Thermodynamics HW #11
Due Monday, November 18th

Note: Questions 1-4 are, of course, from the previous assignment, and I've included them for your convenience. Please just complete questions 5-8 for this assignment. Also note that though questions 6, 7, and 8 ask you to construct graphs, I am only requiring you to include the graph from question 8 on your submission.

This homework has you applying the mathematical results from the previous homework to the real world system of a gas of hydrogen (H_2) molecules. By comparing your predictions to (real!) experimental evidence you will trace the steps of an important development in the history of physics (see the cited work in the footnotes) and gain experience in the (very) practical skills of numerical computation and graphing.

1. The partition function Z is introduced simply as a normalization factor relating "Boltzmann factors" $e^{-\frac{E}{kT}}$ to probabilities. It turns out, however, that the partition function is a key quantity in statistical physics. Many quantities of thermodynamic interest are related to the partition function by surprisingly simple formulas. Show, for example, that the average energy $\langle U \rangle$ of a thermodynamic system in contact with a reservoir with a temperature T is given by the formula

$$\langle U \rangle = -(d/d\beta) \ln Z$$

where Z is the partition function and $\beta \equiv \frac{1}{kT}$.

Solution:

$$\langle E \rangle = \frac{\sum_n E_n e^{-\beta E_n}}{Z} = \frac{-\frac{d}{d\beta} Z}{Z} = -\frac{d}{d\beta} \ln Z$$

2. If we let our system contain a large number of particles, we know that under normal conditions the system never strays far from its expectation values, so that we can say $U = \langle U \rangle$. Though the energy U is a fundamental thermodynamic quantity, it is less accessible experimentally than, say, the heat capacity C_v, which can be measured by simply adding heat to system and noting the resulting temperature change. Show further that C_v can be calculated from the partition function via

$$C_v = k\sigma^2 (d^2/d\sigma^2) \ln Z$$

where k is Boltzmann's constant and σ is any constant multiple of β.

Solution:

$$\begin{aligned} C_v &= \frac{dU}{dT} \\ &= \frac{dU}{d\beta}\frac{d\beta}{dT} \\ &= \left(-\frac{d^2 \ln Z}{d\beta^2}\right)\left(-\frac{1}{kT^2}\right) \\ &= k\beta^2 \frac{d^2 \ln Z}{d\beta^2} \\ &= k(cbeta)^2 \frac{d^2 \ln Z}{d(c\beta)^2} \\ &= k\sigma^2 \frac{d^2 \ln Z}{d\sigma^2} \end{aligned}$$

3. Though the partition function of a microscopic system (like a single harmonic oscillator) can be easy to calculate, the partition function of a macroscopic system can be quite difficult because of the large number of degrees of freedom it contains. Oftentimes, however, the system can be broken up into smaller subsystems that do not interact with other and as a result the partition function takes on a simplified form.

   In detail, let us suppose a microstate of our system is described by a series of indices $n_1, n_2, \ldots, n_i, \ldots, n_M$ so that we can specify a microstate by specifying a value for each of the ${n_i}^{1,2}$. Further suppose that the energy $E(n_1, n_2, \ldots, n_M)$ of a microstate is a *sum* of terms that only depend on one index, i.e.

   $$E(n_1, n_2, \ldots, n_M) = E_1(n_1) + E_2(n_2) + \cdots + E_N(n_M)$$

   [3]. It is in this sense that we say that the i^{th} subsystem "does not interact" with the j^{th} subsystem, where $j \neq i$.

   Assuming that all possible combinations of indices are allowed[4], show then that the partition function Z of this system *factorizes* so that

   $$Z = Z_1 \times Z_2 \times \cdots \times Z_M$$

   where Z_i depends only on E_i. Show that this implies that the energy U (and thus the heat capacity C_v) of the system can be partitioned into a *sum* $U_1 + U_2 + \cdots + U_M$ (and $C_{v1} + C_{v2} + \cdots + C_{vM}$) different pieces, each depending only on one particular E_i.

   Solution:

$$\begin{aligned}
Z &= \sum_{n_1=1}^{M_1} \sum_{n_2=1}^{M_2} \cdots \sum_{n_M=1}^{M_M} e^{-\beta E(n_1, n_2, \ldots, n_M)} \\
&= \sum_{n_1=1}^{M_1} \sum_{n_2=1}^{M_2} \cdots \sum_{n_M=1}^{M_M} e^{-\beta \sum_{i=1}^{M} E_i(n_i)} \\
&= \sum_{n_1=1}^{M_1} e^{-\beta E_1(n_1)} \sum_{n_2=1}^{M_2} e^{-\beta E_2(n_2)} \cdots \sum_{n_M=1}^{M_M} e^{-\beta E_M(n_M)} \\
&= \prod_{i}^{M} \sum_{n_i=1}^{M_i} e^{-\beta E_i(n_i)} \\
&= \prod_{i}^{M} Z_i
\end{aligned}$$

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[1] e.g. if $M = 3$ we could specify a microstate by specifying, e.g., $n_1 = 22, n_2 = 41, n_3 = 88$

[2] For concreteness suppose that the i^{th} index runs from $1, 2, \ldots, M_i$.

[3] For example, the energy of a collection of gas particles can to a good approximation be written as a sum of the kinetic energies plus vibrational energy plus rotational energy. In this case $M = 3$ and E_1 might be the kinetic energy of *all* the particles, and likewise for the other two.

[4] This ignores any difficulties associated with the possible *indistinguishability* of the particles in the system. If we consider a gas, which is by definition low density, we can in a rough sense ignore the possibility of multiple occupation of a single state, and thus correct for indistinguishability by inserting the $1/N!$ "Gibbs Factor" into the partition function at the end.

We then have

$$\begin{aligned}
U &= \langle E \rangle \\
&= -\frac{d \ln Z}{d\beta} \\
&= -\frac{d}{d\beta} \ln \prod_{i=1}^{M} Z_i \\
&= -\frac{d}{d\beta} \sum_{i=1}^{M} \ln Z_i \\
&= \sum_{i=1}^{M} -\frac{d}{d\beta} \ln Z_i \\
&= \sum_{i=1}^{M} U_i
\end{aligned}$$

and likewise for C_{vi}.

4. Many systems also can (at least approximately) be represented as a collection of non-interacting particles. In this case, we would like to treat each index n_i as a *vector* of indices $\mathbf{n}_i = [\mathbf{n}_i]_1, [\mathbf{n}_i]_2, \ldots, [\mathbf{n}_i]_N$ of length N, the number of particles in the system. The j^{th} component $[\mathbf{n}_i]_j$ of the vector specifies a quantum number for the j^{th} particle. So long as the particles do not interact, the energy E_i for a system in a microstate $\mathbf{n}_1, \mathbf{n}_2, \ldots, \mathbf{n}_i, \ldots, \mathbf{n}_M$ is given by

$$E_i(\mathbf{n}_i) = \sum_{j=1}^{N} \varepsilon_i([\mathbf{n}_i]_j)$$

Show then that the partition function Z_i simplifies to

$$Z_i = z_i^N$$

where z_i is indepedent of N and is the partition function for the i^{th} index of a single particle. Show that this in turn implies that i^{th} *molar* heat capacity $(c_v)_i$ is given by

$$(c_v)_i = R\sigma^2 (d^2/d\sigma^2) \ln z_i \tag{1}$$

where $R \equiv N_A k$ is the universal gas constant.

Solution:

To calculate Z_i we sum over all possible $\mathbf{n}_i$ their associated Boltzmann factor $e^{-\beta E_i(\mathbf{n}_i)}$. To sum over every possible vector of indices $\mathbf{n}_i$ we must sum over every combination of *components* $[\mathbf{n}_i]_1, [\mathbf{n}_i]_2, \ldots, [\mathbf{n}_i]_N$. Assume that any component $[\mathbf{n}_i]_j$ can take values $1, \ldots, m_i$, where, crucially, m_i is independent of j because the *species* of particle does not change as you vary j. We find then for Z_i we get

$$\begin{aligned}
Z_i &= \sum_{[\mathbf{n}_i]_1=1}^{m_i} \sum_{[\mathbf{n}_i]_2=1}^{m_i} \cdots \sum_{[\mathbf{n}_i]_N=1}^{m_i} e^{-\beta E_i(\mathbf{n}_i)} \\
&= \sum_{[\mathbf{n}_i]_1=1}^{m_i} \sum_{[\mathbf{n}_i]_2=1}^{m_i} \cdots \sum_{[\mathbf{n}_i]_N=1}^{m_i} e^{-\beta \sum_{j=1}^{N} \epsilon_i([\mathbf{n}_i]_j)} \\
&= \sum_{[\mathbf{n}_i]_1=1}^{m_i} e^{-\beta\epsilon_i([\mathbf{n}_i]_1)} \sum_{[\mathbf{n}_i]_2=1}^{m_i} e^{-\beta\epsilon_i([\mathbf{n}_i]_2)} \cdots \sum_{[\mathbf{n}_i]_N=1}^{m_i} e^{-\beta\epsilon_i([\mathbf{n}_i]_N)} \\
&= \left(\sum_{n=1}^{m_i} e^{-\beta\epsilon_i(n)}\right)\left(\sum_{n=1}^{m_i} e^{-\beta\epsilon_i(n)}\right)\cdots\left(\sum_{n=1}^{m_i} e^{-\beta\epsilon_i(n)}\right) \\
&= z_i^N
\end{aligned}$$

From which we find

$$U_i = N u_i$$

and thus for $N = N_A$

$$(C_v)_i = k N_A (c_v)_i = R (c_v)_i$$

5. Let's now apply the formula derived in question 4 to calculate the temperature dependence of the heat capacity of a gas of hydrogen (H_2) molecules. With this assignment you will gain experience connecting theories about microscopic objects to measurable quantities that can be used to test these theories.

   To begin we note that a hydrogen molecule possesses

   - a momentum $\mathbf{p}$, and
   - angular momentum quantum numbers j and m_j, and

   The energy ε of a hydrogen molecule is given in terms of these quantum numbers[5] by

   $$\varepsilon(\mathbf{p}, j, m_j) = \frac{p^2}{2M} + Bj(j+1)$$

   where $B \equiv \frac{2\hbar^2}{MR^2} \approx 7.5\text{meV}$.

   Recalling that j can take integer values from $0, 1, \ldots, \infty$ and that for each j we have $2j+1$ possible values of m_j, write down an expression $z_r(\sigma)$ for the single molecule rotational partition function as a function of $\sigma \equiv \beta B = \frac{B}{kT}$. Assume for now that the protons in the molecule are distinguishable (and spin zero), so that for any pair j, m_j we have only one possible nuclear spin state. In other words, ignore nuclear spin.

   Hint:

   $$z_r(\sigma) = 1 + 3e^{-2\sigma} + 5e^{-6\sigma} + 7e^{-12\sigma} + \ldots$$

   What are the rest of the terms? Write it in terms of a sum from $j = 0, 1, \ldots, \infty$.

   Solution:

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[5] At the temperatures we consider we can ignore the molecule's *vibrational* motion since it is frozen out (i.e. $\frac{h\nu}{kT} > \frac{546\text{meV}}{25meV} \gg 1$).

Since the rotational energy is independent of the translational energy, we find (a la problem 3) that we can factorize the total system partition function Z into a product $Z_r Z_t$ of partition functions for the rotational and translational functions. Further, the total rotational energy is a sum over individual single particle rotational energies, so that (a la problem 4) we can write Z_r as a single partiticle rotational partition function z_r raised to the N^{th} power, where N is the number of particles, i.e. $Z_r = z_r^N$

Now the recipe for constructing the partition function is to sum over all possible microstates their associated Boltzmann factor. The single particle rotational states are described by quantum numbers j, m, where $j = 0, \ldots, \infty$ and for a given j $m = -j, -j+1, \ldots, j-1, j$. The energy for a particle in the j, m rotational state is $Bj(j+1)$. Therefore

$$z_r = \sum_{j=0}^{\infty} \sum_{m=-j}^{+j} e^{-\beta B j(j+1)} = \sum_{j=0}^{\infty} \sum_{m=-j}^{+j} e^{-\beta \sigma j(j+1)}$$

Since the rotational energy is independent of m the m-sum is easy:

$$z_r = \sum_{j=0}^{\infty} (2j+1) e^{-\sigma j(j+1)}$$

since $\sum_{n=1}^{N} c = c \sum_{n=1}^{N} = cN$ if c is *constant*, i.e. independent of n. See the blue curve on figure 1 for a plot of the resulting heat capacity.

6. In the accompany file “HW#11data.tsv” is a table of molar heat capacities[6] (in units of R) versus temperature (in K). The contributions to the heat capacity from the translational degrees of freedom have been subtracted out so that only the rotational component remains. Construct a scatter plot of this data (do not join the data points by lines).

   Then, using equation (1) with the z_r calculated in the previous section, construct a table of predicted rotational heat capacity vs. temperature, from the lowest measured temperature to the highest in 1K steps. Do not include this table in your homework. Instead, plot this data on the same graph as the experimental data, joining the data points by straight lines. How would you rate the agreement between experiment and theory?

   Note: Questions 6, 7, and 8 all ask you to produce graphs. It is only necessary to include the final graph (from question 8) on the work you turn in.

   Tip: Do the calculations numerically, including the derivatives. For the sum over j in the partition functions, neglect all terms with $j > 5$ (why?). For the second derivative, use the following recipe

$$f''(x) \approx \frac{f(x+\Delta x) + f(x-\Delta x) - 2f(x)}{\Delta x^2}$$

   where Δx is small. For our application a value $\Delta\sigma = .01$ will work fine.

   Solution:

   See HW#11solutions.nb for a Mathematica notebook to see how I computed the heat capacity.

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[6] Dennison, D. M., & Fowler, R. H. (1927). *Proc. Roy. Soc.* A, 115(771), 483–486. https://doi.org/10.1098/rspa.1927.0105

7. This "anomalous" behavior of the H_2 heat capacity led physicists to speculate that protons may be subject to the same Pauli exclusion principle that electrons were found to obey. Without going into details, the exclusion principle implies the following modifications to the model of the hydrogen molecule:

   - for every pair j, m_j where j is even we have only one possible nuclear spin state, while
   - for every pair j, m_j with j odd we have three possible nuclear spin states.

   Write down an expression for the modified z_r' which takes the above complication into account, and plot the associated molar heat capacity on the same plot from problem 6 so that the graph now contains three datasets: z_r, z_r', and the experimental data. Does the modification demanded by the exclusion principle improve the agreement between theory and experiment? Over what temperature ranges?

   Solution:

   Now in addition to the quantum numbers j, m we need to include a quantum number $s_o = 1, 2, 3$ for the odd j nuclear spin states and $s_e = 1$ for the even j nuclear spin states. Repeating then our steps from the last problem:

$$\begin{aligned} z_r &= \sum_{j=1,3,\ldots} \sum_{m=-j}^{+j} \sum_{s_o=1,2,3} e^{-\sigma j(j+1)} + \sum_{j=0,2,\ldots} \sum_{m=-j}^{+j} \sum_{s_e=1} e^{-\sigma j(j+1)} \\ &= \sum_{j=1,3,\ldots} (2j+1)(3)e^{-\sigma j(j+1)} + \sum_{j=0,2,\ldots} (2j+1)(1)e^{-\sigma j(j+1)} \\ &= \sum_{j=0}^{\infty} (2j+1)(2-(-1)^j)e^{-\sigma j(j+1)} \end{aligned}$$

   see the orange curve for the resulting heat capacity. Notice how it describes the experimental data better than the previous result, especially near room temperature.

8. Let us see if we can do better. The heat capacities calculated above assume that the gas is fully equilibriated at all temperatures. However, in order to convert hydrogen molecules with odd j into even j and vice versa, it is necessary to flip their nuclear spins. Perhaps under ordinary circumstances (i.e. in a glass or steel vessel) this flip occurs very rarely, so that over the course of an experiment we can assume that the odd j ("orthohydrogen") and even j ("parahydrogen") molecules are distinct species and *can not interconvert.*

   (a) Compute the ratio $\rho \equiv p_o/p_p$ of orthohydrogen and parahydrogen at 300K. State the answer to at least two decimal places. Retain the assumption from question 7, i.e. that the protons obey the Pauli principle.

   (b) Suppose we have a mole of hydrogen gas that has fully equilibriated at 300K so that the ortho-para ratio is ρ. Assuming this ratio stays fixed as the temperature of the gas is lowered, show that the heat capacity now takes the form

$$c_v = \frac{\rho c_o + c_p}{\rho + 1}$$

   where c_o and c_p are the molar heat capacities of orthohydrogen and parahydrogen respectively.

(c) Plot this new predicted molar heat capacity along with the experimental data and previous two predictions. Pretty neat, huh?

Solution:

(a) The relative probability p_A/p_B of finding a system in some subset A of microstates vs. another subset B is obtained by taking the ratio of the sums over their Boltzmann factors, i.e.:

$$p_A/p_B = \frac{\sum_{s_A \in A} e^{-\beta E(s_A)}}{\sum_{s_B \in B} e^{-\beta E(s_B)}}$$

In our case subset A is the microstates with odd j, and B is the microstates with even j. Anticipating the next question, we can think then of the numerator as the *partition function* z_o for the ortho-hydrogen, and the denominator as the partition function z_p for the para-hydrogen, since they constitute sums over all the states for that particular species of hydrogen (i.e. ortho or para). In other words we define

$$z_{\substack{o \\ p}} = \sum_{j=0}^{\infty} \frac{1}{2} \left(1 \pm (-1)^j\right) \left(2 - (-1)^j\right) (2j+1) \, e^{-\sigma j(j+1)}$$

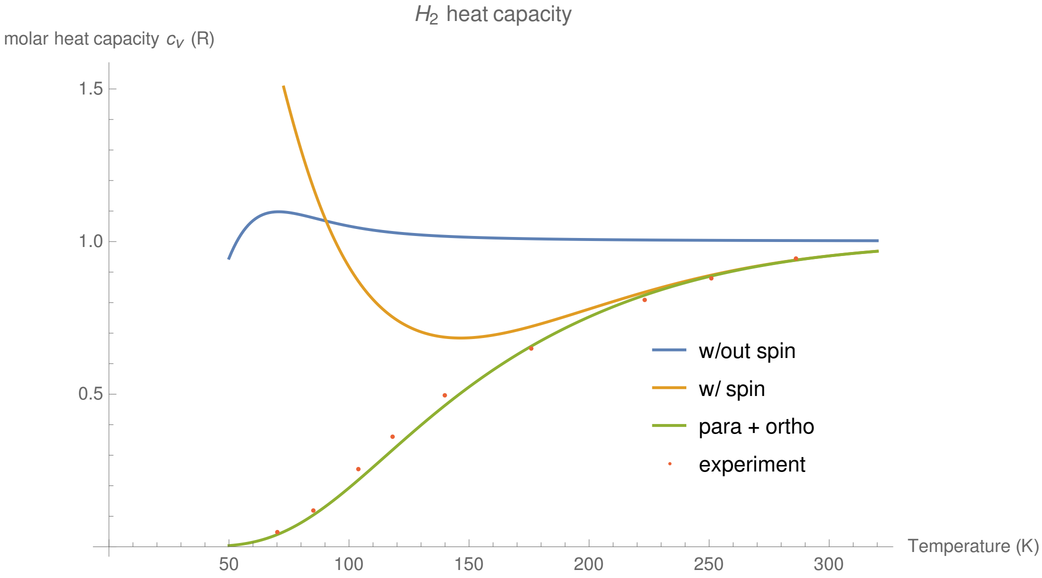
so that

$$\rho = z_o/z_p$$

evaluated at $\sigma = \frac{B}{kT_r}$ where $T_r = 300\text{K}$. I get a value of $\rho = 2.98719$. Check for yourself that in the high temperature limit we get $\rho \to 3$.

(b) We begin with a mixture containing $\frac{\rho}{\rho+1}$ moles of orthohydrogen and $\frac{1}{\rho+1}$ moles of parahydrogen. The heat capacities of a mixture of ideal gases are the sum of the heat capacities of the components, and each component's heat capacity is given by the product of its mole number and molar heat capacity. These properties are fairly in line with our intuition, but please go through the relevant equations if you are not convinced. Anyways, the heat capacities of the different hydrogen species are given by equation 1 applied to z_o and z_p. Combining all this we arrive at the desired expression.

(c) Refer to figure 1 and to the Mathematica notebook for the details. All agree that the result is pretty neat.



H_2 heat capacity
molar heat capacity c_V (R)
1.5
1.0
0.5
50
100
150
200
250
300
Temperature (K)
w/out spin
w/ spin
para + ortho
experiment

Figure 1: