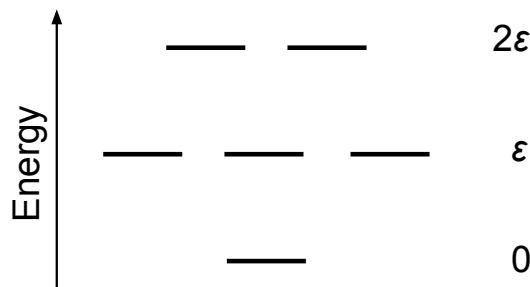Solve each problem on separate sheets of paper, and clearly indicate the problem number and your name on each. Carefully and neatly document your answers. You may use a mathematical solver like Matlab or Mathematica. Use plotting software for all plots.

1 It all adds up now

The diagram below describes the energy states available to some molecule.

1. Construct the partition function q for the molecule at thermal equilibrium at a temperature $\beta = 1/k_b T$.

2. Plot the probability for the molecules to have each of the three possible energies as a function of temperature. Be sure to indicate the probabilities in the limits $T \to 0$ and $T \to \infty$.

3. Derive an expression for the energy u per molecule by summing over the possible configurations weighted by their probabilities. Plot this average energy vs. temperature. Be sure to indicate the probabilities in the limits $T \to 0$ and $T \to \infty$.

4. Derive an expression for the energy u per molecule by taking the appropriate derivative of the partition function from question 1. Does your result agree with that from question 3?

5. Derive an expression for the Helmholtz free energy f per molecule from the partition function. Plot f vs. temperature, assuming $\epsilon/k_b = 300$ K.

6. Derive an expression for the entropy s per molecule from the partition function. Plot s vs. temperature, again assuming $\epsilon/k_b = 300$ K.

7. Look at your answers for questions 2 and 6. Can you use them to rationalize the Third Low of thermodynamics?

8. What would happen to the Third Law if the ground ($\epsilon = 0$) state was degenerate?

2 Thermodynamics from scratch

Let's calculate the thermodynamic properties of an ideal gas of CO_2 at 1 bar pressure. CO_2 is a linear molecule (you knew that, right?), has a rotational constant $B = 0.3836$ cm^{-1} and vibrational frequencies $\mu_i = 2349, 1388, 667,$ and 667~cm^{-1}.

1. Calculate the translational, rotational, and four vibrational temperatures of CO_2.

2. Plot the total translational, rotational, and total vibrational *energies* of CO_2 from $T = 200$ to $2000\,K$. Which (if any) of the three types of motions dominate the internal energy?

3. Plot the total translational, rotational, and total vibrational *Helmholtz energies* of CO_2 from $T = 200$ to $2000\,K$. Which (if any) of the three types of motions dominate the Helmholtz energy?

4. Plot the total translational, rotational, and total vibrational *constant volume molar heat capacities* of CO_2 from $T = 200$ to $2000\,K$. Which (if any) of the three types of motions dominate the heat capacity?

3 How'd the scratching turn out?

Ideal gas thermodynamic quantities are often tabulated in polynomials of temperature. The molar heat heat capacity of CO_2 is reported by a source to be:

$$C_p^{\text{ig}}(t) = -11.401074 - 55.231532t + 5.149108t^2 - 0.29158t^3 + 0.110128t^{-2} + 115.93493t^{1/2}$$

where $t = T(K)/1000$. Compare (by plotting) this expression to your $C_v^{\text{ig}}(T)$ from scratch. Recall $C_p^{\text{ig}} = C_v^{\text{ig}} + R$.

4 Langmuir isotherm

Let's estimate an adsorption isotherm for CO on Pt at $600\,K$, a temperature of practical relevance to catalysis:

$$* + CO(g) \rightleftharpoons CO* \tag{1}$$

Suppose the CO gas is ideal, has a rotational constant $B = 1.931\,\text{cm}^{-1}$ and a harmonic $C-O$ stretch frequency of $2150\,\text{cm}^{-1}$. CO binds C-end down, one CO/Pt, with a constant binding energy of about $150\,\text{kJ}\,\text{mol}^{-1}$. The surface-bound CO has (about) the same $C-O$ stretch frequency and rotational constants as in the gas. In addition, the CO vibrates againt the metal surface with a frequency of about $500\,\text{cm}^{-1}$ and parallel to the surface with frequency $150\,\text{cm}^{-1}$ (2-fold degenerate because the CO can move in two orthogonal directions parallel to the surface).

1. Estimate the adsorption equilibrium constant $K(T)$ at $600\,K$. Use a gas standard state of $1\,\text{bar}$. Recall we derived in class that

$$K(T) = \frac{q_{\text{site}}(T)}{q_{\text{gas}}^{\circ}(T)} e^{-\Delta E/k_B T}$$

1. Plot the adsorption isotherm vs. pressure. At what pressure do you expect the surface to be 50% covered with CO?