3$ the mass of the carbon nucleus, so it should be $3/4$ as far from the molecule’s center of mass. If the bond length is b , then the distance of the oxygen from the center of mass is $3b/7$, while the distance of the carbon from the center of mass is $4b/7$. The moment of inertia about the center of mass is the sum over masses of $m_i r_i^2$, so for this atom,

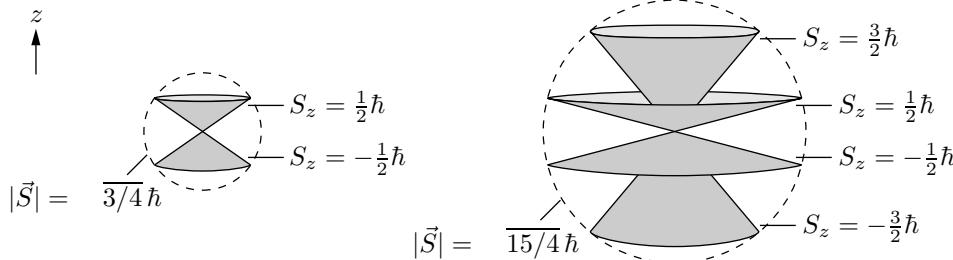
$$I = m_C r_C^2 + m_O r_O^2 = m_C \left(\frac{4b}{7}\right)^2 + \frac{4}{3} m_C \left(\frac{3b}{7}\right)^2 = m_C b^2 \left(\frac{16+12}{49}\right) = \frac{4}{7} m_C b^2.$$

Solving for b then gives

$$b = \sqrt{\frac{7I}{4m_C}} = \sqrt{\frac{7(1.45 \times 10^{-46} \text{ kg m}^2)}{4 \cdot 12(1.66 \times 10^{-27} \text{ kg})}} = 1.13 \times 10^{-10} \text{ m},$$

or 1.13 ångstroms, a very reasonable result.

Problem A.23. For $s = 1/2$, the z component of the spin vector is $\pm\hbar/2$, while the magnitude of the spin vector is $\sqrt{3/4}\hbar = (0.87)\hbar$. The opening angle of the cone should therefore be $\cos^{-1}(0.5/0.87) = 55^\circ$, as shown below (left). For $s = 3/2$, the z component of the spin can be $\pm 3\hbar/2$ or $\pm\hbar/2$, and the magnitude of the spin is $\sqrt{15/4}\hbar = (1.94)\hbar$; the corresponding cones are shown below (right).



Problem A.24. (The cosmological constant.)

- a) The total zero-point energy of all modes in the box would be a triple-sum over mode number of $\frac{1}{2}hf$, multiplied by 2 to count the two polarization states for each mode:

$$U_0 = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \frac{1}{2} hf = \sum_{n_x, n_y, n_z} \epsilon,$$

where $\epsilon = hf$. As in equation 7.80, we can write ϵ as $hc n / 2L$, where $n = |\vec{n}|$. It's then convenient to convert the triple sum to an integral in spherical coordinates:

$$U_0 = \frac{\pi}{2} \int_0^\infty n^2 \frac{hc n}{2L} dn = \frac{\pi hc}{4L} \int_0^\infty n^3 dn,$$

where the factor of $\pi/2$ is from the angular integrals over the positive octant of n -space. Note that the integral diverges at its upper limit.

- b) The quantity $\ell_{\text{Pl}} = \sqrt{G\hbar/c^3}$ is numerically equal to

$$\sqrt{\frac{(6.67 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(6.63 \times 10^{-34} \text{ J s})/2\pi}{(3 \times 10^8 \text{ m/s})^3}} = 1.6 \times 10^{-35} \sqrt{\frac{\text{N m}^2 \text{ J s}^4}{\text{kg}^2 \text{ m}^3}}.$$

If we replace N with kg m/s^2 and J with $\text{kg m}^2/\text{s}^2$, then we find that the kilograms and seconds cancel, leaving us with units of $\sqrt{\text{m}^5/\text{m}^3} = \text{m}$.

- c) The allowed wavelengths are $\lambda = 2L/n$, so a wavelength of ℓ_{Pl} corresponds to a mode number of $n_{\text{max}} = 2L/\ell_{\text{Pl}}$. Cutting off our integral at this value, we obtain

$$U_0 = \frac{\pi hc}{4L} \int_0^{n_{\text{max}}} n^3 dn = \frac{\pi hc}{4L} \frac{n_{\text{max}}^4}{4} = \frac{\pi hc}{16L} \left(\frac{2L}{\ell_{\text{Pl}}}\right)^4 = \frac{\pi hc V}{\ell_{\text{Pl}}^4}.$$

Numerically, we have

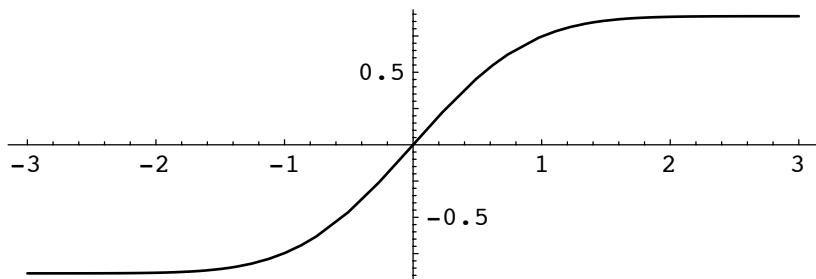
$$\frac{U_0}{V} = \frac{\pi(6.63 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m/s})}{(1.6 \times 10^{-35} \text{ m})^4} = 9.2 \times 10^{114} \text{ J/m}^3,$$

larger than the observational limit by a factor of 10^{122} . Dividing by c^2 gives a mass density of $1.0 \times 10^{98} \text{ kg/m}^3$, about 10^{95} times greater than that of ordinary matter.

B Mathematical Results

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Problem B.1. An antiderivative of the function e^{-x^2} should be a function whose slope has the following properties: positive everywhere; largest, and equal to 1, at $x = 0$; and asymptotically tending to zero as $x \rightarrow \pm\infty$. Furthermore, the function should differ in value by $\sqrt{\pi}$ between $x = -\infty$ and $x = \infty$. Here's a graph of such a function, with the value arbitrarily set to zero at $x = 0$:



Problem B.2. Differentiating equation B.8 with respect to a gives

$$\begin{aligned} \int_0^\infty x^2 \frac{d}{da}(e^{-ax^2}) dx &= \frac{1}{4}\sqrt{\pi} \frac{d}{da}(a^{-3/2}) \\ \Rightarrow \quad \int_0^\infty x^2(-x^2)e^{-ax^2} dx &= \frac{1}{4}\sqrt{\pi} \left(-\frac{3}{2}\right) a^{-5/2}. \end{aligned}$$

Canceling the minus signs then gives

$$\int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{8}\sqrt{\frac{\pi}{a^5}}.$$

Problem B.3. (Gaussian integrals with odd powers of x .)

- a) Since the integrand xe^{-ax^2} is an odd function of x , its integral from $-\infty$ to ∞ must equal zero: For every positive contribution to the integral from positive x , there is an equal and opposite negative contribution from the corresponding negative x .
- b) If we substitute $u = ax^2$, then $du = 2ax dx$, so

$$\int xe^{-ax^2} dx = -\frac{1}{2a} \int e^u du = -\frac{1}{2a} e^u = -\frac{1}{2a} e^{-ax^2}.$$

c)

$$\int_0^\infty xe^{-ax^2} dx = \left. -\frac{1}{2a}e^{-ax^2} \right|_0^\infty = -\frac{1}{2a} [0 - 1] = \frac{1}{2a}.$$

d) Differentiating the previous result with respect to a , we have

$$\begin{aligned} \int_0^\infty x \frac{d}{da}(e^{-ax^2}) dx &= \frac{1}{2} \frac{d}{da}(a^{-1}) \\ \Rightarrow \int_0^\infty x(-x^2)e^{-ax^2} dx &= \frac{1}{2}(-1)a^{-2}. \end{aligned}$$

Canceling the minus sign then gives

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}.$$

Problem B.4. With the substitution $s = t^2$, $t = s^{1/2}$, $dt = \frac{1}{2}s^{-1/2}ds$, our integral becomes

$$\int_x^\infty e^{-t^2} dt = \frac{1}{2} \int_{x^2}^\infty s^{-1/2} e^{-s} ds.$$

When $x \gg 1$, this integral is dominated by the region near its lower limit. Expanding $s^{-1/2}$ in a Taylor series about $s = x^2$ gives

$$\begin{aligned} s^{-1/2} &= (x^2)^{-1/2} + \left. \frac{d}{ds}(s^{-1/2}) \right|_{x^2} (s - x^2) + \frac{1}{2} \left. \frac{d^2}{ds^2}(s^{-1/2}) \right|_{x^2} (s - x^2)^2 + \\ &= (x^2)^{-1/2} - \frac{1}{2}(x^2)^{-3/2}(s - x^2) + \frac{3}{8}(x^2)^{-5/2}(s - x^2)^2 \\ &= \frac{1}{x} - \frac{1}{2x^3}(s - x^2) + \frac{3}{8x^5}(s - x^2)^2 - \frac{135}{(3!)2^3x^7}(s - x^2)^3 + \frac{1357}{(4!)2^4x^9}(s - x^2)^4, \end{aligned}$$

so we can obtain an approximate expression for the integral if we can evaluate integrals of $(s - x^2)^n e^{-s}$. Changing variables to $r = s - x^2$, we have

$$\int_{x^2}^\infty (s - x^2)^n e^{-s} ds = e^{-x^2} \int_0^\infty r^n e^{-r} dr = e^{-x^2} n!,$$

by equation B.11. Our original integral is therefore

$$\begin{aligned} \int_x^\infty e^{-t^2} dt &= \frac{1}{2} \left[\frac{1}{x} e^{-x^2} (0!) - \frac{1}{2x^3} e^{-x^2} (1!) + \frac{3}{8x^5} e^{-x^2} (2!) - \frac{135}{(3!)2^3x^7} e^{-x^2} + \frac{1357}{(4!)2^4x^9} e^{-x^2} \right] \\ &= e^{-x^2} \left[\frac{1}{2x} - \frac{1}{4x^3} + \frac{3}{8x^5} - \frac{135}{24x^7} + \frac{1357}{25x^9} \right]. \end{aligned}$$

If we number the terms starting with zero, then the ratio of the n th term to the previous one is $(2n-1)/2x^2$. When x is large and n is small, this ratio is quite small so the series appears to be converging. But for any fixed x , there will eventually be a term where n exceeds x^2 ; the terms then start to grow, so the series diverges.

Problem B.5. As in the previous problem, change variables to $s = t^2$:

$$\int_x^\infty t^2 e^{-t^2} dt = \frac{1}{2} \int_{x^2}^\infty s^{1/2} e^{-s} ds.$$

Now expand $s^{1/2}$ in a Taylor series about $s = x^2$:

$$\begin{aligned} s^{1/2} &= (x^2)^{1/2} + \frac{d}{ds}(s^{1/2})\Big|_{x^2}(s - x^2) + \frac{1}{2} \frac{d^2}{ds^2}(s^{1/2})\Big|_{x^2}(s - x^2)^2 + \\ &= (x^2)^{1/2} + \frac{1}{2}(x^2)^{-1/2}(s - x^2) - \frac{1}{8}(x^2)^{-3/2}(s - x^2)^2 \\ &= x + \frac{1}{2x}(s - x^2) - \frac{1}{8x^3}(s - x^2)^2 + \frac{1}{(3!)2^3x^5}(s - x^2)^3 - \frac{1}{(4!)2^4x^7}(s - x^2)^4. \end{aligned}$$

The integrals are the same as in the previous problem,

$$\int_{x^2}^\infty (s - x^2)^n e^{-s} ds = e^{-x^2} \int_0^\infty r^n e^{-r} dr = e^{-x^2} n!,$$

where $r = s - x^2$ and again I've used equation B.11. Assembling the pieces gives

$$\begin{aligned} \int_x^\infty t^2 e^{-t^2} dt &= \frac{1}{2} \left[xe^{-x^2}(0!) + \frac{1}{2x} e^{-x^2}(1!) - \frac{1}{8x^3} e^{-x^2}(2!) + \frac{1}{2^3 x^5} e^{-x^2} - \frac{1}{2^4 x^7} e^{-x^2} + \dots \right] \\ &= e^{-x^2} \left[\frac{x}{2} + \frac{1}{4x} - \frac{1}{8x^3} + \frac{1}{2^4 x^5} - \frac{1}{2^5 x^7} + \dots \right]. \end{aligned}$$

(You can also derive this result by integration by parts; see Problem B.6(b).)

Problem B.6. (The error function.)

a) By equation B.6,

$$\operatorname{erf}(\infty) = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-t^2} dt = \frac{2}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2} = 1,$$

while

$$\operatorname{erf}(-\infty) = \frac{2}{\sqrt{\pi}} \int_0^{-\infty} e^{-t^2} dt = -\frac{2}{\sqrt{\pi}} \int_0^\infty e^{-t^2} dt = -1.$$

b) Separate the integrand into the factors $(t)(te^{-t^2})$, then integrate by parts:

$$\int_0^x t^2 e^{-t^2} dt = (t) \left(-\frac{1}{2} e^{-t^2} \right) \Big|_0^x - \int_0^x (1) \left(-\frac{1}{2} e^{-t^2} \right) dt = -\frac{1}{2} x e^{-x^2} + \frac{\sqrt{\pi}}{4} \operatorname{erf} x.$$

c) Since we know the value of the integral from 0 to ∞ , we can write

$$\begin{aligned} \operatorname{erf} x &= \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-t^2} dt - \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt \\ &= 1 - \frac{2}{\sqrt{\pi}} e^{-x^2} \left[\frac{1}{2x} - \frac{1}{4x^3} + \frac{3}{8x^5} \right], \end{aligned}$$

where in the last step I've plugged in the asymptotic expansion from Problem B.4.

Problem B.7. To derive the recursion formula for the gamma function, just start with the definition and integrate by parts:

$$\begin{aligned} (n+1) &= \int_0^\infty x^n e^{-x} dx = (x^n)(-e^{-x}) \Big|_0^\infty - \int_0^\infty (nx^{n-1})(-e^{-x}) dx \\ &= 0 + n \int_0^\infty x^{n-1} e^{-x} dx = n \Gamma(n). \end{aligned}$$

Problem B.8. Starting from the definition and changing variables to $t = \sqrt{x}$, we have

$$\Gamma(\frac{1}{2}) = \int_0^\infty x^{-1/2} e^{-x} dx = \int_0^\infty (t^2)^{-1/2} e^{-t^2} (2t dt) = 2 \int_0^\infty e^{-t^2} dt = \sqrt{\pi},$$

by equation B.6. Therefore, by the recursion formula,

$$\Gamma(\frac{3}{2}) = \frac{1}{2} \Gamma(\frac{1}{2}) = \frac{1}{2} \sqrt{\pi}; \quad \Gamma(\frac{1}{2}) = \Gamma(\frac{1}{2}) / (\frac{1}{2}) = 2\sqrt{\pi}.$$

Problem B.9. To evaluate $\Gamma(\frac{1}{3})$, I gave *Mathematica* the instruction

```
NIntegrate[x^(-2/3) Exp[-x], {x, 0, Infinity}]
```

which returned 2.67894. Similarly, to evaluate $\Gamma(2/3)$, I typed

```
NIntegrate[x^(-1/3) Exp[-x], {x, 0, Infinity}]
```

and got the result 1.35412. According to the quoted identity, we should therefore have

$$(2.67894)(1.35412) = \frac{\pi}{\sin(\pi/3)}.$$

The right-hand side evaluates to $\pi/(\sqrt{3}/2) = 2\pi/\sqrt{3} = 3.62760$, while the left-hand side evaluates to 3.62761, equal within a bit of round-off error.

Problem B.10. Looking at Figure B.4, you can see that to include all of the last bar in the bar graph, the integral should go up to $n + \frac{1}{2}$ instead of n . At the lower end of the integral, the choice of 0 for the limit includes quite a bit of extra negative white space. We could do better by choosing 1 for the limit, but then there would be a bit too much positive white space. Still, there's no obvious better choice, so here goes:

$$\begin{aligned} \ln n! &\approx \int_1^{n+\frac{1}{2}} \ln x dx = (x \ln x - x) \Big|_1^{n+\frac{1}{2}} = [(n + \frac{1}{2}) \ln(n + \frac{1}{2}) - (n + \frac{1}{2})] - [1 \ln 1 - 1] \\ &= (n + \frac{1}{2}) \ln(n + \frac{1}{2}) - n + \frac{1}{2}. \end{aligned}$$

To compare this formula to Stirling's approximation, it's useful to expand the logarithm:

$$\ln(n + \frac{1}{2}) = \ln n + \ln\left(1 + \frac{1}{2n}\right) \approx \ln n + \frac{1}{2n}.$$

With this approximation,

$$\ln n! \approx (n + \frac{1}{2}) \left(\ln n + \frac{1}{2n} \right) \quad n + \frac{1}{2} = n \ln n + \frac{1}{2} \ln n - n + 1,$$

where I've dropped the term $1/4n$ since it's much smaller than any of the others. Exponentiating this expression now gives

$$n! \approx n^n n^{1/2} e^{-n} e^1 = n^n e^{-n} \sqrt{e^2 n}.$$

Comparing to equation B.16, we see that this expression is too large by a factor of $\sqrt{e^2/2\pi} = 1.084$. Still, we've improved greatly on equation B.18, by picking up the factor of \sqrt{n} (which came from the upper limit of the integral). In principle, a better choice of the lower limit could get rid of the 8.4% error, but I know of no way to find the right choice other than working backward from the desired answer.

Problem B.11. To find the maximum of the function $x^n e^{-x}$, just set its derivative equal to zero:

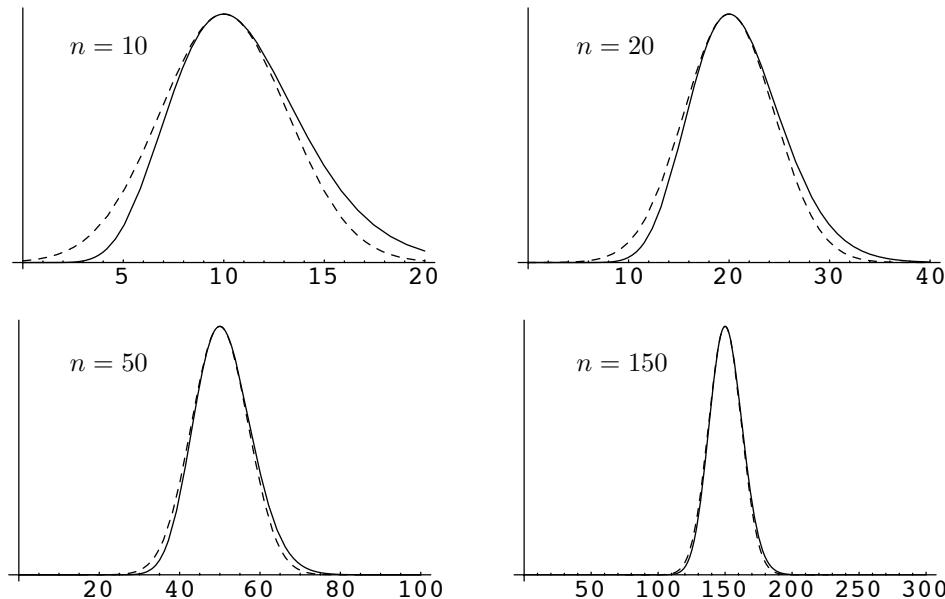
$$0 = \frac{d}{dx}(x^n e^{-x}) = nx^{n-1} e^{-x} + x^n(-e^{-x}) = nx^{n-1} e^{-x} - x^n e^{-x} = x^{n-1} e^{-x}(n-x).$$

The solutions are $x = 0$, $x = \infty$, and $x = n$. However, we know that this function is positive everywhere and goes to zero at $x = 0$ and $x = \infty$, so of the three solutions, the one at $x = n$ must be the maximum.

Problem B.12. To plot these functions I used the following *Mathematica* instructions:

```
n = 50;
Plot[{(x^n)*Exp[-x], (n^n)*Exp[-n]*Exp[-(x-n)^2/(2n)]},
      {x, 0, 2n}, PlotRange->All, Ticks->{Automatic, None}]
```

Changing n in the first line to 10, 20, 50, and 150 then produced the following plots:



In the plots I've kept the original function, $x^n e^{-x}$, as a solid line, and changed the Gaussian approximation to a dashed line. *Mathematica* gave overflow errors when I raised n above about 170. Notice that even for $n = 10$, the area under the Gaussian curve gives a good approximation to the area under the original curve. The fit improves further as n is increased. (For clarity, I've suppressed the scales on the vertical axes. The heights of the peaks, if you're curious, are of order 10^6 , 10^{17} , 10^{63} , and 10^{261} , respectively.)

Problem B.13. To improve upon Stirling's approximation, we need to take the expansion in equation B.22 to fourth order:

$$\ln\left(1 + \frac{y}{n}\right) \approx \frac{y}{n} - \frac{1}{2}\left(\frac{y}{n}\right)^2 + \frac{1}{3}\left(\frac{y}{n}\right)^3 - \frac{1}{4}\left(\frac{y}{n}\right)^4.$$

Plugging this expansion into equation B.21, we obtain

$$n \ln x - x \approx n \ln n - n - \frac{y^2}{2n} + \frac{y^3}{3n^2} - \frac{y^4}{4n^3}.$$

Exponentiating this expression gives

$$\begin{aligned} x^n e^{-x} &\approx n^n e^{-n} e^{-y^2/2n} e^{y^3/3n^2 - y^4/4n^3} \\ &= n^n e^{-n} e^{-y^2/2n} \left[1 + \left(\frac{y^3}{3n^2} - \frac{y^4}{4n^3} \right) + \frac{1}{2} \left(\frac{y^3}{3n^2} - \frac{y^4}{4n^3} \right)^2 \right]. \end{aligned}$$

In the second line I've expanded the exponential of the new terms in a Taylor series to second order. Now let's estimate the sizes of the various terms. When we integrate over y , the Gaussian function will cut off the integral at $y \sim \sqrt{n}$, so for the purpose of estimation, we can set $y = \sqrt{n}$. Then y^3/n^2 is of order $1/\sqrt{n}$, while y^4/n^3 is of order $1/n$, the size of the correction we are looking for. The next term in the original expansion of the logarithm would have given something proportional to y^5/n^4 , which would be of order $1/n^{3/2}$, so there's no need to keep this term. Furthermore, the next term in the Taylor expansion of the exponential would be of order $(1/\sqrt{n})^3$, also smaller than the desired correction. We can even drop the final y^4/n^3 term written in the last line above, since it becomes negligible when squared or when multiplied by y^3/n^2 . The remaining terms give

$$n! \approx n^n e^{-n} \int_{-\infty}^{\infty} e^{-y^2/2n} \left[1 + \frac{y^3}{3n^2} - \frac{y^4}{4n^3} + \frac{y^6}{18n^4} \right],$$

where I've extended the lower limit of the integral down to $-\infty$ as in equation B.24. The y^3 term in the brackets is an odd function, so it integrates to zero. To integrate the y^4 term, we can use the result of Problem B.2,

$$\int_0^{\infty} x^4 e^{-ax^2} dx = \frac{3\sqrt{\pi}}{8} a^{-5/2}.$$

And to integrate the y^6 term, we can differentiate this equation with respect to a to obtain

$$\int_0^{\infty} x^6 e^{-ax^2} dx = \frac{15\sqrt{\pi}}{16} a^{-7/2}.$$

Assembling all the terms, we finally have

$$\begin{aligned} n! &\approx n^n e^{-n} \left[\sqrt{2\pi n} - \frac{1}{4n^3} - \frac{3\sqrt{\pi}}{4} (2n)^{5/2} + \frac{1}{18n^4} - \frac{15\sqrt{\pi}}{8} (2n)^{7/2} \right] \\ &= n^n e^{-n} \sqrt{2\pi n} \left[1 - \frac{1}{4n^3} - \frac{3}{4} \cdot 4n^2 + \frac{1}{18n^4} - \frac{15}{8} \cdot 8n^3 \right] \\ &= n^n e^{-n} \sqrt{2\pi n} \left[1 - \frac{3}{4n} + \frac{5}{6n} \right] = n^n e^{-n} \sqrt{2\pi n} \left[1 + \frac{1}{12n} \right]. \end{aligned}$$

For $n = 1$, this improved version of Stirling's approximation gives $e^{-1}\sqrt{2\pi}(13/12) = 0.9990$, too small by only one part in a thousand. For $n = 10$, it gives $10^{10}e^{-10}\sqrt{20\pi}(121/120) = 3,628,684$, whereas $10! = 3,628,800$, so the approximation is too low by 0.003%.

Problem B.14. (Integration of $(\sin \theta)^n$ from 0 to π .)

- a) For $n = 0$, equation B.28 gives

$$\int_0^\pi 1 d\theta = \frac{\sqrt{\pi} \binom{1}{2}}{(1)}.$$

The left-hand side is simply π , while on the right-hand side, $\binom{1}{2} = \sqrt{\pi}$ (by Problem B.8) and $(1) = 1$. Therefore the identity holds. For $n = 1$, we have

$$\int_0^\pi \sin \theta d\theta = \frac{\sqrt{\pi} \binom{1}{2}}{(1)}.$$

Here the left-hand side is 2, while on the right-hand side, $\binom{3}{2} = \frac{1}{2}\sqrt{\pi}$. So the identity holds once again.

- b) Following the hint, for $n \geq 2$,

$$\begin{aligned} \int_0^\pi (\sin \theta)^n d\theta &= \int_0^\pi (\sin \theta)^{n-2} (1 - \cos^2 \theta) d\theta \\ &= \int_0^\pi (\sin \theta)^{n-2} d\theta - \int_0^\pi (\cos \theta) [(\cos \theta)(\sin \theta)^{n-2}] d\theta \\ &= \int_0^\pi (\sin \theta)^{n-2} d\theta - \left[(\cos \theta) \frac{(\sin \theta)^{n-1}}{n-1} \right]_0^\pi - \int_0^\pi (-\sin \theta) \frac{(\sin \theta)^{n-1}}{n-1} d\theta \\ &= \int_0^\pi (\sin \theta)^{n-2} d\theta - \frac{1}{n-1} \int_0^\pi (\sin \theta)^n d\theta. \end{aligned}$$

Taking the second term over to the left-hand side then gives

$$\left(1 + \frac{1}{n-1}\right) \int_0^\pi (\sin \theta)^n d\theta = \int_0^\pi (\sin \theta)^{n-2} d\theta.$$

The factor in parentheses is $n/(n-1)$, so we have

$$\int_0^\pi (\sin \theta)^n d\theta = \left(\frac{n-1}{n}\right) \int_0^\pi (\sin \theta)^{n-2} d\theta.$$

- c) In part (a) I showed that equation B.28 holds for $n = 0$ and $n = 1$. For any $n \geq 2$, we can then assume by induction that the equation holds for $n - 2$; the result of part (b) then implies

$$\int_0^\pi (\sin \theta)^n d\theta = \left(\frac{n-1}{n}\right) \frac{\sqrt{\pi} \left(\frac{n-2}{2} + \frac{1}{2}\right)}{\left(\frac{n-2}{2} + 1\right)} = \frac{\sqrt{\pi} \left(\frac{n}{2} - \frac{1}{2}\right) \left(\frac{n}{2} - \frac{1}{2}\right)}{\left(\frac{n}{2}\right) \left(\frac{n}{2}\right)} = \frac{\sqrt{\pi} \left(\frac{n}{2} + \frac{1}{2}\right)}{\left(\frac{n}{2} + 1\right)},$$

where in the last step I've used the recursion relation B.14 in both the numerator and the denominator. This establishes equation B.28 for any nonnegative integer n .

Problem B.15. (Alternative calculation of the area of a hypersphere.)

- a) Evaluating the integral in rectangular coordinates,

$$\int e^{-r^2} d^d x = \int e^{-x_1^2 - x_2^2 - \dots - x_d^2} dx_1 \dots dx_d = \left(\int e^{-x^2} dx \right)^d = (\sqrt{\pi})^d = \pi^{d/2}.$$

- b) Imagine breaking the integration volume into a series of concentric spherical shells. A shell of radius r and thickness dr has a volume (within the shell itself, not the region enclosed) of $A_d(r) dr$, so

$$\int e^{-r^2} d^d x = \sum_{\text{shells}} e^{-r^2} \text{ (volume of shell)} = \int_0^\infty e^{-r^2} A_d(r) dr.$$

By dimensional analysis, $A_d(r)$ must be proportional to r^{d-1} ; setting $r = 1$ tells us that the coefficient of proportionality is $A_d(1)$. Therefore,

$$\int e^{-r^2} d^d x = A_d(1) \int_0^\infty r^{d-1} e^{-r^2} dr.$$

- c) Change variables to $t = r^2$ (so $dt = 2r dr$, $r^{d-2} = t^{(d-2)/2}$), then use the definition (B.12) of the gamma function:

$$\int e^{-r^2} d^d x = \frac{1}{2} A_d(1) \int_0^\infty t^{(d-2)/2} e^{-t} dt = \frac{1}{2} A_d(1) \left(\frac{d-2}{2} + 1\right) = \frac{1}{2} A_d(1) \left(\frac{d}{2}\right).$$

Combining this result with the result of part (a) gives

$$\pi^{d/2} = \frac{1}{2} A_d(1) \left(\frac{d}{2}\right), \quad \text{or} \quad A_d(1) = \frac{2\pi^{d/2}}{\left(\frac{d}{2}\right)},$$

in agreement with equation B.29.

Problem B.16. The easiest way to find the volume V of a hypersphere is from equation B.29 for the surface area, as follows. If the radius of the hypersphere increases by dr , then its volume increases by dV , such that

$$dV = \frac{dV}{dr} dr.$$

On the other hand, dV is just the thickness dr of the additional shell, times its surface area, $A_d(r)$:

$$dV = A_d(r) dr.$$

Combining these two relations gives

$$\frac{dV}{dr} = A_d(r), \quad \text{or} \quad V = \int A_d(r) dr = \frac{2\pi^{d/2}}{\left(\frac{d}{2}\right)} \int r^{d-1} dr = \frac{2\pi^{d/2}}{\left(\frac{d}{2}\right)} \frac{r^d}{d},$$

where I've set the integration constant to zero because a zero-radius hypersphere has zero volume.

Problem B.17. Generalizing equation B.32 to the case where the numerator is x^n , we have

$$\int_0^\infty \frac{x^n}{e^x \pm 1} dx = \int_0^\infty x^n e^{-x} \mp x^n e^{-2x} + x^n e^{-3x} \mp \dots dx.$$

To integrate the k th term, change variables to $y = kx$:

$$\int_0^\infty x^n e^{-kx} dx = \frac{1}{k^{n+1}} \int_0^\infty y^n e^{-y} dy = \frac{1}{k^{n+1}} (n+1),$$

by the definition (B.12) of the gamma function. Our integral is therefore

$$\int_0^\infty \frac{x^n}{e^x \pm 1} dx = \left(1 \mp \frac{1}{2^{n+1}} + \frac{1}{3^{n+1}} \mp \frac{1}{4^{n+1}} + \dots \right) (n+1).$$

For the case of the $-$ in the denominator of the integrand, the series is simply $\zeta(n+1)$, so

$$\int_0^\infty \frac{x^n}{e^x - 1} dx = (n+1)\zeta(n+1),$$

which is the first equation in B.36. For the case of the $+$ in the denominator, manipulate the series as in equation B.35:

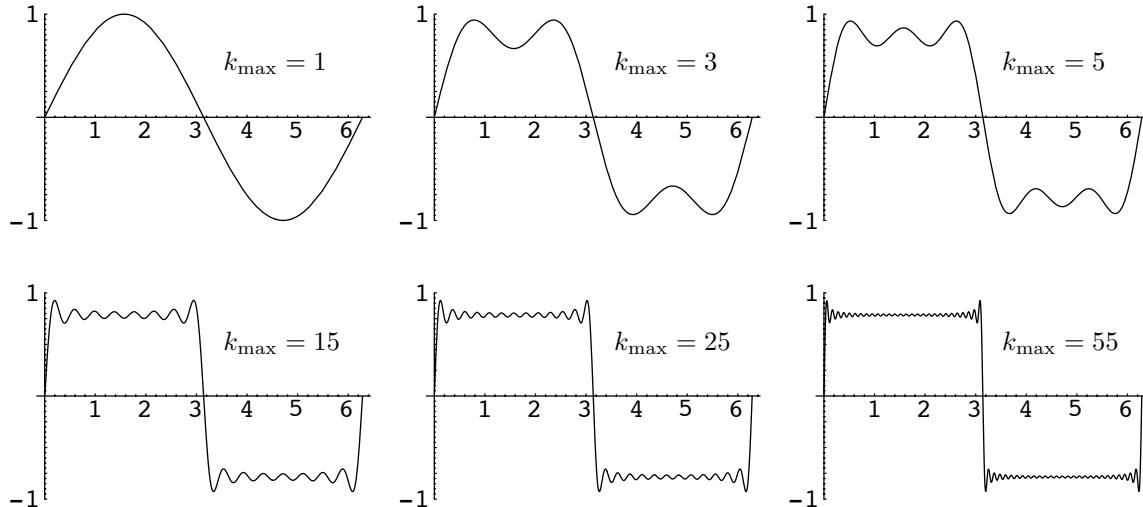
$$\begin{aligned} \frac{1}{(n+1)} \int_0^\infty \frac{x^n}{e^x + 1} dx &= \left(1 + \frac{1}{2^{n+1}} + \frac{1}{3^{n+1}} + \dots \right) - 2 \left(\frac{1}{2^{n+1}} + \frac{1}{4^{n+1}} + \frac{1}{6^{n+1}} + \dots \right) \\ &= \zeta(n+1) - \frac{2}{2^{n+1}} \left(1 + \frac{1}{2^{n+1}} + \frac{1}{3^{n+1}} + \dots \right) \\ &= \zeta(n+1) - \frac{1}{2^n} \zeta(n+1) = \left(1 - \frac{1}{2^n} \right) \zeta(n+1). \end{aligned}$$

This is the second equation in B.36.

Problem B.18. To plot the partial Fourier series in equation B.41, I gave *Mathematica* the instruction

```
Plot[Sum[Sin[k*x]/k, {k, 1, 25, 2}], {x, 0, 2Pi}]
```

which adds up all terms from $k = 1$ to $k = 25$, in steps of $\Delta k = 2$. To terminate the sum at other k values, I just changed the upper limit from 25 to something else. Here are the graphs produced with various upper limits:



Indeed, the series is converging to the desired square wave. The wiggles at the corners, however, are still pretty large even when we include lots of terms in the sum.

Problem B.19. Starting with equation B.42,

$$\frac{\pi x'}{4} = \sum_{\text{odd } k} \frac{1}{k^2} (1 - \cos kx'),$$

integrating over x' from 0 to x gives

$$\frac{\pi x^2}{8} = \sum_{\text{odd } k} \frac{1}{k^2} \left(x - \frac{1}{k} \sin kx \right), \quad (1)$$

and integrating again (from $x = 0$ to $x = x'$) gives

$$\frac{\pi(x')^3}{24} = \sum_{\text{odd } k} \frac{1}{k^2} \left(\frac{(x')^2}{2} + \frac{1}{k^2} (\cos kx' - 1) \right).$$

Setting $x' = \pi/2$, we now have

$$\frac{\pi^4}{192} = \sum_{\text{odd } k} \frac{1}{k^2} \left(\frac{\pi^2}{8} - \frac{1}{k^2} \right) = \frac{\pi^2}{8} \left(\sum_{\text{odd } k} \frac{1}{k^2} \right) - \sum_{\text{odd } k} \frac{1}{k^4}.$$

But the sum of $1/k^2$ is $\pi^2/8$ (by equation B.43), so

$$\sum_{\text{odd } k} \frac{1}{k^4} = \frac{\pi^2}{8} - \frac{\pi^2}{8} = \frac{\pi^4}{192} = \frac{\pi^4}{64} - \frac{\pi^4}{192} = \frac{\pi^4}{96}.$$

But $\zeta(4)$ is the sum of $1/k^4$ over all positive k :

$$\begin{aligned}\zeta(4) &= \sum_{\text{odd } k} \frac{1}{k^4} + \sum_{\text{even } k} \frac{1}{k^4} \\ &= \frac{\pi^4}{96} + \left(\frac{1}{2^4} + \frac{1}{4^4} + \frac{1}{6^4} + \dots \right) \\ &= \frac{\pi^4}{96} + \frac{1}{16} \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots \right) \\ &= \frac{\pi^4}{96} + \frac{1}{16} \zeta(4).\end{aligned}$$

Therefore,

$$\left(1 - \frac{1}{16}\right) \zeta(4) = \frac{\pi^4}{96}, \quad \text{or} \quad \zeta(4) = \frac{16}{15} \cdot \frac{\pi^4}{96} = \frac{\pi^4}{90}.$$

Plugging this value into the integrals in equation B.36, we have

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = (4)\zeta(4) = (3!) \left(\frac{\pi^4}{90} \right) = \frac{\pi^4}{15}$$

(as quoted on page 294), and

$$\int_0^\infty \frac{x^3}{e^x + 1} dx = \left(1 - \frac{1}{8}\right) (4)\zeta(4) = \frac{7}{8} \cdot \frac{\pi^4}{15} = \frac{7\pi^4}{120}$$

(as quoted in the solution to Problem 7.48). Why can't this method be used to evaluate $\zeta(3)$? For this we would need the sum of $1/k^3$, which appears in equation 1. However, plugging $x = \pi/2$ into that equation gives

$$\frac{\pi^3}{32} = \sum_{\text{odd } k} \frac{1}{k^2} \left(\frac{\pi}{2} - \frac{1}{k} \sin \frac{k\pi}{2} \right) = \frac{\pi^3}{16} - \sum_{\text{odd } k} \frac{1}{k^3} \sin \frac{k\pi}{2}.$$

The sine function in the last term is 1 for $k = 1, 5, 9, \dots$, and -1 for $k = 3, 7, 11, \dots$. Thus, we get a series of terms with alternating signs, and there's no way to manipulate this series into the one we want.

Problem B.20. Plugging $x = \pi/2$ into equation B.41 gives

$$\frac{\pi}{4} = \sum_{\text{odd } k} \frac{1}{k} \sin \frac{k\pi}{2} = 1 - \frac{1}{3} + \frac{1}{5} - \frac{1}{7} + \frac{1}{9} - \frac{1}{11} + \dots,$$

since the sine function is 1 for $k = 1, 5, 9, \dots$, and -1 for $k = 3, 7, 11, \dots$. A handy way to write the sign of each term is $(-1)^{(k-1)/2}$. If you add up the first few terms on a pocket

calculator, you'll find that this series does not converge very fast; for instance, summing the terms shown explicitly above gives $\pi \approx 2.976$. To sum a large number of terms, I used the *Mathematica* instruction

```
4*Sum[(-1)^((k-1)/2)/k,{k,1,499,2}] //N
```

and adjusted the upper limit of the sum until I got 3.14. Summing up to $k = 499$ gave 3.13759, which does round to 3.14, although stopping at $k = 501$ gives 3.14558, which rounds to 3.15. In any case, we need approximately 250 terms, just to get three significant figures! If you really want to compute π numerically, you should use a different series; the series in equation B.43 gives π to three significant figures after about 50 terms, for example.

Problem B.21. To see that the integrand is an even function, write the squared quantity in the denominator as two separate factors, then group one of them with the e^x in the numerator:

$$\frac{x^2 e^x}{(e^x + 1)^2} = \frac{x^2}{(e^x + 1)(e^x/e^x + 1/e^x)} = \frac{x^2}{(e^x + 1)(e^{-x} + 1)}.$$

Now it's clear that replacing x with $-x$ leaves this expression unchanged; therefore we can just integrate from 0 to ∞ and multiply by 2. Integrating by parts (differentiating the x^2 and integrating the rest), we then have

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx &= 2 \int_0^{\infty} x^2 e^x (e^x + 1)^{-2} dx \\ &= 2 \left[x^2 \frac{(e^x + 1)^{-1}}{-1} \Big|_0^{\infty} - \int_0^{\infty} 2x \frac{(e^x + 1)^{-1}}{-1} dx \right] \\ &= 2 \left[0 + 2 \int_0^{\infty} \frac{x}{e^x + 1} dx \right] = 4 \cdot \frac{1}{2} \zeta(2) = 2\zeta(2) = \frac{\pi^2}{3}, \end{aligned}$$

where in the last line I've used equations B.35 and B.45.

Problem B.22. You can sum the series on a pocket calculator, but it gets tedious after a few terms. I used the *Mathematica* instruction

```
Sum[1/k^3,{k,1,1000}] //N
```

to sum the first 1000 terms, and got the result 1.20206. I then raised the upper limit to 2000, and noted that this didn't affect any of the digits displayed. To get just three significant figures, or 1.20, I found that the upper limit could be lowered to only 8. To get four significant figures, or 1.202, I found that the upper limit needs to be at least 30.