

## Molecular Motion

ID code \_\_\_\_\_  
Section \_\_\_\_\_

Date \_\_\_\_\_  
Instructor \_\_\_\_\_

**OBJECTIVE:** To visualize the distribution of molecular speeds and how it depends on mass and temperature.

**CONCEPTS:** Molecular motion, effusion, diffusion, Maxwell-Boltzmann distribution, gas laws

**INTRODUCTION:** Use a computer in the computer lab or download the program **Boltzmann 3D** from [http://people.chem.byu.edu/rbshirts/research/boltzmann\\_3d](http://people.chem.byu.edu/rbshirts/research/boltzmann_3d) onto your own computer. **Boltzmann 3D** simulates the motion of hard disks (2 dimensions) and hard spheres (3 dimensions) in a box. These are classical simulations of particles with no intermolecular forces except when they bounce off each other in a collision, but the behavior should be very much the same for real molecules above the boiling point. The program uses mouse controls and has online help by clicking "Help" in the help menu. It may take some time to get the hang of, but it can be fun.

When you start **Boltzmann 3D**, particles are started out with random positions and random directions but with identical velocities. However, when particles collide, they exchange energy. After they collide a few times, they should forget this highly unlikely velocity distribution and settle into a more probable one (i.e. the Maxwell-Boltzmann distribution). This lab exercise is to help you find out if that is really true and to help you visualize molecular motion in a gas. Work with a partner if one is available; otherwise you may work alone.

### Procedure

1. Before starting, fill in the following table of velocities and energies for H<sub>2</sub> and O<sub>2</sub> molecules in 2- and 3-dimensions. (Hint: since there are two rather than three directions in which to move, replace 3/2 by 2/2(=1) in the formula for kinetic energy, and 3 by 2 in the formula for rms velocity.)

	3D avg. kinetic energy (kJ/mol)	3D avg. RMS velocity (m/s)	3D avg. kinetic energy (kJ/mol)	3D avg. RMS velocity (m/s)
H <sub>2</sub> at 1000 K				
O <sub>2</sub> at 1000 K				
H <sub>2</sub> at 100 K				
O <sub>2</sub> at 100 K				

2. Calculate the ratio of effusion rates for H<sub>2</sub> molecules compared to O<sub>2</sub> molecules both at the same temperature? \_\_\_\_\_
3. Click "Load" in the **Boltzmann 3D** file menu and pick the file "2Dhyd1000.set", or start up a 2D simulation on your own with about 50 particles each with mass 2 amu (H<sub>2</sub>) at a temperature of 1000K (use the buttons at the lower left and press reset (return arrow) when you have the parameters adjusted). Select "Kinetic Energy" in the dropdown menu above the graph in the upper left to display a histogram of the kinetic energy distribution in the plot window at the upper left. The black line is the Boltzmann distribution and the vertical green line is the instantaneous average energy. Is the average kinetic energy correctly predicted (orange vertical line and your calculation in #1)? \_\_\_\_\_ The actual numbers for these computed and predicted averages are shown in boxes. Is the distribution accurately predicted? \_\_\_\_\_ Is the distribution of energies over a long time in better agreement (press "Cum" button after letting the simulation proceed a while, about 500 ps to 1 ns)? \_\_\_\_\_ You can speed up the simulation by clicking - several times on the simulation speed box. While you are waiting for the simulation to propagate, switch the plot display to the rms velocity plot by selecting "RMS Velocity" in the dropdown menu above the graph. The black line is the Maxwell-Boltzmann distribution of velocities, and the vertical green line is the actual rms velocity. Is the rms velocity correctly predicted (orange line and your calculation in #1)? \_\_\_\_\_ Is the instantaneous distribution exactly predicted? \_\_\_\_\_ Is the cumulative distribution in better agreement with the black line? \_\_\_\_\_

4. Adjust the simulation speed so you can follow one particle around. Pick one that is moving slowly. Is it slow all the time, or does it sometimes gain energy in a collision and become a fast particle temporarily? \_\_\_\_\_ Now pick one particle that is moving fast. It is fast all the time, or does it sometimes lose energy in a collision and become a slow particle temporarily? \_\_\_\_\_ Do you think there would be any difference between the average velocity or average energy of a large number of particles at one time and that of one particle averaged over a large time? \_\_\_\_\_ If you want to check, there are plots of the average velocity and energy of each particle averaged over the time of the simulation (see the clock in the lower left). All the particles do not have the same average velocity or energy in a short simulation, but the width of the distribution can be seen to decrease over a long simulation.
5. Start a new simulation with 450 particles by entering "450" in the "# of particles" box and then pressing reset (you may have to reduce the radius or resize the box to get them all in). Are the fluctuations about the black line smaller if you use more particles? \_\_\_\_\_ Estimate by approximately what factor the fluctuations decrease when you increased the number of particles by 9 from 50 to 450? \_\_\_\_\_ (Statisticians predict that the fluctuations should go down by a factor of  $9^{1/2} = 3$ .) How big do you expect fluctuations to be with  $10^{24}$  particles? \_\_\_\_\_
6. Use "Load" in the file menu and pick the file "2Doxy1000.set", or start a new simulation on your own with 50 particles of mass 32 amu ( $O_2$ ) at 1000K and repeat the observations you made in step #3. Why do oxygen particles have a lower average velocity than hydrogen particles at the same temperature? \_\_\_\_\_
7. Repeat your observations with  $H_2$  and  $O_2$  particles at 100K (you can use the files "2Dhyd100.set" and "2Doxy100.set") and see how the velocities and kinetic energies change. Are they in agreement with your predictions in #1? \_\_\_\_\_
8. Start a simulation with a mixture of  $H_2$  and  $O_2$  particles at a relatively high temperature (or click "Load" and pick "2Dmixture.set") or create your own by adding mass 32 particles after starting with mass 2 particles. Use about 30 particles of each. Watch the "RMS velocity" distribution (from the dropdown graph menu) for light and heavy particles and the sum of the two by clicking "Red," "Blue," and "Both" buttons at the top left. Do the light ones go faster than the heavy ones on average? \_\_\_\_\_ By what factor? \_\_\_\_\_ Why? \_\_\_\_\_ Now check the "Kinetic Energy" distribution. How does the kinetic energy average and distribution compare for the two sets? \_\_\_\_\_ Try to explain why? \_\_\_\_\_
9. Start a simulation with a mixture of  $H_2$  and  $O_2$  particles all on the left of a divided box (choose "Load" and pick "2Ddiffuse.set") or create your own by adding particles of the appropriate mass with the box divided (click the box shape button with a wall). Open an opening between the halves by clicking the box shape button with a hole in the wall. Watch how fast the heavy particles escape into the right-hand-side relative to the light ones. Are the two rates of escape in the ratio predicted by Graham's Law and your calculation in #2? \_\_\_\_\_ If not, try to guess why not. (Hint: Would you expect it be more accurate with  $10^{24}$  particles?) \_\_\_\_\_
10. Start a simulation like in #1 with a single type of particle and choose "RMS Velocity" in the graph. Look carefully at the predicted 2-dimensional velocity distribution. Then, change to a 3-dimensional simulation by clicking dimension under the simulation menu. How does the velocity distribution change? (Hint: look for curvature at low velocity) \_\_\_\_\_

Explore some of the other features of **Boltzmann 3D** if you have time.