

EXPERIMENT 2000.05.2: Gases, Diffusion, and Reactions

Topics of investigation: Coherent and incoherent atomic motion; diffusion; thermal equilibrium; fractals

Read about this topic in: Serway, Ch. 16, C&J, Ch. 14

Toolkit: Computer
LifeMaker (© Jesse Jones, 1990) Software

This set of laboratory exercises involves the study of a *simulation* of atomic motion using the freeware program LifeMaker[®], written by Jesse Jones, and modified by David Peak. In this study we will probe the differences between coherent and incoherent atomic motion, how a system of a large number of atoms approaches thermal equilibrium, and the nature of chemical reactions whose rates are determined by how fast reactant atoms can get to the site of the reaction.

The basic premises of this laboratory are: bulk matter consists of a very large number of atoms; atoms undergo unceasing, microscopic motion; and microscopic atomic motion can be usefully approximated as a series of constant velocity flights punctuated by elastic collisions with other atoms. Recall that an elastic collision conserves kinetic energy as well as momentum. Elastic collisions between atoms of equal mass basically interchange the velocities of the atoms.

Simulations are often incredibly useful for developing insight into the workings of real, physical (or biological or social) systems that are too difficult or expensive to create, or too hard to control, or too small to actually see, or too dangerous to play with. In this simulation, we will be able to manipulate and observe mobile atoms that can bounce off each other and off the walls of their container, and that can “stick” to immobile atoms to form a growing cluster. Atoms, in this simulation, can reside only on a square grid. (Technically, such a simulation is called a “lattice gas.”) When they move they jump from one site to another one grid spacing away.

First Exercise – A Dilute Gas; Preliminaries

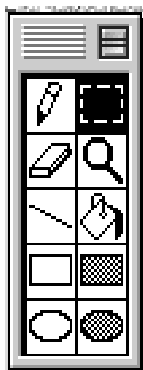
•E1.1 Launch the program *Gasstick.start*. *Gasstick.start* is a saved starting condition for LifeMaker.

Your computer monitor has to be set to 256 colors. To check

pull out the control strip  and click on the monitor colors panel, as shown to the right.

In addition to a large, white-filled window (the “space”), you should see (a) a toolbox, (b) a state menu, and (c) a clock (as shown left to right below). (If you don’t ask your TA for help.)

You can drag these windows around and place them anywhere you find convenient. Note that they *are* windows, and as such can be overlaid by other windows, such as the white-filled space.



•E1.2 Click on (select) the **rectangle outline tool** (row 4, column 1) in the toolbox. Click on (select) the **red state**. In the white space window click and drag diagonally to **form an unfilled rectangle of red states**. **Note: If at any time, you wish to undo a drawing action you have just made, click on Undo in the Edit Menu.** In the Gasstick simulation, a **red state represents a perfectly reflecting atom of infinite mass**. Thus, the rectangle you have created can be used as a two-dimensional “corral” in which other, mobile atoms can be trapped. **Mobile atoms are represented by the blue state**. Select the **pencil tool** (row 1, column 1) and the **blue state**, and create **one blue atom inside your corral** by clicking once. Under the Control Menu, **Reset Time**, then **Run**. Observe the motion of the blue atom for about a few hundred time steps. Depending on where you first created your atom it will move off along one of the four diagonal directions (NE, NW, SE, SW). Such a blue atom moves with constant velocity (speed = one diagonal grid spacing per time step) until it encounters a red atom, after which its velocity is redirected so that the angle of reflection equals the angle of incidence (a condition called “specular reflection”). The speed after the collision is exactly the same as the speed before. The red atom doesn’t budge (“infinite mass”). In Gasstick, a wall is a perfect reflector. Under Control click on **Stop**.

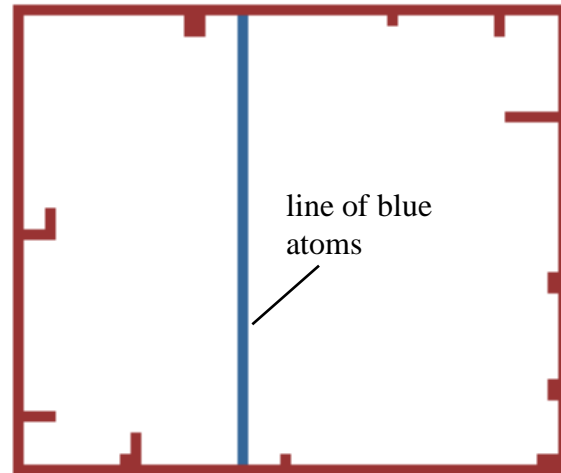
•E1.3 To see how two blue atoms interact with each other create a **second blue atom immediately above** or below the first. Run and track the two as they move about. What can you conclude about their motion and their interactions? Next, **erase one** of the atoms with the eraser tool (row 2, column 1). (The eraser makes a black smudge that disappears as soon as you Run again. Incidentally, if you accidentally erase some wall atoms, you can repair the hole by selecting red and the pencil tool, and putting them back one atom at a time.) Place a **second atom immediately to the left** or right side of the first. Run and track. Now what happens? Finally, **erase one** and place a **second adjacent to the unerased one along a diagonal**. Now what happens?

•E1.4 Some cool things to do: Erase previous atoms. **Note: You can remove large quantities of atoms with the dotted rectangle select tool (row 1, column 2). Surround the atoms you wish to remove by clicking and dragging the select tool over them. Then choose Clear in the Edit Menu.** (You can always clear everything then redraw your corral.) In each of the following cases, Run and say what you observe. • Create an L-shaped wedge of three blue atoms. • Create two blue atoms in a corner in along one wall. • Create two blue atoms in one corner pointing out diagonally. • Create a line of three blue atoms in a corner along one wall. • Create three blue atoms in one corner pointing out diagonally. • Create an L-shaped wedge of three blue atoms in a corner. • Create a vertical or horizontal line of an odd number atoms and of an even number. • Create a diagonal line of odd and even numbers. • With the rectangular fill or disk fill tools (row 4, column 2 and row 5, column 2, respectively), create a packed group of blue atoms near the center of the corral. • With the line tool (row 3, column 1) make a vertical or horizontal line of blue atoms that stretches from one side of the corral to the other. • Create two parallel lines like the previous one. **Do any of these lead to irregular or disordered motion?**

•E1.5 The following configurations are better viewed at a lower magnification. Under the View Menu **Zoom Out** once. **Clear** everything from your space using the select tool and redraw a **rectangular (red atom) corral**. Select as much of the interior of the corral as you can with the rectangular select tool. Be careful, the select tool sometimes selects the corral boundaries or outside them. If so, just click anywhere outside the selected area to deselect, then select again. Under the Transform Menu click on **Randomize > Low Bit**. Then, again Under Transform, click on **Density > 25%**. Finally, under Transform click on **Random**. 25% of the sites in the selected area should now be filled with blue atoms, with no special pattern. This is called a “random fill.” Guess what will happen when you let this starting pattern Run. Now **Run** for a minute or so. Is your guess confirmed? (You may observe some patterns moving through the display that are due to initially unfilled gaps near the walls.) **Clear** everything and create a **new corral**. Instead of filling

the whole interior now fill only about the **leftmost half with 25% fill**. Guess what will happen when you let this starting pattern Run. Now **Run** for a minute or so. Is your guess confirmed? Fill the **entire interior with 25% fill** again. With the line tool create a **vertical line of blue atoms** going from top to bottom somewhere inside the corral. Guess what will happen to the line when you Run it through a background of randomly created atoms. **Run**. What happens? The latter situation is equivalent to the passage of a “sound wave” through a tube of air (like a clarinet). A sound wave exists in a background fluid or solid medium and is a series of regions of more densely packed atoms that appear to travel coherently together over long distances. In the perfectly elastic collision model of this simulation with perfectly rectangular walls, the wave will continue to travel back and forth through the tube without weakening or spreading out.

•E1.6 In all of the cases examined so far, any initial collective motion of gas atoms is retained indefinitely. Of course, such perpetual coherent motion is *not* observed in nature. In nature, waves dissipate. Unequal concentrations equilibrate. How does this happen? Start with a **new corral** and a nicely coherent **vertical line of blue atoms**. With the pencil tool and the red state selected, **decorate the inner walls of the corral with 10 or so irregularly spaced protuberances**, like those shown to the right. **Reset Time**. **Run**. How long does it take for the initial line state of blue atoms to lose all recognizable coherence? The state that eventually emerges from these collisions is very similar to a state with randomly assigned initial positions of blue atoms, though **nothing** about the evolution of this state is random. The motions of all atoms in this corral are perfectly deterministic (the future is completely determined by the past). The imperfections in the walls of the corral cause the blue atoms to mix as if they were randomly placed. This highly mixed—as-good-as-random—final state is what we call “thermal equilibrium.” Thermal equilibrium is a state of maximal mixing caused by microscopic irregularities.



•E1.7 Create **two corrals of approximately the same size and shape** next to each other. Fill **one with 5% random fill**, the **second with 50%**. **Run**. Watch both very closely. Do you ever see in the 5% corral fairly large empty areas and fairly large clumps? Do you see similar density variations in the 50% corral? Sudden appearances of unusual areas of atomic clustering or evacuation are called **density fluctuations**. Large density fluctuations are *much* more likely when dealing with small numbers of randomly placed atoms than with large numbers of randomly placed atoms—though such fluctuations *could* happen in the larger system. (In a container with 10^{25} or so atoms, the likelihood that any significant fraction of the volume will spontaneously become empty is *incredibly low*, though, in principle, it *could* happen.)

Second Exercise – Diffusion in a Dense Medium

•E2.1 **Clear** the space. Under View, **Zoom In** once. Under Space, select **Margolus > Dendcoll**. Create a **corral**. Create a **single blue atom**. **Run**. What is the difference between the motion of a blue atom for the rule Dendcoll and a blue atom for the previous rule Gasstick? (There’s a trivial difference: the blue atom now goes either N, S, E, or W. But there’s a much more significant difference.) The rule Dendcoll simulates the motion of an atom in a background sea of other atoms. The background atoms in this simulation are unimportant and are colored white. You can’t see them, but they’re there. All of the atoms are flying around as before (except for the diagonal versus vertical-horizontal difference), but the packing is so dense that none of them get very far

before suffering a collision. The motion of the blue atom appears willy-nilly. Its motion is called a *random walk* or *Brownian motion*. When there is no net flow (convection) of the solvent, molecules in solution undergo Brownian motion.

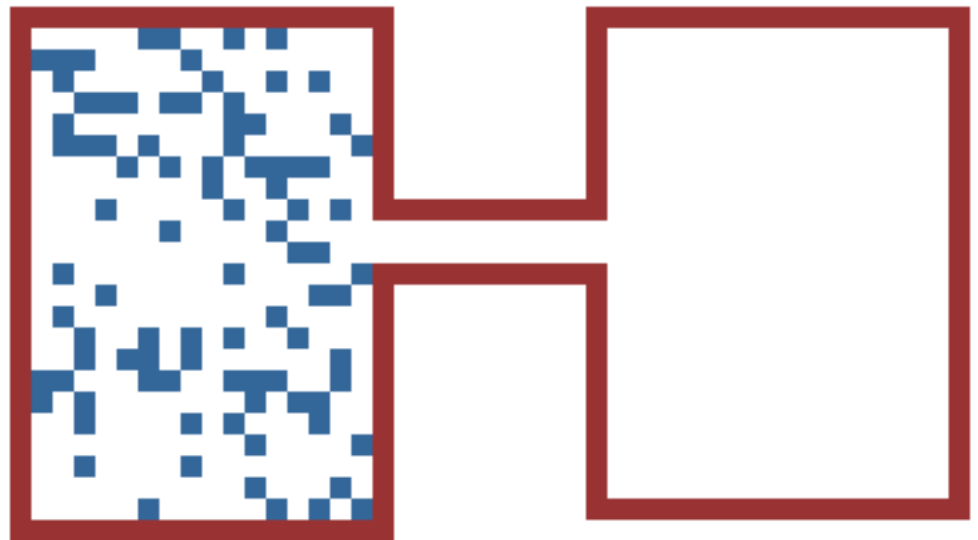
•E2.2 Create a **second blue atom** with a gap of one space near the first. **Run** for a few hundred time steps. For gas atoms freely moving in empty space and colliding with perfect walls, two such atoms starting close, stay close. But this isn't so for two atoms diffusing through a dense medium. There they stay close only for a brief period—occasionally returning, occasionally drifting far apart.

•E2.3 **Clear** the space. Under View, **Zoom Out twice**. Create a **new corral** and, with the disk fill tool, a **small blob of blue atoms near the center** of the corral. **Run**. Does the resulting motion remind you of anything? What you observe is like what happens, for example, when a drop of ink is placed in a glass of water. Gradually the sharp boundaries of the drop blur. The drop spreads and eventually fills the interior of the corral fairly uniformly.

•E2.4 **Clear** the space. **Zoom In twice**. Create a **corral**. Fill the **left hand half** of the corral **with 100% blue atoms using the rectangular fill tool**. **Reset Time**. **Run**. What does the corral look like after about **500 time steps**? How does this differ from what would have happened had you done the same thing with the Gasstick rule, that is, with gas atoms rushing into a vacuum? Diffusion is a mechanism for mixing in which atoms tend to migrate from regions of high concentration to regions of low concentration.

Third Exercise – Diffusion versus Gas Flow: Consequences for Biology and Chemistry

•E3.1 **Clear** the space. Create a **corral with two large chambers connected by a narrow channel**, such as the one to the right. Such a corral can be thought of as a model for molecules passing across a cell membrane, for example. Here the left hand side can be thought of as outside the membrane, the right hand side as inside the membrane, and the channel as channel through the membrane through which molecules



can be exchanged between the inside and outside. Fill the in the interior of the **left hand side with blue atoms using 25% random fill**. Select **Margolus > Gasstick** under the Space Menu. **Reset Time**. Run for **150 time steps**. Note how atoms are distributed throughout the corral. **Erase all of the blue atoms** (repairing the walls with the red pencil if necessary). Replace the **fill on the left hand side with 25% blue atoms**. Select **Margolus > Dendcoll** under Space. **Reset Time**. Run for **150 time steps**. Compare the distribution of blue atoms now with the former case. Diffusion doesn't require much machinery, such as a pump, so it is structurally "cheap." But it is also exceedingly slow. Where it is essential to transport molecules across a cell membrane rapidly, evolution has discovered faster mechanisms than diffusion. Calcium and potassium ions, for example, are transported across cell membranes by electrical pumps. They cost energy to run, but chemical reactions using these ions get done in a reasonable time as a result.

•E3.2 **Clear** the space. Create an approximately **square corral**. Fill the corral with **10% blue atoms**. Select **green** and with the pencil tool insert **one green atom at the center** of the corral. Green atoms don't move and they are sticky. When a blue atom collides with a green one it sticks and gets converted to green. Select **Margolus > Gasstick. Reset Time. Run**. During the run note the shape of the developing cluster of green atoms and also note the distribution of blue atoms in the vicinity of the green cluster. **Stop as soon as there are no blue atoms left. Note the time** necessary to completely use up blue atoms. Describe the green cluster that is formed. **Erase the cluster** and repeat the previous steps, but now using **Margolus > Dendcoll. Compare the times** to use up blues in each case and compare the cluster structures. You should have observed a "depletion region" around the growing cluster in the diffusion case that wasn't present in the gas flow case. The depletion region occurs because the reaction $blue \rightarrow green$ happens abruptly, while replacing a blue atom near the green cluster by diffusion can take a long time. (Replacement in gas flow is much quicker.)

Local depletion due to a rapid reaction fed by slow diffusion is a quite common phenomenon in chemistry and biology. Such a reaction is called *diffusion limited*—the rate of the reaction is limited only by the ability of diffusion to resupply reactants. The green cluster formed by blue atom diffusion is an example of what is called a *diffusion limited aggregate (DLA)*. The green cluster formed by free gas flow is called a *ballistic aggregate (BA)*. DLA's are much less compact than BA's. They have stringy structures called *dendrites* (that is, "fingers") and large holes called *fjords*. The fjords in a DLA don't fill in because diffusing blue atoms have a really hard time going long distances in a straight line. DLA structures are found in electroplating (as when copper ions diffuse to an electrode to form a copper deposit) and in the growth of cell colonies (as when a single bacterium, placed on the surface of a nutrient in a petri dish, divides again and again). An oil deposit in rocky subsurface soil is DLA-like as are the paths electrical current travels over when a power line falls on the ground. Even city neighborhoods have dendritic shapes reminiscent of DLA.

*****You are done using the software. Please Quit LifeMaker (under File) and click NO when it asks if you want to save changes.*****

Project: We can distinguish between a compact ballistic aggregate and a DLA by a statistical property called *mass dimension*. We think of a sheet of paper as being essentially 2-dimensional—it is characterized by a length and a width. (Of course, it also has thickness, but let's assume that thickness is unimportant.) The mass dimension of a sheet of paper is determined by cutting out a series of disks of different radii and weighing them. Suppose the mass of a disk of radius 1 cm is found to be 1 g. The mass of a disk of the same paper of radius 2 cm will be 4 g and that of a disk of radius 3 cm will be 9 g and so on. In other words, the relation between mass, M , and radius, R , for disks of paper is $M = AR^2$, where A depends on the units of mass and radius used. *The exponent 2 is the mass dimension of a sheet of paper.* It agrees with our primitive idea of dimension.

You are supplied with a DLA and a ballistic aggregate grown with LifeMaker. Superposed on top of the aggregates are a series of concentric disks. For each, count the number of atoms in disks of radii 1, 2, 3, and 4, respectively. Here 1 atom = 1 unit of mass. For each we seek a relation $N = AR^d$, where d is the mass-dimension of the respective cluster. How do you find d ? One way is to plot the log of N as a function of the log of R and fit the data with a straight line. The slope of such a fit should be an experimental value for d . (**Be sure you understand why.**) (People have evaluated d for really large BA's and really large DLA's and have found $d_{BA} = 2.00$ and $d_{DLA} = 1.71$. What do you find? Objects that have a weird, non-integer dimension like 1.71 are called *fractals*. Fractals are typically made up of subpieces that are basically just shrunken copies of the whole thing. For a DLA, a piece of a dendrite can look pretty much like the whole DLA; that piece will have even smaller pieces that look like the whole thing. Rivers have tributaries that look like the

whole river. The tributaries, in turn, have smaller tributaries that also look like the whole river. This branching structure repeats again and again down to tiny rivulets. A tree also has branches, and each of these looks like a shrunken tree; each branch has stems that also look like little trees. A lung, again, consists of branches, having subbranches, having subbranches. The brain has large folds that have smaller, similar folds that have smaller similar folds. Fractal structures abound in the natural world, especially in biology. Recently it has been shown that the surfaces of some tumors form fractal shapes similar to DLA's. It has been shown that the rougher the surface of a tumor the more likely it is to metastasize. By calculating the fractal dimension of the surface of a tumor mass, it is possible to predict whether the tumor is malignant or benign.

Incidentally, turbulent swirls in a fluid are also fractal—made up of similar smaller swirls, that also contains similar even smaller swirls. The fractal shape of turbulence obviously is associated with the appearance of chaotic dynamics. This appears not to be an accident. Frequently, when a process is infected with chaotic time-keeping there are also fractal shapes lurking around, and *vice versa*. Of course, since many physiological systems appear to be chaotic it should be no surprise that anatomy is filled with fractal structures. One wonders to what extent the one actually creates the other (as opposed to just being an artifact). As yet this is an unanswered question.

(If you want to know more about fractal structures in nature you could read about them in the book, *Chaos Under Control*, by Peak and Frame (Freeman, 1994).)