NAME:

Instructions:

1. Please silence any noisy electronic devices you have and put any communications devices out of reach. Calculators are the only electronics permitted for the exam.

2. **Please write your name on this page but not on any other page.**

3. You may work on this part of the exam for 50 minutes.

4. You may detach the last sheet, containing tables and equations, from the exam.

5. To receive full credit for your work, please

   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;

   (b) specify the correct units, if any, for your final answers;

   (c) use an appropriate number of significant digits for final numerical answers;

   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- The first portion of this exam (problem 1) is several short questions worth 60 points total. Partial credit for these problems is not necessarily available. Part 2 of the final exam will also have a 60-point "short answer" section, so these problems will total 120 points across both halves.

- Your 5 best scores of the remaining problems, counted across *both* halves of the final exam will be worth 36 points each, for a total of 180 points. Partial credit is available for these problems, so try each problem and do not erase any of your work. The total final exam score is 300 points.

- These final exam scores and final course grades will be posted to Blackboard after all the exams have been graded.

1. 60 pts

   (a) Calculate the temperature at which 2.00 mol of an ideal gas occupies 40.0 L at a pressure of 1.50 bar.

   (b) According to the equipartition principle, what is the molar heat capacity at constant pressure (in **SI** units) for tetrachloroethene (C_2H_4) in the limit that k_BT is less than the lowest vibrational constant.

   (c) The mean free path of N_2 at 1.00 bar and 288 K is 790 Å. What is the mean free path at 0.020 bar and 298 K?

   (d) The Maxwell-Boltzmann distribution for CO at 300 K is labeled below. Which of the unlabeled curves a–d gives the distribution for the Maxwell-Boltzmann distribution of C_2O_2 at 600 K?
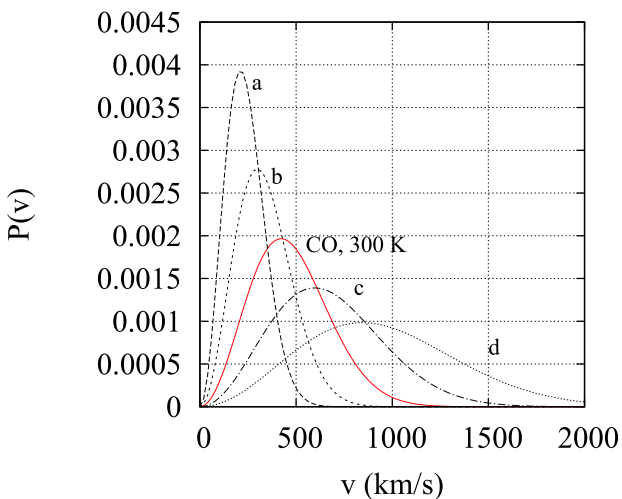
(e) Which of the following approximations did we use to obtain the van der Waals equation for non-ideal gases starting from the intermolecular potential energy function? Circle the Roman numeral; there may be more than one correct answer.

    i. The magnitude of the repulsive potential energy is much less than the thermal energy.

    ii. The magnitude of the attractive potential energy is much less than the thermal energy.

    iii. The total potential energy of the N molecules is the sum of all the pair potential energy functions.

    iv. The potential energy at interaction distances less than R_{LJ} is essentially infinite.

    v. The integral of the product of $N(N-1)/2$ integrands can be set equal to the a one-dimensional integral raised to the $N(N-1)/2$ power.

(f) Complete the Maxwell relation which is started below:

$$-\left(\frac{\partial S}{\partial n}\right)_{T,V} = \left[\frac{\partial}{\partial n}\left(\frac{\partial F}{\partial T}\right)_{V,n}\right]_{T,V} =$$

2. Shown below is the ensemble used in Fig. 2.5, showing three fluorine atoms, one of them in an excited electronic state, in four different translation states. The electronic energy of the one excited fluorine atom is $404\,\mathrm{cm}^{-1}$ above the ground state.

   (a) Calculate the Boltzmann entropy of this system in SI units.
   (b) Calculate the Gibbs entropy of this system in SI units.
   (c) Using the energy and entropy, estimate the temperature of this system.
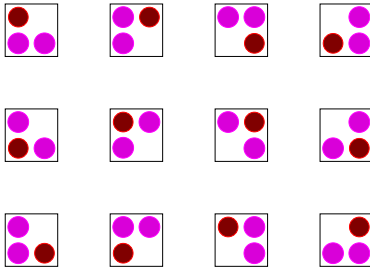
3. If $d\rho/dt = D\rho/a$ at a point Z_0 in our system, where a is a distance, then find an expression for the flux at that point.

4. A gas-phase sample of a diatomic molecule is placed in a chamber at $298\,\mathrm{K}$. Spectroscopy determines the populations of vibrational and rotational states graphed below. Use the data to *roughly* estimate the values of the rotational and vibrational constants.
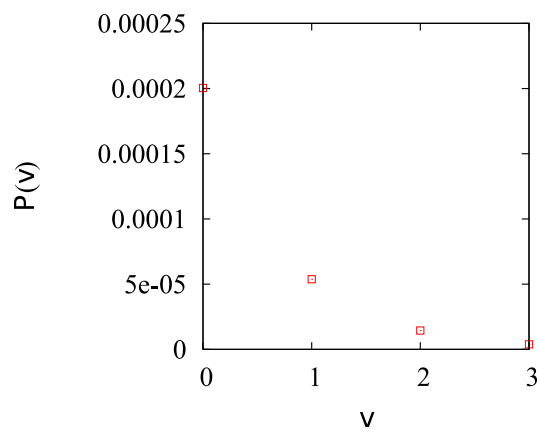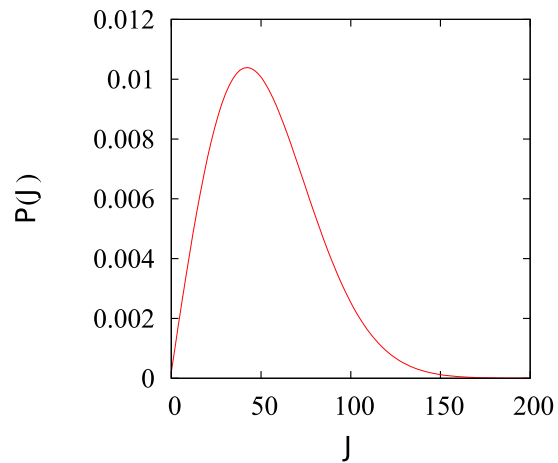
5. Imagine a blackbody composed of rigid, rotating molecules, so that the emission arises from **rotational** transitions rather than vibrational transitions. To find the average energy $\langle \epsilon_{\mathrm{rot}} \rangle$ (in order to get its contribution to ρ_{rad}), we must use a sum over all the states, rather than an integral (otherwise we have the same problem as in the case of classical vibrations). Write $\langle \epsilon_{\mathrm{rot}} \rangle$ for a linear molecule as a power series in x, where $x = e^{-B/(k_{\mathrm{B}} T)}$. Treat q_{rot} as a constant that can be factored out.

6. Sodium chloride is a relatively compressible solid, and has an internal pressure $\left(\frac{\partial E}{\partial V} \right)_{T,n} = 83 \, \mathrm{kbar}$, a density of $2.16 \, \mathrm{g\,cm^{-3}}$, and a coefficient of thermal expansion $39.8 \cdot 10^{-6} \, \mathrm{K^{-1}}$. Use these data to calculate the total work w **in kJ** when $50.00 \, \mathrm{g}$ of solid NaCl is warmed from $285.0 \, \mathrm{K}$ to $335.0 \, \mathrm{K}$ at a constant pressure of $1.00 \, \mathrm{bar}$.