10.34 – Fall 2006

Homework #4

Due Date: Monday, Oct. 2nd, 2006 – 7 PM

(Turn in hard copies in class or at the TA help session Monday evening.)

Problem 1:

Do problem 3.A.3 in Beers's textbook.

Problem 2:

The heat capacity of many organic molecules is dominated by the torsions or internal-rotations about C-C single bonds, but unfortunately this is a bit tricky to calculate. Often a good approach is to first find the eigenvalues {E} of this 1-D Schrödinger equation:

$$\frac{-h^2}{8\pi^2 I}\cdot\frac{d^2\Psi}{d\phi^2}+V(\phi)\Psi(\phi)=E\Psi(\phi) \qquad \text{Eq.(1)}$$

where ϕ, which runs from 0 to 2π, is the dihedral angle between substituents on the two carbon atoms making the single bond, $V(\phi)$ is the potential energy associated with this torsional motion, and I is its effective reduced moment of inertia. With the $\{E\}$, one can then compute the heat capacity using the statistical-mechanics formula

$$C(T)=\left(\langle E^2\rangle-\langle E\rangle^2\right)\Big/k_B T^2 \qquad \text{Eq.(2)}$$

where: $$\langle E\rangle=\frac{\sum E_j \exp\left(-E_j/k_B T\right)}{\sum \exp\left(-E_j/k_B T\right)} \quad \text{and} \quad \langle E^2\rangle=\frac{\sum E_j^2 \exp\left(-E_j/k_B T\right)}{\sum \exp\left(-E_j/k_B T\right)}$$

which you will see soon in 10.40 and again in the Spring in 10.65. The potential energy function $V(\phi)$ is typically obtained by computing V at a half-dozen values of ϕ using quantum chemistry techniques, e.g.

ϕ	0	$\pi/3$	$2\pi/3$	π	$4\pi/3$	$5\pi/3$	*radians*
V	0	2.1	0.5	8.6	0.4	1.8	x10^{-20} *Joules*

and then interpolating, e.g.

$$V(\phi)\sim\sum y_n\cos(n\phi) \qquad n=0,1,\ldots,N_{\max} \qquad \text{Eq.(3)}$$

For the case of N_{max} = 4, a least-squares fitting yields the following:

$$(y_0 = 2.067 \quad y_1 = -2.033 \quad y_2 = 1.056 \quad y_3 = -1.767 \quad y_4 = 0.678) \times 10^{-20} \ Joules$$

It is very convenient to convert the Schrödinger equation from a differential equation into a linear algebra equation by searching for solutions where

$$\Psi(\phi) \sim \sum x_m \exp(i \cdot m\phi) \qquad m = -M, -(M-1), \ldots, (M-1), M \quad \text{Eq.(4)}$$

(a) Write the linear algebra equation that corresponds to Equation 1. [Hint: multiply through by exp($-ip\phi$) and integrate over ϕ]. Give an algebraic expression for the $(m,n)^{th}$ element in the matrix, assuming $V(\phi)$ is given exactly by Eq.(3).

(b) Write a Matlab function that makes use of your answer in part A to compute the energy values *E* corresponding to Eqn. 1, taking in the moment of inertia, *I*, and the number of basis functions, *M*. For the case of $I = 3\text{x}10^{-45}$ kg-m^2 and M = 50, calculate the zero point energy of the system (you do not need to show all of the eigenvalues). Make a plot showing $V(\phi)$ from 0 to 2π, with a horizontal line shown on the plot for each eigenvalue of the system.

(c) Write a set of Matlab functions which cumulatively compute $C(T,M)$ using expansions Eq.(4) for the case $I = 3\text{x}10^{-45}$ kg-m^2. Calculate the value of the heat capacity for M = 100 at 300 K (in J/mol-K).

(d) Make a plot of $C(T)$ from T = 100 K to T = 2000 K for a series of M's to show how the calculation converges as M is increased. Use the following values of M: 20, 50, 100, 300, and 500. Plot the curves.

N.B. The smallest *E* value you obtain is called the "zero-point energy". Quantum mechanically it is impossible to remove the zero-point energy from the torsional degree of freedom, so even at T = 0 K the atoms in the molecule are not quite stationary. The zero-point energy depends on the value of "*I*", and hence on the masses of the atoms in the molecule. This mass-dependence leads to small differences between the enthalpies and hence chemistry of different isotopes of the same molecule. Also note that for a given M and I, the energy values do not change, meaning that the eigenvalue problem only needs to solved once to calculate an entire C(T) curve. It may be useful to recall that:

$$\cos(n\phi) = \frac{e^{in\phi} + e^{-in\phi}}{2}$$