Physics 401  
Computer Assignment 1: Molecular Hydrogen

The goal of this computer assignment is to predict the molar specific heat of H$_2$ molecules, as seen experimentally in Figure 1.13 in the textbook. Hydrogen molecules have translational energy, rotational energy, and vibrational energy. All play a role. Being able to predict and understand such a complex thermal property will be a nice culmination of Boltzmann statistics.

Part 1: Translational energy

Q1: Discuss the significance of the quantity $kT/\varepsilon$. What does it tell you? Why would we want to examine the conditions giving $kT/\varepsilon = 1$?

Q2: Consider hydrogen molecules in a three-dimensional cube with sides $L$ and volume $L^3$. The energy levels are those of a particle in a box. Are the quantum statistics of these energy levels important for understanding the heat capacity of hydrogen? Or will classical thermodynamics (i.e., the equipartition theorem) suffice?

Look up the equation for energy levels for a 3D particle in a box. What is $\varepsilon$, the characteristic quantum of energy? This is an expression in terms of $L$, not a number. At $T = 20$ K, the condensation temperature for hydrogen and thus the lowest temperature for the gas (at atmospheric pressure), what numerical value of $L$ gives $kT/\varepsilon = 1$?

Explain why, even at the very lowest temperatures, the translational energy of H$_2$ can be thought of purely classically. Your answer should be based on your answer to Q1 and on your value of $L$.

As a result, the translational energy of a mole of molecules is

$$U_{\text{trans}} = \frac{3}{2} N_A kT = \frac{3}{2} R T$$

and thus the translational contribution to the molar specific heat is the well known

$$c_V = \frac{dU_{\text{trans}}}{dT} = \frac{3}{2} R$$

There’s no computation for Part 1. Just turn in the answers to questions Q1 – Q2.

Part 2: Vibrational energy

The single-molecule partition function for vibrational energy is

$$Z_{1\text{vib}} = \sum_{\text{vibrational states}} e^{-\beta E_{\text{vib}}} = \sum_{\text{vibrational states}} e^{-E_{\text{vib}}/kT}$$

Although we often think of molecular vibrations as simple harmonic oscillators, whose quantized energies would be given by $E_{\text{vib}} = nh\omega$, the potential well is actually somewhat anharmonic. As a result, the vibrational energy levels of H$_2$ are
\[ E_{\text{vib}} = (1.03n - 0.03n^2) \varepsilon_{\text{vib}}, \quad n = 0, 1, 2, 3, \ldots \]

where the quantum energy of vibration is known to be \( \varepsilon_{\text{vib}} = hf = 0.53 \text{ eV} \).

The quantum energy levels of a true simple harmonic oscillator, given by \( E_{\text{sho}} = n\varepsilon_{\text{vib}} \), are equally spaced at \( \varepsilon_{\text{vib}} \). The first few vibrational energy levels of H\(_2\) are nearly equally spaced, but, because of the anharmonicity, the energy levels gradually get closer together as \( n \) increases.

**Q3:** Calculate the vibrational energy levels \( E_n \) for \( n = 0 \) to \( n = 8 \) both for a true simple harmonic oscillator and for the hydrogen molecule. You can leave your answers as multiples of \( \varepsilon \), such as \( E_4 = 4\varepsilon \) for a true SHO or \( E_4 = 3.64\varepsilon \) for hydrogen. Then draw side-by-side accurate energy-level diagrams for the two. You can draw these by hand if you use a ruler to make the energy-level positions accurate and the energy-level lines straight. Or figure out a way to do it in Excel or some other graphing program. Be sure to label which is which.

Set up a spreadsheet with the first column being temperature \( T \), going from 0 to 5100 K in steps of 50 K. Except let the first cell be 1 K rather than 0 K to avoid divide-by-zero errors. Let the next 11 columns calculate the individual terms in the sum of the partition function, for \( n = 0 \) to 10. To make your spreadsheet neat, put (and label!) the values of \( k \) (in eV/K) and \( \varepsilon_{\text{vib}} \) at the top of your spreadsheet and refer to them with absolute addressing, rather than putting numerical values in your formulas.

At lower temperatures, most of the terms in the sum will be zero to many decimal places. But at the highest temperatures, you really do need to sum through \( n = 10 \) to have good accuracy. I’ve already checked this for you, saving you the effort of figuring out how many terms are needed.

Let the next column do the sum to find \( Z_1 \) at that temperature, then the next column be \( \ln(Z_1) \). Then graph \( Z_1 \) versus \( T \) and \( \ln(Z_1) \) versus \( T \) for \( T = 0 \) to 5000 K (not 5100). We frequently talk about partition functions in statistical mechanics, but we rarely do we “see” what the function actually looks like.

**Note:** This is theory, not data like you would have from experimental measurements. To draw theory graphs, turn \textbf{off} plotted points, turn \textbf{off} shadowing, and turn \textbf{on} plotted lines. Use a fairly small line weight so that Excel draws narrow \textbf{lines} for your graphs rather than plotting a huge number of discrete data points. Also, don’t forget that (1) both axes of your graph need a label (showing units, if that’s relevant) and (2) your graph needs a title.

**Q4:** What is \( Z_1 \) at \( T = 0 \)? Why?

You’re learning in Chapter 6 that the energy of a system is given by

\[ U = -\frac{\partial \ln Z}{\partial \beta} \]
But two issues arise. First, \( Z \) is the partition function of the gas, whereas what you’ve just calculated is the partition function of one molecule. For indistinguishable particles,

\[
Z = \frac{(Z_1)^N}{N!}
\]

Second, while writing the derivative in terms of \( \beta = 1/kT \) makes equations look neat, we’re going to want to plot results versus \( T \), not \( \beta \), so we want equally spaced values of \( T \) rather than the equally spaced values of \( \beta \) that would be appropriate for finding numerical derivatives with respect to \( \beta \).

**Q5:** Prove (show your work), that the energy of an \( N \)-particle system is related to the single-particle partition function \( Z_1 \) by

\[
U = NkT^2 \frac{\partial \ln Z_1}{\partial T}
\]

Add another column to your spreadsheet to calculate the average vibrational energy per molecule, which is \( U/N \). Use the centered-difference method of approximating derivatives, as you learned in Computer Assignment 2. That is, use the rows above and below your target row for taking differences. This means you won’t have a \( U \) for \( T = 1 \text{ K} \) or 5100 K. However, you should be able to see what \( U \) is for 1 K and fill in that value manually.

Make a graph of \( U/N \) versus \( T \) for \( T \) from 0 to 5000 K. **Note that \( U/N \) has units**, so be sure to figure our what those units are and include them as part of your axis label.

**Q6:** Over what range of energies does \( U/N \) vary as \( T \) increases? Does this seem reasonable? Why?

Finally, let your last column calculate the heat capacity \( C/Nk \), again using centered differences to approximate derivatives. This means you won’t have a \( C \) for \( T = 1 \text{ K} \) or 5050 K. However, you should be able to see what \( C \) is for 1 K and fill in that value manually. **Note that asks for \( C/Nk \), not \( C/N \), so you’ll have to divide by \( k \) after taking derivatives.** If \( N = N_A \), then \( Nk = N_A k = R \). Thus what you’ve really calculated is the molar specific heat \( c_V \) in units of \( R \).

Make a graph of \( c_V/R \) versus \( T \) for \( T \) from 0 to 5000 K. This is the vibrational contribution to the specific heat of \( \text{H}_2 \) molecules.

**Q7:** At roughly what temperature does vibrational motion begin to contribute to specific heat? Over what range does \( c_V/R \) vary? Do both of these seem reasonable? Why? (Hint: The answer may have something to do with \( kT/\varepsilon \).)

For Part 2, turn in the first page of your spreadsheet, 4 graphs, and answers to questions Q3–Q6.

**Part 3: Rotational energy**
The single-molecule partition function for rotational energy is
\[ Z_{\text{rot}} = \sum_{\text{rotational states } j} (2j + 1)e^{-\beta E_{\text{rot}}} = \sum_{\text{rotational states } j} (2j + 1)e^{-E_{\text{rot}}/kT} \]

It’s found in PHYS 405 that the energy levels of a “rigid rotor” are
\[ E_{\text{rot}} = j(j + 1) \varepsilon_{\text{rot}}, \quad j = 0, 1, 2, 3, \ldots \]

and for hydrogen molecules the quantum of energy (which depends on the molecule’s moment of inertia) is \( \varepsilon_{\text{rot}} = 0.0076 \) eV. The factor \( (2j + 1) \) appears in the partition function because these energy levels are degenerate. That is, there really are \( (2j + 1) \) states having each energy. Recall in hydrogen atoms how each orbital angular momentum quantum number \( l \) has \( 2l + 1 \) degenerate states having the quantum number \( m \) (going from \( -l \) to \( l \)) associated with it. The same thing is happening with molecular rotation. Thus there are \( (2j + 1) \) equal terms in the partition function sum for each value if \( E_{\text{rot}} \).

Set up a spreadsheet with the first column being temperature \( T \), going from 0 to 504 K in steps of 2 K. Except let the first cell be 0.01 K rather than 0 K to avoid divide-by-zero errors. Let the next 11 columns calculate the individual terms in the sum of the partition function, for \( j = 0 \) to 10, including the \( 2j + 1 \) factor. Then, as in Part 2, do the sum to find \( Z_{\text{rot}} \) at that temperature, calculate \( \ln(Z) \), calculate \( U/N \) to 502 K, and finally calculate \( C/Nk = c_V/R \) to 500 K. Then make and print a graph of \( c_V/R \) versus \( T \) for \( T \) from 0 to 500 K.

Your graph should have the correct high-temperature limit (what should it be?), but, in comparison with Figure 1.13, does not have the right shape at lower temperatures.

What’s wrong? The problem is related to the Pauli exclusion principle. For reasons that we can’t justify here, the allowed values of \( j \) depend on the orientations of the nuclear spins – that is, the spins of the two protons that are the nuclei of the H atoms. Each proton has spin \( s = 1/2 \), and the two protons in \( \text{H}_2 \) can combine to be a total nuclear spin \( S = 0 \) (singlet states) or \( S = 1 \) (triplet states). Molecules with total nuclear spin \( S = 0 \) are called parahydrogen, and it turns out that only even values of \( j \) are allowed in parahydrogen. Molecules with total nuclear spin \( S = 1 \) are called orthohydrogen, and only odd values of \( j \) are allowed in orthohydrogen.

Transitions between orthohydrogen and parahydrogen are rare, so you can think of hydrogen gas as really being two separate gases, each with its own energy and heat capacity. So return to your spreadsheet and calculate separate partition functions and heat capacities for orthohydrogen and parahydrogen, summing only over odd or even values of \( j \).

Make a graph showing (on the same graph) the two partition functions versus \( kT/\varepsilon \). Be sure to label which is which. It’s better to do this with actual labels on the graph rather than using a legend at the side.
Q8: At approximately what value of $kT/\varepsilon$ do the heat capacities begin to curve upward. Does this make sense? Explain.

Heat capacity is additive. This follows from the fact that energy is additive: $U_{\text{total}} = U_{\text{ortho}} + U_{\text{para}}$. But there are three times as many orthohydrogen molecules as parahydrogen molecules because the nuclear spin $S = 1$ has three values of $m_S$, namely $-1$, $0$, and $1$, whereas the nuclear spin $S = 0$ has only $m_S = 0$. Thus the heat capacity is $C = 0.25C_{\text{para}} + 0.75C_{\text{ortho}}$.

Calculate the rotational heat capacity of the gas. Make a graph showing (and labeling) the $c_V/R$ for orthohydrogen, parahydrogen, and the full gas of hydrogen molecules, from $T = 0$ to 500 K.

Q9: Does your net result now look pretty similar to Figure 1.13? (Keep in mind that you have a linear horizontal scale while the figure has a logarithmic scale.) What is the high-temperature value of $c_V$? Is this expected? Why?

For Part 3, turn in the first page of your spreadsheet, 3 graphs, and answers to questions Q7–Q9.

Part 4: Adding It All Up

Make a new spreadsheet with the first column being temperature, going 0 to 500 K in steps of 2 K, then 500 to 5000 K in steps of 50 K. The translational $c_V = 3/2$ at all temperatures. You have rotational specific heats for 0–500 K. At that point the rotational $c_V$ has reached a steady value, and you can continue that value out to 5000 K. You have vibrational specific heats for 500–5000 K, and you should have found it to be zero (to 3 decimal places) for $T < 500$. So enter all these values and add them up!

Make two graphs: One, a graph of $c_V/R$ for $T = 0$ to 5000 K with a regular linear temperature scale. Second, a graph of $c_V/R$ for $T = 1$ to 10,000 K with a logarithmic temperature scale. You can do this as an option in Excel in the Format Axis control window; you don’t have to actually calculate and plot logarithms of the temperatures.

Q10: How well did you do? Don’t just say “OK,” but make an actual comparison to Figure 1.13.