

## Homework #6: Boundary Value Problems (BVPs)

**Problem 1.** (10 points)

Most entropies of gas phase molecules tabulated in databases were not directly determined experimentally, instead they were computed using statistical mechanics. The biggest challenge in these computations is to determine the entropy contribution from internal rotations in the molecule, e.g. when a methyl ( $-\text{CH}_3$ ) group spins around relative to the rest of the molecule.

Statistical mechanics formulas for the Boltzmann-weighted energy ( $U$ ) and Helmholtz free energy ( $A$ ) are known in terms of the allowed (quantized) energy levels  $\{E_n\}$  of the molecule:

$$U = N_A \frac{\sum_n E_n e^{\left(\frac{-E_n}{k_B T}\right)}}{\sum_n e^{\left(\frac{-E_n}{k_B T}\right)}}$$

$$A = U - TS = -N_A k_B T \ln \left[ \sum_n e^{\left(\frac{-E_n}{k_B T}\right)} \right]$$

From the computed  $U$  and  $A$ , you can compute  $S$ . In this problem, we'll compute the  $\{E_n\}$  and then the  $S$  associated with the internal rotation of methanol  $\text{HO} - \text{CH}_3$ .

1. To find  $\{E_n\}$  we will use the Schroedinger equation. The Schroedinger equation associated with the angle  $\theta$  between the  $O - H$  and one of the  $C - H$ 's is

$$\left(\frac{-h^2}{8\pi I}\right) \frac{d^2 \Psi_n}{d\theta^2} + V_3(1 - \cos(3\theta)) \Psi_n = E_n \Psi_n \quad (1)$$

where  $I \in \mathbb{R}$  is the reduced moment of inertia associate with rotating the methyl group relative to the OH group,  $h$  is Planck's constant and  $V_3 \in \mathbb{R}$  is half of the height of the potential energy barrier to spinning the methyl group. (Note that we are assuming the potential energy surface is given by a simple cosine shape.) We will find the numerical solution by approximating the wavefunction,  $\Psi_n$ , using a basis set expansion

$$\Psi_n(\theta) = \sum_{m=-M}^M C_{mn} \Phi_m(\theta) \quad (2)$$

and use Galerkin's method (multiplying both sides by one of the basis functions and integrating) to convert the differential equation into  $N = 2M + 1$  algebraic equations:

$$\int_0^{2\pi} \Phi_k^*(\theta) \left( \frac{-h^2}{8\pi I} \frac{d^2 \Psi_n}{d\theta^2} + V_3(1 - \cos(3\theta)) \Psi_n(\theta) - E_n \Psi_n(\theta) \right) d\theta = 0 \quad \text{for } k = -M, \dots, M \quad (3)$$

where  $\Phi_k^*(\theta)$  is the complex conjugate.

Use the basis

$$\Phi_m(\theta) = e^{im\theta}$$

to simplify the algebra. For example, using this basis

$$\frac{d^2\Phi_m}{d\theta^2} = -m^2\Phi_m(\theta)$$

This form of basis automatically satisfies many physical conditions on the wavefunctions for these types of problems, e.g. that  $\Psi_n(\theta) = \Psi_n(\theta + 2\pi)$ . Conveniently, all of the integrals that arise can be computed analytically, see below for some hints.

Write out one of the Schroedinger equations. Show how the integrals are simplified by evaluating them analytically.

*HINT:* You will find the following integral formulas to be useful:

$$\int_0^{2\pi} e^{-ik\theta} e^{im\theta} d\theta = \begin{cases} 0, & \text{if } k \neq m \\ 2\pi, & \text{if } k = m \end{cases}$$

$$\int_0^{2\pi} e^{-ik\theta} \cos(3\theta) e^{im\theta} d\theta = \int_0^{2\pi} e^{-ik\theta} \left( \frac{e^{i3\theta} + e^{-i3\theta}}{2} \right) e^{im\theta} d\theta = \begin{cases} 0, & \text{if } m - k \neq \pm 3 \\ \pi, & \text{if } m - k = \pm 3 \end{cases}$$

- Now consider the full set of Schroedinger equations. We want to write the system of equations in the form

$$\mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{E}$$

What is the sparsity pattern of  $\mathbf{H}$ ? Report  $\mathbf{H}$  for  $M = 2$  (i.e.  $\mathbf{H} \in \mathbb{R}^{5 \times 5}$ ).

- Write a MATLAB<sup>®</sup> function to solve for  $\{E_n\}$  using MATLAB's `eig` function

$$\mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{E}$$

Your function should take the effective moment of inertia ( $I$ , in  $kg\ m^2$ ), the parameter  $V_3$  (in  $J$ ) and the temperature  $T$  (in  $K$ ) as inputs. Your function should also read in  $M_{max}$  which will set the number of basis functions to use in your expansion for  $\Psi$ .

- Write a MATLAB function that calls the function you wrote to calculate the entropy for the following parameters:

$$\begin{aligned} I &= 1.2 \times 10^{-45} \text{ kg } m^2 \\ V_3 &= 0.81 \times 10^{-20} \text{ J} \\ T &= 300 \text{ K} \end{aligned}$$

This function should generate a plot of the computed entropy as a function of  $M$ . Approximately how big a basis is needed for the computed value of  $S(300K)$  to be converged to 1%? What is the converged value of the entropy associated with this internal rotation at 300K ?

By construction, if you take your computed lowest-energy eigenvalue  $E_0$  and its corresponding eigenvector  $\mathbf{c}_0$ , use the definition of  $\Psi$  in eqn. 2 and plug into eqn. 3, that equation will be satisfied to good numerical precision. Do you think this numerical solution of eqn. 3 also satisfies the original eqn. 1 at all angles?

Note: The molecular constants  $I$  and  $V_3$  can be determined experimentally using high-resolution microwave or infrared spectroscopy. Now  $I$  and  $V_3$  (and better representations of the shape of the potential energy surface than a simple cosine) can be computed pretty accurately using quantum chemistry, which is becoming the most common way to determine entropies for molecules in the gas phase.

**Problem 2.** (10 points)

Consider the following steady-state reaction-diffusion problem, which describes the simple consumption of a reactant with concentration  $C$  in a porous bed of thickness  $H$  where there is no convection. The porous bed could be either a slab of cells (in which case the reactant might be dissolved oxygen), or a catalytic washcoat (in which case the reactant might be carbon monoxide in exhaust gases). Here is the equation for the steady-state concentration of  $C$ , where a reactant with effective diffusivity inside the bed of  $D$  is being consumed at reaction rate  $r(C, T)$  at temperature  $T$ , but new reactant is diffusing in to maintain a steady concentration:

$$\begin{aligned} D \frac{d^2 C}{dx^2} - r(C, T) &= 0 \\ \left. \frac{dC}{dx} \right|_{x=0} &= 0 \\ C(H) &= C_0 \end{aligned}$$

The above boundary conditions are appropriate if the porous bed is resting on an impermeable wall at  $x = 0$ , and if the concentration  $C_0$  of the reactant at the top of the bed  $x = H$  is known. The reaction will have an associated heat of reaction  $\Delta H_{rxn}$ , so there is a coupled temperature equation from energy balance:

$$\begin{aligned} \frac{d^2 T}{dx^2} - \gamma r(C, T) &= 0 \\ \left. \frac{dT}{dx} \right|_{x=0} &= 0 \\ T(H) &= T_0 \end{aligned}$$

where  $\gamma = \frac{\Delta H_{rxn}}{\alpha C_P}$ . These boundary conditions shown are appropriate if the temperature at the top of the bed is known, and the impermeable wall is a perfect insulator. Your task is to use the shooting method to compute the concentration and temperature profiles  $C(x)$  and  $T(x)$  inside the bed. Note that the total molar flow rate  $F$  of the reactant flowing into the bed and consumed is given by

$$F = AD \frac{dC}{dx}$$

where  $A$  is the area of the bed.

First, rewrite the system of differential equations in the standard form  $\frac{dy}{dx} = f(y)$ . Arrange the equations so  $x_0$  corresponds to  $x = H$  and  $x_f$  corresponds to  $x = 0$ .

Note that you do not know all 4 initial conditions, so you will need to guess the missing initial conditions, and then iteratively improve them until the solution satisfies the other boundary conditions. This is the shooting method. We suggest you use `fsolve` to do the iterative improvement, and `ode45` to solve the ODE-IVP corresponding to each set of initial conditions.

In this problem, solve the system for these three different rate laws  $r(C, T)$ :

1.  $r(C, T) = kC$ . This is a simple linear-kinetics test case for debugging your code; it can be solved analytically. The analytical solution is

$$C(x) = C_0 \frac{\cosh\left(\frac{x}{L}\right)}{\cosh\left(\frac{H}{L}\right)}$$

where  $L = \sqrt{\frac{D}{k}}$ . For your test use these values of the parameters:  $C_0 = 1.2 \times 10^{-6} \frac{\text{mol}}{\text{cm}^3}$ ,  $T_0 = 300\text{K}$ ,  $k = 0.041\text{s}^{-1}$ ,  $D = 0.022 \frac{\text{cm}^2}{\text{s}}$ ,  $\Delta H_{rxn} = -50 \frac{\text{kJ}}{\text{mol}}$ ,  $\alpha = 0.11 \frac{\text{cm}^2}{\text{s}}$ ,  $C_P = 0.004 \frac{\text{J}}{\text{cm}^3\text{K}}$ , and  $H = 2.2\text{cm}$ . Make a plot comparing your numerical solution from shooting versus the analytical solution. Hint: the two should be identical. If you are getting problems with `fsolve`, it may help to convert everything into a dimensionless system in order to have the system properly scaled.

What is the Thiele modulus of the system? Does the plot agree with the modulus?

2.  $r(C, T) = \frac{kC_{sat}(C-C_{min})^2}{(C+C_{sat})^2}$  if  $C > C_{min}$ , 0 otherwise. This is a typical case for cell metabolism, where the reactant is  $\text{O}_2$ . When  $C$  drops to  $C_{min}$  the cells cannot function and stop metabolizing so  $r \rightarrow 0$ . As  $C$  gets large the consumption rate saturates. The diffusivity is smaller in this liquid-phase case:  $D = 10^{-5} \frac{\text{cm}^2}{\text{s}}$ . Also, assume that  $\Delta H = 0$ . Note that you will need to initialize  $\frac{dT}{dx} = 0$  as well to satisfy the boundary conditions. Compute and plot results using the same parameters as in Part 1, with  $C_{min} = 5 \times 10^{-8} \frac{\text{mol}}{\text{cm}^3}$  and  $C_{sat} = 10^{-6} \frac{\text{mol}}{\text{cm}^3}$ . Approximately what fraction of the cells in the bed are not metabolizing effectively because they are starved for  $\text{O}_2$ ? (Note here we assumed  $r(C, T)$  has no  $T$  dependence, but in reality the water would boil and the cells would die if  $T$  went too high).
3.  $r(C, T) = AC \exp\left(-\frac{E_a}{RT}\right)$  This is a typical case for catalytic chemistry, for example the reactant could be carbon monoxide in an exhaust stream.  $R = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ . Use these parameter values:  $A = 1.1 \times 10^9 \text{s}^{-1}$ ,  $E_a = 101 \frac{\text{kJ}}{\text{mol}}$ , and  $T_0 = 503\text{K}$ ; all other parameters the same as in part 1. Plot the  $T$  profile as well as the  $C$  profile. Also plot the analytical solution from part 1. Why are they different?

N.B. This model ignores the volumetric expansion of gases due to change in temperature.

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