1. Read the Feynman Lectures on "Superconductivity".

https://www.feynmanlectures.caltech.edu/III_21.html

- 2. Solve the attached problem 6.30 on the spin isomers of hydrogen. Your plot should look exactly like that for molar heat capacities on the Wikipedia page for Spin_isomers_of_hydrogen. You can skip part (e) on deuterium if you wish.
- 3. Solve the attached problem 7.70 on the BEC heat capacity. Use a computer to plot the heat capacity and verify that it looks like the lecture notes.
- 4. In the van der Waals equation of state,

$$P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}$$

the critical point is the unique point where both the first and second derivatives of pressure with respect to volume at fixed temperature are zero. Find the critical pressure, volume, and temperature in terms of a and b.

5. Rewrite the van der Waals equation of state in terms of the dimensionless variables $t \equiv \frac{T}{T_C}$, $p \equiv \frac{P}{P_C}$, and $v \equiv \frac{V}{V_C}$. Plot some isotherms above and below the critical point.

Bonus

1. Solve the attached problem 7.41 on the Einstein A and B coefficients for spontaneous and stimulated emission.

Problem 6.28. Use a computer to sum the rotational partition function (equation 6.30) algebraically, keeping terms through j = 6. Then calculate the average energy and the heat capacity. Plot the heat capacity for values of kT/ϵ ranging from 0 to 3. Have you kept enough terms in Z to give accurate results within this temperature range?

Problem 6.30. In this problem you will investigate the behavior of ordinary hydrogen, H_2 , at low temperatures. The constant ϵ is 0.0076 eV. As noted in the text, only half of the terms in the rotational partition function, equation 6.30, contribute for any given molecule. More precisely, the set of allowed j values is determined by the *spin* configuration of the two atomic nuclei. There are four independent spin configurations, classified as a single "singlet" state and three "triplet" states. The time required for a molecule to convert between the singlet and triplet configurations is ordinarily quite long, so the properties of the two types of molecules can be studied independently. The singlet molecules are known as **parahydrogen** while the triplet molecules are known as **orthohydrogen**.

(a) For parahydrogen, only the rotational states with even values of j are allowed.^{*} Use a computer (as in Problem 6.28) to calculate the rotational

*For those who have studied quantum mechanics, here's why: Even-*j* wavefunctions are symmetric (unchanged) under the operation of replacing \vec{r} with $-\vec{r}$, which is equivalent to interchanging the two nuclei; odd-*j* wavefunctions are antisymmetric under this operation. The two hydrogen nuclei (protons) are fermions, so their overall wavefunction must be antisymmetric under interchange. The singlet state $(\uparrow\downarrow - \downarrow\uparrow)$ is already antisymmetric in

partition function, average energy, and heat capacity of a parahydrogen molecule. Plot the heat capacity as a function of kT/ϵ .*

- (b) For orthohydrogen, only the rotational states with odd values of j are allowed. Repeat part (a) for orthohydrogen.
- (c) At high temperature, where the number of accessible even-j states is essentially the same as the number of accessible odd-j states, a sample of hydrogen gas will ordinarily consist of a mixture of 1/4 parahydrogen and 3/4 orthohydrogen. A mixture with these proportions is called **normal hydrogen**. Suppose that normal hydrogen is cooled to low temperature without allowing the spin configurations of the molecules to change. Plot the rotational heat capacity of this mixture as a function of temperature. At what temperature does the rotational heat capacity fall to half its high-temperature value (i.e., to k/2 per molecule)?
- (d) Suppose now that some hydrogen is cooled in the presence of a catalyst that allows the nuclear spins to frequently change alignment. In this case all terms in the original partition function are allowed, but the odd-j terms should be counted three times each because of the nuclear spin degeneracy. Calculate the rotational partition function, average energy, and heat capacity of this system, and plot the heat capacity as a function of kT/ϵ .
- (e) A deuterium molecule, D₂, has nine independent nuclear spin configurations, of which six are "symmetric" and three are "antisymmetric." The rule for nomenclature is that the variety with more independent states gets called "ortho-," while the other gets called "para-." For orthodeuterium only even-j rotational states are allowed, while for paradeuterium only oddj states are allowed.[†] Suppose, then, that a sample of D₂ gas, consisting of a normal equilibrium mixture of 2/3 ortho and 1/3 para, is cooled without allowing the nuclear spin configurations to change. Calculate and plot the rotational heat capacity of this system as a function of temperature.[‡]

spin, so its spatial wavefunction must be symmetric, while the triplet states $(\uparrow\uparrow, \downarrow\downarrow)$, and $\uparrow\downarrow + \downarrow\uparrow)$ are symmetric in spin, so their spatial wavefunctions must be antisymmetric.

^{*}For a molecule such as O_2 with spin-0 nuclei, this graph is the whole story; the only nuclear spin configuration is a singlet and only the even-j states are allowed.

[†]Deuterium nuclei are bosons, so the overall wavefunction must be symmetric under interchange.

[‡]For a good discussion of hydrogen at low temperature, with references to experiments, see Gopal (1966).

$$N = \int_0^\infty g(\epsilon) \frac{1}{e^{(\epsilon-\mu)/kT} - 1} d\epsilon.$$
(7.122)

Problem 7.69. If you have a computer system that can do numerical integrals, it's not particularly difficult to evaluate μ for $T > T_c$.

(a) As usual when solving a problem on a computer, it's best to start by putting everything in terms of dimensionless variables. So define $t = T/T_c$,

 $c = \mu/kT_c$, and $x = \epsilon/kT_c$. Express the integral that defines μ , equation 7.122, in terms of these variables. You should obtain the equation

$$2.315 = \int_0^\infty \frac{\sqrt{x} \, dx}{e^{(x-c)/t} - 1}$$

- (b) According to Figure 7.33, the correct value of c when $T = 2T_c$ is approximately -0.8. Plug in these values and check that the equation above is approximately satisfied.
- (c) Now vary μ , holding T fixed, to find the precise value of μ for $T = 2T_c$. Repeat for values of T/T_c ranging from 1.2 up to 3.0, in increments of 0.2. Plot a graph of μ as a function of temperature.

Problem 7.70. Figure 7.37 shows the heat capacity of a Bose gas as a function of temperature. In this problem you will calculate the shape of this unusual graph.

- (a) Write down an expression for the total energy of a gas of N bosons confined to a volume V, in terms of an integral (analogous to equation 7.122).
- (b) For $T < T_c$ you can set $\mu = 0$. Evaluate the integral numerically in this case, then differentiate the result with respect to T to obtain the heat capacity. Compare to Figure 7.37.
- (c) Explain why the heat capacity must approach $\frac{3}{2}Nk$ in the high-T limit.
- (d) For $T > T_c$ you can evaluate the integral using the values of μ calculated in Problem 7.69. Do this to obtain the energy as a function of temperature, then numerically differentiate the result to obtain the heat capacity. Plot the heat capacity, and check that your graph agrees with Figure 7.37.



Figure 7.37. Heat capacity of an ideal Bose gas in a three-dimensional box.

Problem 7.41. Consider any two internal states, s_1 and s_2 , of an atom. Let s_2 be the higher-energy state, so that $E(s_2) - E(s_1) = \epsilon$ for some positive constant ϵ . If the atom is currently in state s_2 , then there is a certain probability per unit time for it to spontaneously decay down to state s_1 , emitting a photon with energy ϵ . This probability per unit time is called the **Einstein A coefficient**:

A = probability of spontaneous decay per unit time.

On the other hand, if the atom is currently in state s_1 and we shine light on it with frequency $f = \epsilon/h$, then there is a chance that it will absorb a photon, jumping into state s_2 . The probability for this to occur is proportional not only to the amount of time elapsed but also to the intensity of the light, or more precisely, the energy density of the light per unit frequency, u(f). (This is the function which, when integrated over any frequency interval, gives the energy per unit volume within that frequency interval. For our atomic transition, all that matters is the value of u(f) at $f = \epsilon/h$.) The probability of absorbing a photon, per unit time per unit intensity, is called the **Einstein** *B* coefficient:

$$B = \frac{\text{probability of absorption per unit time}}{u(f)}.$$

Finally, it is also possible for the atom to make a *stimulated* transition from s_2 down to s_1 , again with a probability that is proportional to the intensity of light at frequency f. (Stimulated emission is the fundamental mechanism of the laser: Light Amplification by Stimulated Emission of Radiation.) Thus we define a third coefficient, B', that is analogous to B:

$$B' = \frac{\text{probability of stimulated emission per unit time}}{u(f)}$$

As Einstein showed in 1917, knowing any one of these three coefficients is as good as knowing them all.

- (a) Imagine a collection of many of these atoms, such that N₁ of them are in state s₁ and N₂ are in state s₂. Write down a formula for dN₁/dt in terms of A, B, B', N₁, N₂, and u(f).
- (b) Einstein's trick is to imagine that these atoms are bathed in *thermal* radiation, so that u(f) is the Planck spectral function. At equilibrium, N_1 and N_2 should be constant in time, with their ratio given by a simple Boltzmann factor. Show, then, that the coefficients must be related by

$$B' = B$$
 and $\frac{A}{B} = \frac{8\pi h f^3}{c^3}$.