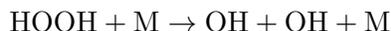


Homework #9: Monte Carlo Methods

Problem 1 (10 points).

Caution: read the entire problem statement carefully before you attempt to structure a response; there is important information throughout!

When heated in air, most fuels form hydrogen peroxide (HOOH), which accumulates to a somewhat high concentration before ignition. One reason ignition is so sudden is that above the ignition temperature (about 1200 K), the HOOH decomposes, forming a large concentration of very reactive OH radicals. The ignition temperature is very sensitive to the rate at which the HOOH decomposes, which in the gas phase is usually limited by the rate at which the thermal bath can supply energy for this endothermic reaction through collisions. That is, the rate-limiting step is:



where M stands for any collision partner (i.e., any other molecule in the system). Experimentally, some collision partners are much more effective than others at transferring energy to HOOH, but no one knows exactly why. One theory proposes that the dipole moment of HOOH allows energy transfer over long distances, but other researchers have suggested that the dipole moment of HOOH is actually very small at these high temperatures, where it is vibrating violently.

In this problem, your task is to estimate the average *magnitude* of the dipole moment, $\langle \|\boldsymbol{\mu}\| \rangle$, of HOOH at 1200 K, based on a molecular mechanics potential energy expression for HOOH and for the charges on the H and O atoms. Note the dipole moment is a vector quantity:

$$\boldsymbol{\mu} = \sum_i q_i (\mathbf{r}_i - \mathbf{R}_{cm}),$$

where \mathbf{r}_i is a vector specifying the (x, y, z) position of the i^{th} atom and q_i is the atom's charge. The vector \mathbf{R}_{cm} is the (x, y, z) position of the center of mass:

$$\mathbf{R}_{cm} = \frac{\sum_i m_i \mathbf{r}_i}{\sum_i m_i},$$

where m_i is the mass of the i^{th} atom.

We do not care about the direction of the dipole vector, only its magnitude $\|\boldsymbol{\mu}\|$ (2-norm).

The symbol " $\langle \cdot \rangle$ " refers to the Boltzmann average over all possible molecular geometries; in the classical limit and neglecting some minor complications due to the integral over the kinetic energy we can write:

$$\langle \|\boldsymbol{\mu}\| \rangle = \frac{1}{Q} \int \cdots \int \exp\left(-\frac{V(\mathbf{r}_1, \dots, \mathbf{r}_N)}{kT}\right) \|\boldsymbol{\mu}(\mathbf{r}_1, \dots, \mathbf{r}_N)\| d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N,$$

where Q is the classical partition function:

$$Q = \int \cdots \int \exp\left(-\frac{V(\mathbf{r}_1, \dots, \mathbf{r}_N)}{kT}\right) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N.$$

Write a set of OCVNCD¹ functions that use the Metropolis Monte Carlo integration method to compute $\langle \|\boldsymbol{\mu}\| \rangle$ at $T = 1200$ K. You should report the following:

1. The value you obtain for $\langle \|\boldsymbol{\mu}\| \rangle$ and the number of Monte Carlo steps attempted and accepted.
2. Your best guess at the variance in $\|\boldsymbol{\mu}\|$ and the uncertainty in your predicted value of $\langle \|\boldsymbol{\mu}\| \rangle$. Explain how you derived these.
3. A plot of the probability density $p(\|\boldsymbol{\mu}\|)$ of observing an HOOH molecule with a dipole moment of magnitude $\|\boldsymbol{\mu}\|$. *Hint: You may find the MATLAB routine `hist` helpful here.*

An expression for the potential, V , and related information are as follows:

$$V(\mathbf{r}) = V_{OH}(\mathbf{R}_{O_1H_1}) + V_{OH}(\mathbf{R}_{O_2H_2}) + \frac{1}{2}k_{OO}(\|\mathbf{R}_{OO}\| - L_O)^2 + \frac{1}{2}k_\theta((\theta_{HOO} - \theta_0)^2 + (\theta_{OOH} - \theta_0)^2) + V_\phi(\theta_{HOO}, \theta_{OOH}, \phi),$$

where

$$V_{OH}(\mathbf{r}) = D_{OH} (1 - \exp(-\alpha(\|\mathbf{r}\| - L_H)))^2, \\ V_\phi(\theta_{HOO}, \theta_{OOH}, \phi) = (2 \times 10^{-20} \text{J})(1 + \cos(\theta_{HOO}))(1 + \cos(\theta_{OOH}))(\cos(\phi) - \cos(\phi_0))^2.$$

\mathbf{R}_{ij} is the vector between atoms i and j (so $\|\mathbf{R}_{ij}\|$ is the Cartesian distance between atoms i and j). θ_{HOO} is the angle defined by H1-O1-O2. θ_{OOH} is the angle defined by O1-O2-H2 (*hint: law of cosines*). ϕ is the dihedral angle, the expression for which depends on your choice of axes; an expression for molecular-fixed axes is given at the end of the problem statement.

The charges on the atoms depend on the OH bond lengths, and are given by:

$$q(\mathbf{r}) = -0.25 \exp(-\alpha(\|\mathbf{r}\| - L_H)), \\ q_{H_1} = -q_{O_1} = q(\mathbf{R}_{H_1O_1}), \\ q_{H_2} = -q_{O_2} = q(\mathbf{R}_{H_2O_2}).$$

The values of q are given in units of the charge of an electron (a negative number with the normal sign convention for charge). It is customary to report molecular dipole moments in units of Debye. System parameters:

$$D_{OH} = 6 \times 10^{-19} \text{ J} \\ L_H = 1.05 \times 10^{-10} \text{ m} \\ L_O = 1.6 \times 10^{-10} \text{ m} \\ k_{OO} = 300 \text{ J/m}^2 \\ k_\theta = 1.1 \times 10^{-18} \text{ J/rad}^2 \\ \alpha = 1.5 \times 10^{10} \text{ m}^{-1} \\ \phi_0 = 1.7 \text{ rad} \\ \theta_0 = 1.8 \text{ rad}$$

Note that it is very easy to figure out the equilibrium geometry from the analytical expression for the potential ($V = 0$ at the equilibrium geometry). Use this equilibrium geometry to compute $\langle \|\boldsymbol{\mu}\| \rangle$ for $T = 0$ K. When you begin the Metropolis MC integration, start your Monte Carlo steps from the equilibrium geometry.

Hint: You can use molecule-fixed axes to reduce the dimensionality of your model. Molecular potentials do not depend on the position of the molecule in space, nor on its orientation, but only

on the relative position of the atoms. Hence, one can usually cut six degrees of freedom (three corresponding to the position of the molecule and three corresponding to its angular orientation—the Euler angles) out of molecular problems. In this particular problem, we suggest using molecule-fixed axes where the position of atom O_1 sets the origin, atom O_2 lies on the x axis, and atom H_1 lies in the x - y plane. In this way, one can remove these 6 degrees of freedom from the problem: $x_{O_1}, y_{O_1}, z_{O_1}, y_{O_2}, z_{O_2}, z_{H_1}$ (that is, these can all be set equal to zero).

When you remove these orientational degrees of freedom you pick up some Jacobian volume elements in the integrals for $\langle \|\boldsymbol{\mu}\| \rangle$ and Q (approximating away some minor terms):

$$\langle \|\boldsymbol{\mu}\| \rangle = \frac{1}{Q} \int \cdots \int (x_{O_2})^2 |y_{H_1}| \exp\left(-\frac{V(\mathbf{x})}{kT}\right) \|\boldsymbol{\mu}(\mathbf{x})\| d^6 \mathbf{x},$$

$$Q = \int \cdots \int (x_{O_2})^2 |y_{H_1}| \exp\left(-\frac{V(\mathbf{x})}{kT}\right) d^6 \mathbf{x},$$

where the vector \mathbf{x} contains the non-zero (x, y, z) coordinates of all the atoms. In this molecule-fixed coordinate system, the dihedral angle is given by

$$\cos(\phi) = \frac{y_{H_1} y_{H_2}}{|y_{H_1}| \sqrt{(y_{H_2})^2 + (z_{H_2})^2}}$$

Problem 2 (10 points). Consider a simple system with a single particle that can be in any one of 5 boxes. This situation is shown in Figure 1.

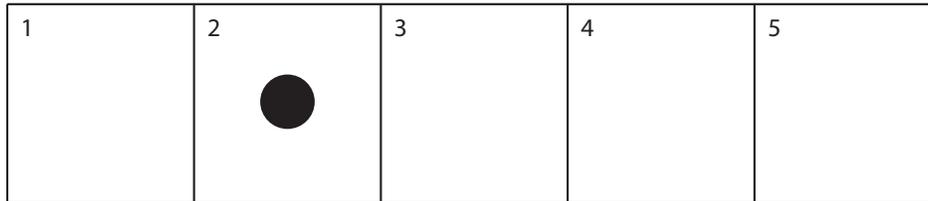


Figure 1: A simple system with a single particle that moves between five boxes.

Suppose that the energy of the system when the particle is in each box, E_1, \dots, E_5 , are known and satisfy

$$E_1 > E_2 > E_3 > E_4 > E_5.$$

Suppose further that the probability of being in box i , $p(i)$, satisfies

$$p(i) \propto \exp(-E_i/kT).$$

You decide to compute an approximation of the PDF p using a Markov process. In each step of your simulation, the particle is initially in box i . First, you select a neighboring box at random (with equal probability). Next, you decide whether or not to accept a move to this neighboring box using the acceptance criterion of Metropolis. A typical simulation of this type results in the histogram in Figure 2.

1. Does it make physical sense that p should look like the histogram in Figure 2? Explain why or why not.

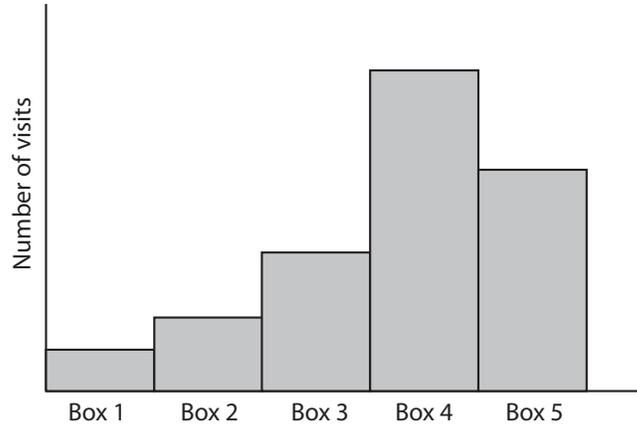


Figure 2: Typical results from Markov process simulation. For each box i , the height of the bar indicates the number of times the configuration where the particle is in box i was visited during the simulation.

2. Analyze the transition probabilities of the Markov process described by the algorithm above. In your report, use the transition probabilities to argue either that the simulation is flawed, or that it is guaranteed to give the correct results.
3. Suggest a second definition of the transition probabilities that leads to a valid simulation and justify your choice. If you believe that the original simulation results are incorrect, explain how your new transition probabilities correct the problem.
4. Suppose that the system described in Figure 1 is being used to model a one dimensional diffusion process. Clearly, it is not physical for a particle to diffuse from box 2 to box 4 without first passing through box 3. Now consider a Markov process with transition probabilities that allow moves between non-neighboring boxes with nonzero probability. Can such a Markov process be used to approximate p ? Explain your answer on physical grounds.

jks: November 23, 2011

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Fall 2015

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