10.34 – Fall 2006
Homework #10 Solution

Monte Carlo Sampling within a molecular potential

The purpose of this problem was to take a representative sampling of molecular configurations at a given temperature for the given molecular potential. Proper sampling from the probability of the molecule having a certain amount of energy will allow for average quantities to be estimated, such as the $<1/R_{HH}^6>$ and $<R_{HH}>$ asked for in the problem statement.

This could be done using internal coordinates of the molecules, but was essentially given to you in terms of Cartesian coordinates in the problem. The pertinent equation for the average of interest was given by the following equation. In this equation, several degrees of freedom have been removed by assuming a fixed position of one oxygen atom (O1), the other oxygen (O2) only moves along one dimension, and that one H atom (H1) is confined to a 2-D plane. This leaves a 6-D phase space to be probed, which in Cartesian coordinates can be written as the following variables: x_{O2}, x_{H1}, y_{H1}, x_{H2}, y_{H2}, and z_{H2}.

$$\left\langle \frac{1}{R_{HH}^6} \right\rangle = \frac{\iiint \left(\frac{1}{[R_{HH}]^6} \cdot w(\underline{q}) \right) dx_{O2}\, dx_{H1}\, dy_{H1}\, dx_{H2}\, dy_{H2}\, dz_{H2}}{\iiint w(\underline{q}) \cdot dx_{O2}\, dx_{H1}\, dy_{H1}\, dx_{H2}\, dy_{H2}\, dz_{H2}}$$

$$where: \qquad w(\underline{q}) = x_{O_2}^2 \cdot \left| y_{H_1} \right| \cdot \exp\left[\frac{-V(\underline{q})}{k_B T} \right]$$

It is easy to see that the weighting function in this case is a modified Boltzmann distribution, which was modified because the degrees of freedom were reduced. This weighting function will then be used in the Metropolis algorithm to accept or reject steps. The acceptance criterion for an uphill step in energy is given by:

$$rand[0,1] < \frac{w_{new}(\underline{q})}{w_{current}(\underline{q})} = \frac{\left(x_{O_2}^2 \cdot \left| y_{H_1} \right| \right)_{new}}{\left(x_{O_2}^2 \cdot \left| y_{H_1} \right| \right)_{current}} \cdot \exp\left[\frac{-\{V_{new} - V_{current}\}}{k_B T} \right] \quad \Rightarrow \quad Accept\ step$$

Generally, a downhill step in energy is always accepted and this formula is not used (you can see that for a pure Boltzmann factor, a downhill step will always be accepted with the above formula). However, this criterion could also be used in this case for a downhill step, and for very small downhill steps in energy, there could be a small chance of rejecting the step based the geometry ratio pre-factor.

Now that the acceptance criterion is defined, we can begin to take steps. In this problem, each coordinate could be changed independently by +/- 0.10 Å.

Part A:

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Equilibrium value at 0 K:
<R_HH> = 2.5836 (Angstroms)
<1/R_HH^6> = 0.0033623 (1/A^6)


Number of MC steps taken: 100000
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Equilibrium Geometry at T = 0 K

One would expect that the equilibrium 0 K distance and the <distance> at elevated are different, though the difference may be small. The main reason why this would be the case is due to asymmetries in the potentials within the molecule. As the temperature increases, the atoms can move to locations of higher energy, with a probability that depends on T. A very much simplified (an rigorously incorrect) way of envisioning this would be to assume that the molecule can exist on a single iso-energy contour at a given temperature. Only if this iso-energy contour was symmetric about the 0 K minimum, would you expect the average value to be centered on the 0 K position for N_{points} → large. A simple example is shown below. If you have a circular contour around (0,0) and could sample anywhere along the circle, you would find that the <(x,y)>= (0,0). However, if the shape is asymmetric (as are the potentials in this problem), you will find some other value for <(x,y)>, denoted by the "X" in the images below, even if the true minimum lies at (0,0). The value would lie at the average position of all points along the contour (in this simple case).
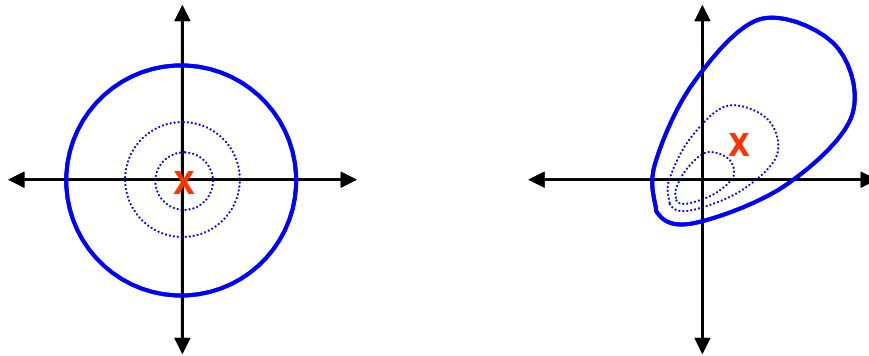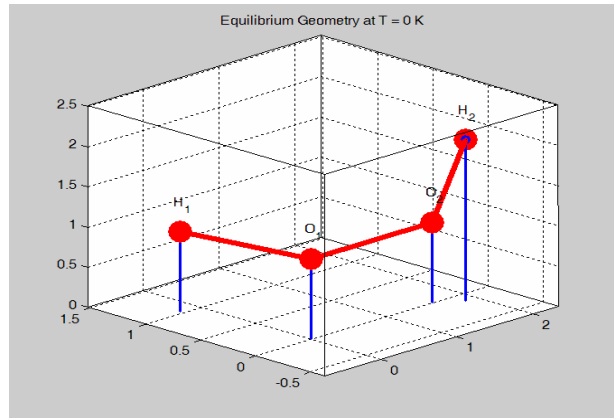
The uncertainties in the values were calculated in two ways, one using the standard deviation and another using the fluctuation formula given in class:

$$\delta f = \sqrt{\frac{1}{N} \cdot \left[\left\langle f^2 \right\rangle - \left\langle f \right\rangle^2 \right]}$$

The "sigma" given in the parts below is the standard deviation of the cumulative $<1/R_{HH}^6>$ taken over the final 50% of the MC points (the final 50000 points in this case). The (+/-) values shown below are calculated using the fluctuation equation as shown above for δf. Both should provide an estimate of the uncertainty in the average value, though they differ by significant amounts.
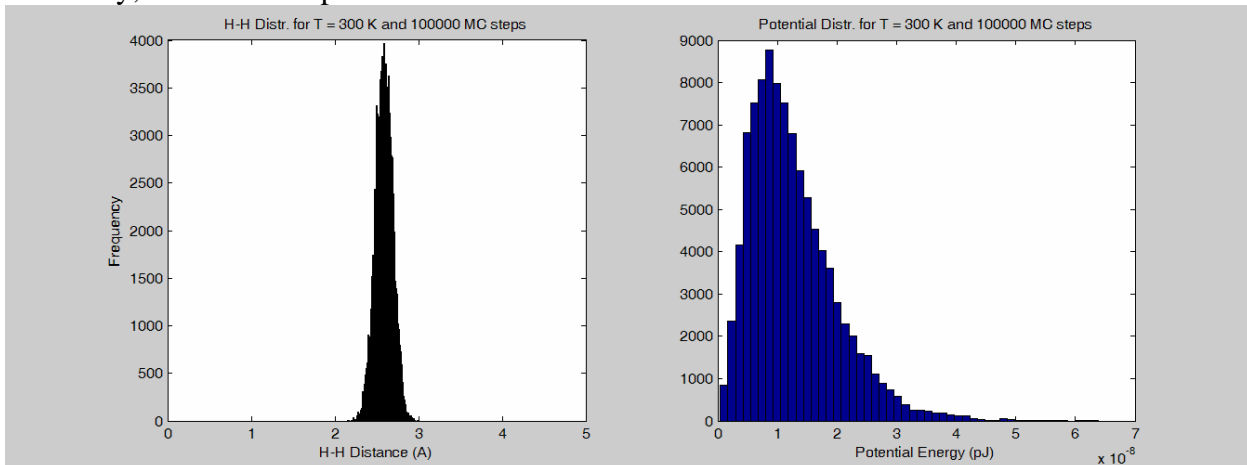
Results for T = 300 K

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<1/R_HH^6> for T = 300 K:  0.0034424  +/-  2.7485e-006
<1/R_HH^6> for T = 300 K:  0.0034424 with sigma = 2.3747e-005
<R_HH> for T = 300 K:  2.5886
There were 17325 steps accepted out of 100000 total steps

Most probable MC V(q) = 8.6703e-009 pJ
Value of kB*T = 4.1421e-009 pJ
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At 300 K, the atoms are confined to a rather limited energy and physical space. This is because the small thermal energy available makes significant uphill steps very unlikely. You should also be able to see that the $<R_{HH}>$ value is slightly larger that at 0 K due to the asymmetry in the dihedral potential. The barrier at the "trans" configuration is smaller than the "cis" barrier, making the potential less steep for H atoms moving away from each other. This is similar to the simple example shown above.
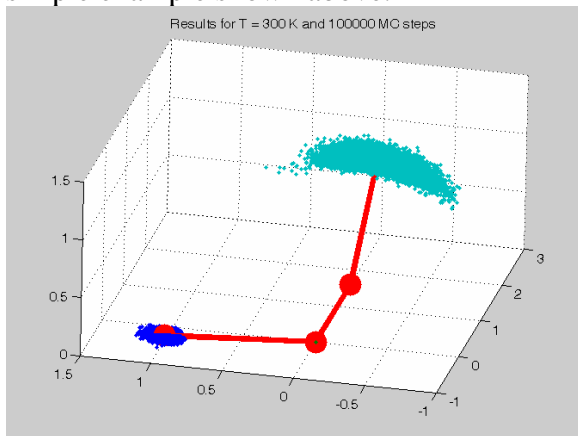
The H-H distance is fairly sharply peaked, as would be expected for a low temperature. The most frequently seen value of the potential is found to be near the thermal energy of the system (k_BT), as would be expected. It is not exactly the same, but we are not sampling from a pure Boltzmann distribution, we have discrete bin sizes, and cannot do an infinite number of points. Generally, one would expect these values to be close to each other.
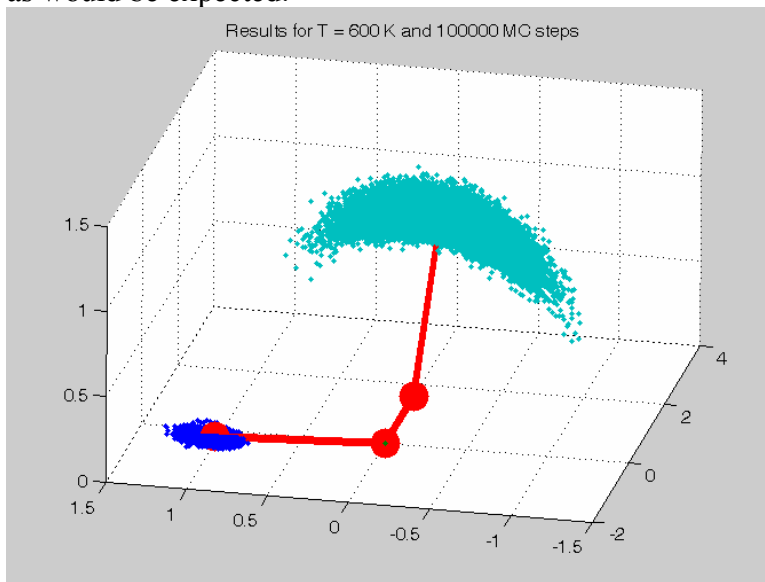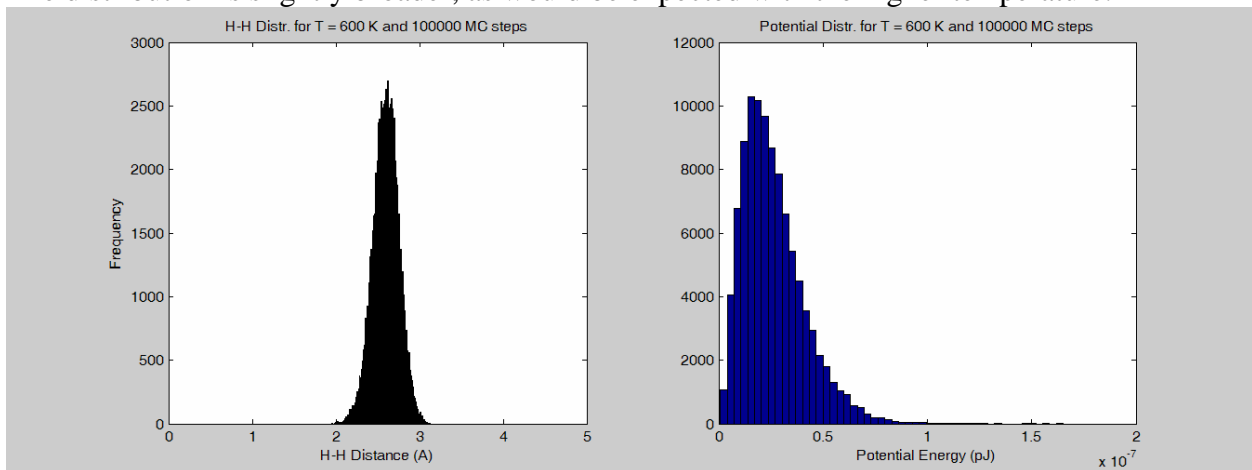
Results for T = 600 K

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<1/R_HH^6> for T = 600 K:   0.0035244  +/-   4.4425e-006
<1/R_HH^6> for T = 600 K:   0.0035244 with sigma = 1.6526e-005
<R_HH> for T = 600 K:   2.5971
There were 32549 steps accepted out of 100000 total steps

Most probable MC V(q) = 1.5515e-008 pJ
Value of kB*T = 8.2842e-009 pJ
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At 600 K, the trends are the same as what was said for the 300 K case. However, now the H atoms can sample a larger energy and physical space. The $<R_{HH}>$ value at 600 K is even larger, as would be expected.

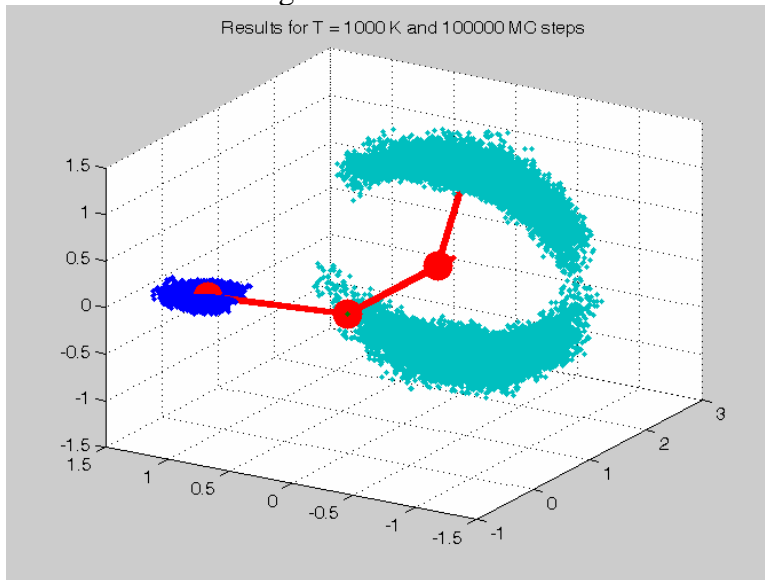The distribution is slightly broader, as would be expected with the higher temperature.
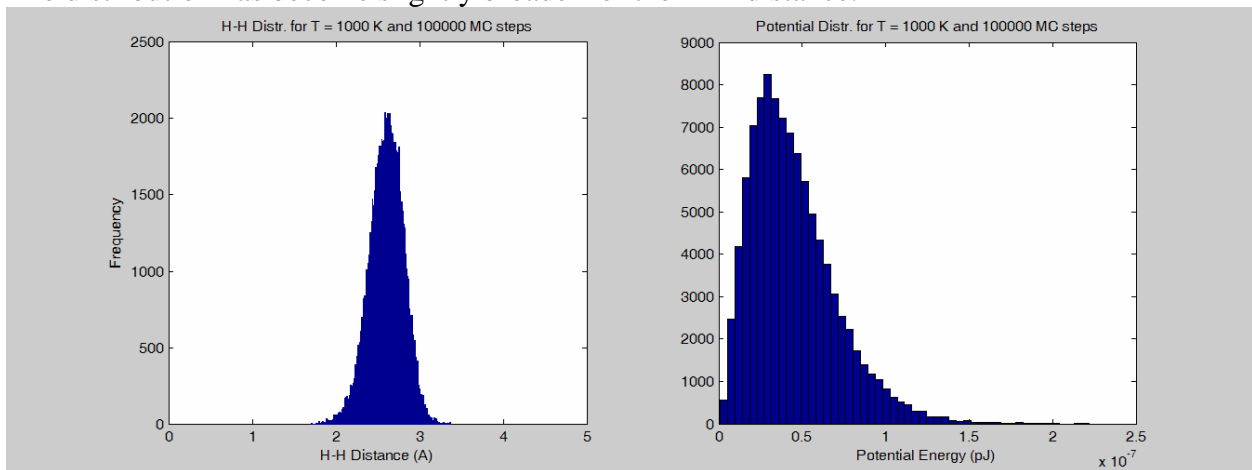
Results for T = 1000 K

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<1/R_HH^6> for T = 1000 K:  0.0037102  +/-  7.0191e-006
<1/R_HH^6> for T = 1000 K:  0.0037102 with sigma = 2.6755e-005
<R_HH> for T = 1000 K:  2.603
There were 44013 steps accepted out of 100000 total steps

Most probable MC V(q) = 2.9491e-008 pJ
Value of kB*T = 1.3807e-008 pJ
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Again, in this case the $<R_{HH}>$ is even larger and the asymmetry in the dihedral potential can be seen easily. At 1000 K, there was enough energy available to traverse the "trans" barrier and create the mirror-image molecule with the H2 atom on the opposite side of the x-y plane.

The distribution has become slightly broader for the H-H distance.

Results for T = 5000 K

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<1/R_HH^6> for T = 5000 K:  0.041604  +/-  0.0067392
<1/R_HH^6> for T = 5000 K:  0.041604 with sigma = 0.010055
<R_HH> for T = 5000 K:  2.7388
There were 74825 steps accepted out of 100000 total steps

Most probable MC V(q) = 1.5169e-007 pJ
Value of kB*T = 6.9035e-008 pJ
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At 5000 K, things become strange because there is enough energy available to break, or nearly break, the O-H bonds. In the figures below, you can see that the bonds break, but the atoms find their ways back into the wells again. The energy is also high enough that nearly all values of the dihedral angle can be sampled equally well (this would essentially act like a free rotor).
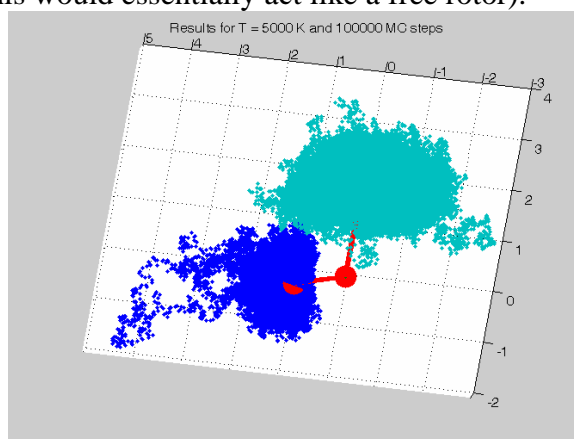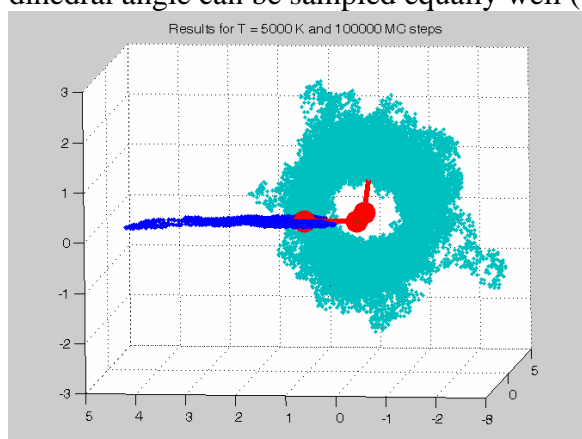

This distribution in this case is very wide, since such a large range of energies and geometries are accessible with a reasonably high probability.
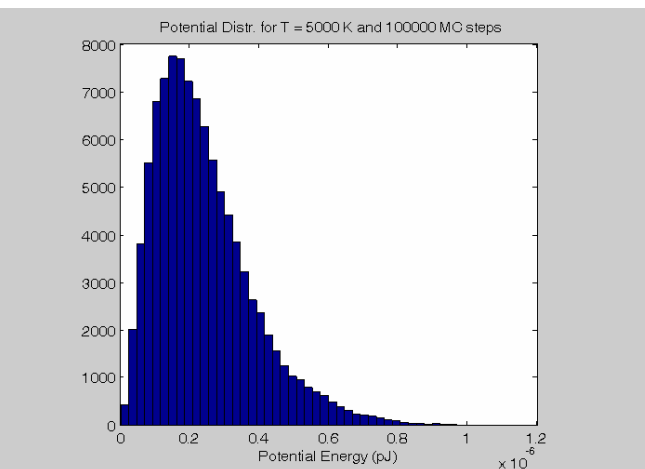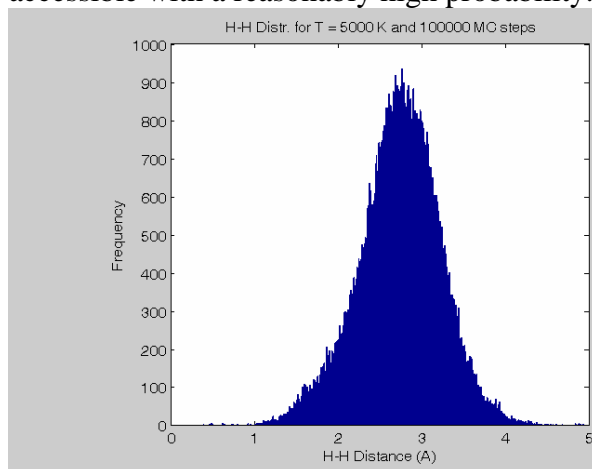
This is an example at 5000 K where the O-H bond was essentially broken, and the H atom was free to roam around on a nearly flat energy surface. It does not appear to have found its way back into the minimum energy well at the end of 100000 steps. This obviously will not give you any meaningful information, other than the fact that the molecule is unstable at such high T's.

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<1/R_HH^6> for T = 5000 K:  0.0050603  +/-  0.00057345
<1/R_HH^6> for T = 5000 K:  0.0050603 with sigma = 0.001415
<R_HH> for T = 5000 K:  12.5612
There were 78295 steps accepted out of 100000 total steps


Most probable MC V(q) = 6.8229e-007 pJ
Value of kB*T = 6.9035e-008 pJ
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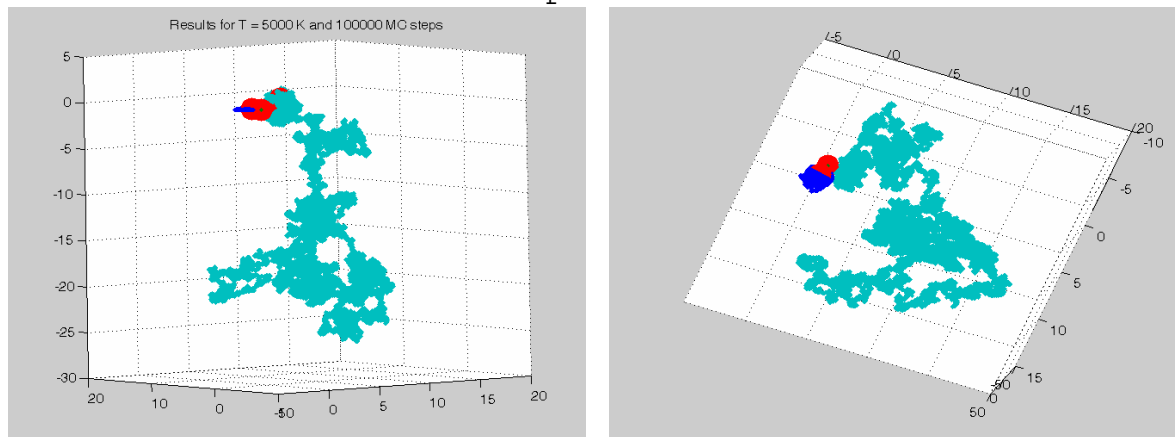

The distributions are interesting in this case because of the strange behavior. There is still a sharp peak in H-H between 2 and 3 Å, but there are also a large range of distances present due to the broken bond. You can also see the bimodal energy distribution. The lower energy peak corresponds to the distribution for a molecule confined within the molecular potential, while the higher energy peak corresponds to the molecule after the O-H bond has been broken. In reality, once the bond has been broken, the supplied potential is no longer valid, since the angular and dihedral potentials given would only be valid for tightly bound atoms in covalent bonds, but the behavior is interesting nonetheless.
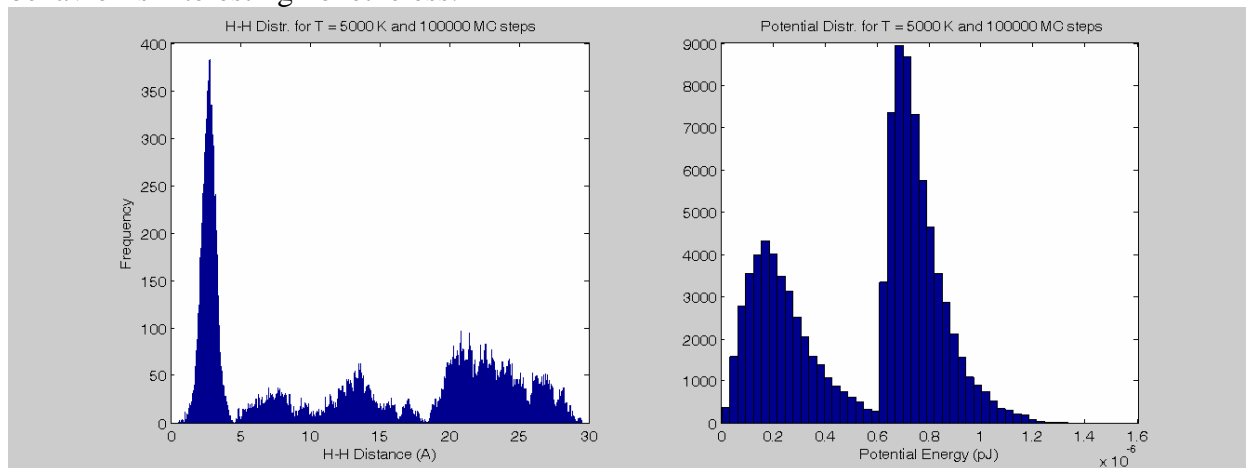
Results for $\langle R_{HH}^6 \rangle$ as the number of points increases for a single MC "trajectory"
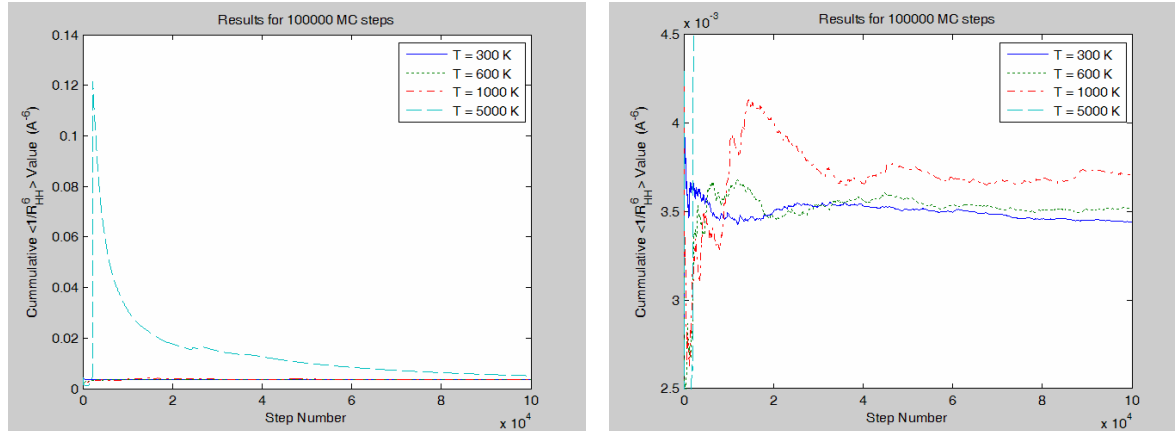
These results are for the average value along the entire MC sampling "trajectory." The word trajectory is used very loosely here since MC does not attempt to trace a true dynamic trajectory in time, but only samples randomly in space.

You can see that the behavior at 300 K, 600 K, and 1000 K is relatively well-confined to a narrow region. This is because the atoms are confined to a relatively narrow range of the physical space defined the molecular potential. You can also see that the high temperatures typically result in larger values of $\langle 1/R_{HH}^6 \rangle$. This is somewhat counter-intuitive because we also think that the $\langle R_{HH} \rangle$ should increase with temperature. However, the larger values of the H-H distance contribute much less to $\langle 1/R_{HH}^6 \rangle$ because they are raise to the 6th power.

What is happening is that at higher temperatures, you can have H-H values that are both larger and smaller that the equilibrium distance (or at a smaller temperature). Due to the asymmetric potential you can go farther to increase H-H than you can to decrease H-H (e.g. if the equilibrium H-H is 2.6 Å, then at 600 K, maybe you can range from 2.4 to 3.0 Å). This will definitely increase the value of $\langle R_{HH} \rangle$ with increasing temperature. However, since the small values of H-H will count much more in the $\langle 1/R_{HH}^6 \rangle$ value, the ability to add some smaller H-H values is much more important to the average value than adding larger values (even if the larger H-H values correspond to a larger displacement than the smaller ones).

The behavior at 5000 K shown here is strange, as expected. The molecule must have seen some very small H-H distances at the beginning that made the function average large, and then returned to more normal behavior as the number of points increased.

As a side note and along the same lines, you should also realize that:

$$\langle R_{HH} \rangle \neq \left\langle \frac{1}{R_{HH}^6} \right\rangle^{-\frac{1}{6}}$$