

- (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}]
```

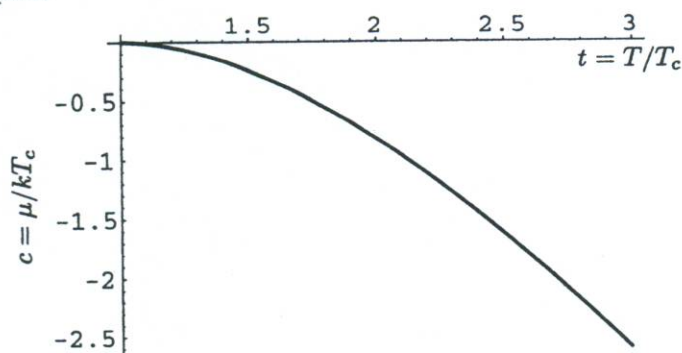
This instruction returned the value $c = -0.820792$. (The values $-.8$ and $-.9$ tell *Mathematica* where to begin the search.) Repeating this instruction for other values of t is now a simple matter, although for smaller t values, you get bad results unless you specify better starting points such as $-.1$ 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:

$$\begin{aligned}
 U &= \sum_{\text{all } s} \frac{\epsilon}{e^{(\epsilon_s - \mu)/kT} - 1} = \int_0^{\infty} \epsilon g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon \\
 &= \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \int_0^{\infty} \frac{\epsilon^{3/2}}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon.
 \end{aligned}$$

(b) For $T < T_c$ we can set $\mu = 0$, 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):

$$U = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V (kT_c)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^{(x-c)/t} - 1} dx = (0.432) NkT_c \int_0^\infty \frac{x^{3/2}}{e^{(x-c)/t} - 1} dx,$$

where I've again used the definition of T_c , equation 7.126. To compute U/NkT_c I defined the following *Mathematica* function:

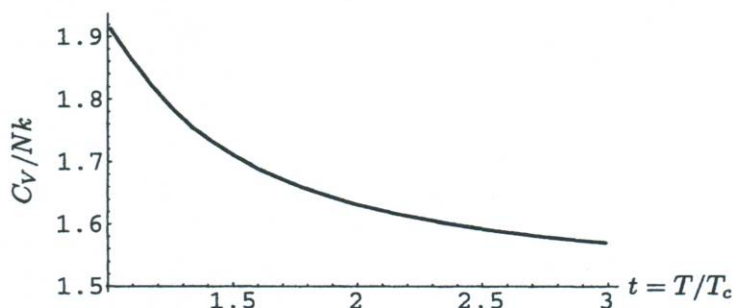
```
u[t_] := .432*NIntegrate[x^1.5/(Exp[(x-muInterp[t])/t]-1),{x,0,Infinity}]
```

Here `muInterp[t]` is the interpolating function for $c = \mu/kT$ 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 μ values that were calculated explicitly, I've avoided the inaccuracies in the interpolating function for μ . 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 μ 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 μ 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 μ 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

$$N = \sum_{n=0}^{\infty} \frac{(n+1)(n+2)}{2} \frac{1}{e^{(\epsilon-\mu)/kT} - 1},$$

where $\epsilon = nhf$. Substituting $\mu = chf$ and $T = thf$, the exponent in the denominator becomes simply $(n-c)/t$, so

$$N = \sum_{n=0}^{\infty} \frac{(n+1)(n+2)}{2} \frac{1}{e^{(n-c)/t} - 1}.$$

- (e) Using the same methods as in part (d), I found the c values listed in the table below. 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.

$t = kT/hf$	$c = \mu/hf$	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

$$\frac{kT_c}{hf} = \left(\frac{2000}{1.202} \right)^{1/3} = 11.85.$$

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 $e^{-(\epsilon-\mu)/kT}$, we get

$$\bar{n}_{\text{BE}}(\epsilon) = \frac{e^{-(\epsilon-\mu)/kT}}{1 - e^{-(\epsilon-\mu)/kT}} = e^{-(\epsilon-\mu)/kT} [1 + e^{-(\epsilon-\mu)/kT} + \dots],$$

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 $e^{-(\epsilon-\mu)/kT}$ 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,

$$\begin{aligned} N &= \frac{\sqrt{\pi}}{2} g_0 e^{\mu/kT} (kT)^{3/2} \left[1 + \frac{1}{\sqrt{8}} e^{\mu/kT} \right] = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} V e^{\mu/kT} \left[1 + \frac{1}{\sqrt{8}} e^{\mu/kT} \right] \\ &= \frac{V}{v_Q} e^{\mu/kT} \left[1 + \frac{1}{\sqrt{8}} e^{\mu/kT} \right], \end{aligned} \quad (1)$$

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 $\mu = -kT \ln(V/Nv_Q)$. 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 $1 + Nv_Q/\sqrt{8}V$ 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 $\Phi = -kT \ln \mathcal{Z}$. Combining these results gives $P = (kT/V) \ln \mathcal{Z}$. 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:

$$\mathcal{Z}_{\text{total}} = \mathcal{Z}_1 \mathcal{Z}_2 \mathcal{Z}_3 \cdots = \prod_n \mathcal{Z}_n,$$

where n labels the various wave modes. Taking the logarithm of both sides of this equation gives

$$\ln \mathcal{Z}_{\text{total}} = \ln \mathcal{Z}_1 + \ln \mathcal{Z}_2 + \ln \mathcal{Z}_3 + \cdots = \sum_n \ln \mathcal{Z}_n.$$

- (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

$$\ln \mathcal{Z}_n \approx e^{-(\epsilon - \mu)/kT} + \frac{1}{2}e^{-2(\epsilon - \mu)/kT} + \cdots.$$

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 $x = \sqrt{\epsilon/kT} = n\sqrt{h^2/8mL^2kT}$:

$$\begin{aligned} \ln \mathcal{Z} &= \frac{\pi}{2} \left(\frac{8mL^2kT}{h^2} \right)^{3/2} e^{\mu/kT} \left[\int_0^\infty x^2 e^{-x^2} dx + \frac{1}{2} e^{\mu/kT} \int_0^\infty x^2 e^{-2x^2} dx \right] \\ &= \frac{\pi}{2} \left(\frac{8mL^2kT}{h^2} \right)^{3/2} e^{\mu/kT} \left[\frac{\sqrt{\pi}}{4} + \frac{1}{2} e^{\mu/kT} \frac{\sqrt{\pi}}{4} \frac{1}{\sqrt{8}} \right] \\ &= \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V e^{\mu/kT} \left[1 + \frac{1}{2\sqrt{8}} e^{\mu/kT} \right] = \frac{V}{v_Q} e^{\mu/kT} \left[1 + \frac{1}{2\sqrt{8}} e^{\mu/kT} \right]. \end{aligned}$$

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, $e^{\mu/kT} = Nv_Q/V$. 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

$$B(T) = -\frac{N_A v_Q}{4\sqrt{2}} = -\frac{N_A}{4\sqrt{2}} \left(\frac{h^2}{2\pi m kT} \right)^{3/2}.$$

For helium-4 atoms, this evaluates to

$$\begin{aligned} B(T) &= -\frac{6.02 \times 10^{23} \text{ mol}^{-1}}{4\sqrt{2}} \left(\frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}{2\pi(4)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})} \right)^{3/2} T^{-3/2} \\ &= -(7.07 \times 10^{-5} \text{ m}^3 \cdot \text{K}^{3/2} / \text{mol}) \cdot T^{-3/2} = -(70.7 \text{ cm}^3 \cdot \text{K}^{3/2} / \text{mol}) \cdot T^{-3/2}. \end{aligned}$$

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

$$N = \frac{2V}{v_Q} e^{\mu/kT} \left[1 - \frac{1}{\sqrt{8}} e^{\mu/kT} \right].$$

The remaining equations of part (b) are similarly modified; in particular,

$$e^{\mu/kT} = \frac{Nv_Q}{2V} \left[1 + \frac{1}{\sqrt{8}} \frac{Nv_Q}{2V} \right].$$

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 $\mathcal{Z}_n = 1 + e^{-(\epsilon-\mu)/kT}$, by equation 7.21. This change converts the relative + sign in the next several lines to a -. Eventually we obtain

$$\ln \mathcal{Z} = \frac{2V}{v_Q} e^{\mu/kT} \left[1 - \frac{1}{2\sqrt{8}} e^{\mu/kT} \right].$$

The overall factor of 2 cancels when we plug in our formula for $e^{\mu/kT}$, 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,

$$B(T) = +\frac{N_A v_Q}{8\sqrt{2}} = +\frac{N_A}{8\sqrt{2}} \left(\frac{h^2}{2\pi m k T} \right)^{3/2}.$$

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, $54.4 \text{ cm}^3/\text{mol}$ at 1 K. The plot below shows the predictions for both isotopes as a function of temperature.

