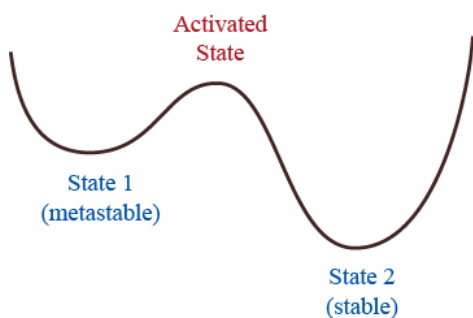


Homework 4 online activity: accompanying handout

I. Introduction

The goal of this activity is to provide insight into the ways modern science views the effects of temperature on chemical reactions, including especially thermally activated processes. Schematic diagrams of the type shown below, and used in lecture, have tremendous power when thinking about such processes at the molecular level.

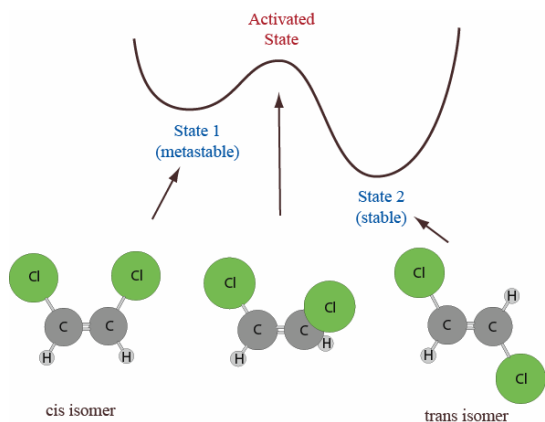


The diagram shows the energy associated with a thermally activated process in which a chemical system transitions between two states, labeled state 1 and state 2. State 2 is a stable state because it corresponds to the lowest energy configuration. State 1 is a metastable because, although it has higher energy than state 2, the system must overcome an activation barrier to transition from state 1 to state 2. In many cases, the barrier is so high that the metastable state can exist for a very long time. For instance, diamond is a higher-energy form of carbon than graphite and so is, in principle, a metastable form of carbon. However, the barrier between the diamond and graphite form of carbon is so high that you are not in any danger of having your diamond necklace spontaneously convert into graphite. For chemical processes with lower barriers, transitions from metastable to stable states do occur and diagrams of the type above are the primary means through which scientists understand such processes. We will therefore begin by exploring the meanings of various features of the above diagram and how it is used to think about chemical processes.

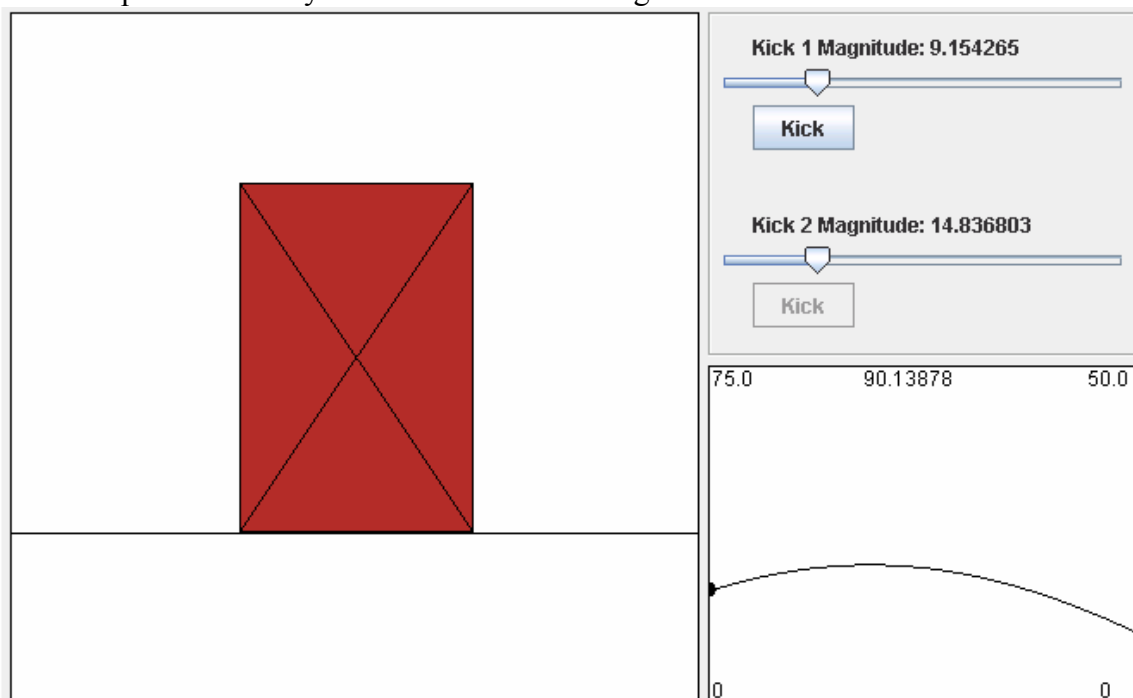
II. The reaction coordinate

The first feature we will explore is the meaning of the x-axis in the above figure, which is known as the reaction coordinate Q . For a system to get from state 1 to state 2 it must follow some pathway. In most cases, we don't have detailed information on the precise nature of this pathway, but it is nevertheless useful to imagine motion along a single dimension and consider the potential energy of the system as it moves along this path. The potential energy along the reaction coordinate is called the "energy landscape".

One example for which the pathway is easy to envision is the cis-trans isomerization shown below. In this case, Q is the dihedral angle about the double bond. The transition state occurs when the dihedral angle is about 90° . We can consider all angles $<90^\circ$ to correspond to the cis isomer (state 1) and all angles $>90^\circ$ to correspond to the trans isomer (state 2).



Our simulations will use a much simpler system, but one that retains the essentials of a thermally activated process. The system is that of the rectangular box demonstrated in lecture.



Activity Try kicking the box over (with the upper kick button). Once it falls over, try kicking it back up (with the lower kick button). Notice the relation between the position of the box and the dot on the energy landscape.

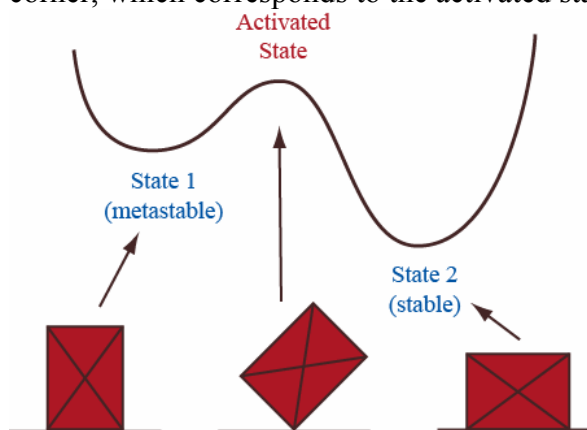
Q: What is the minimum kick needed to knock the box from the metastable to stable state (kick 1)? (Please give answer to 1 point past the decimal point.)

Q: What is the minimum kick needed to knock the box from the stable state to the metastable state (kick 2)? (Please give answer to 1 point past the decimal point.)

Q: Compare your results for the above minimum kicks to the three numbers above the energy landscape. These three numbers give the energy of state 1, the energy at the top of the barrier, and the energy of state 2. What is the relation between these numbers?

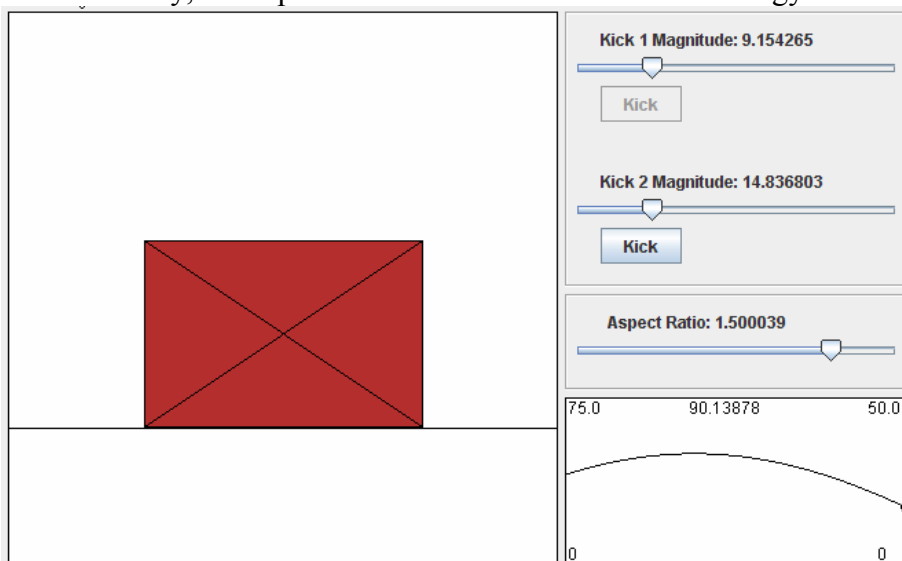
Notice the relation between the position of the box and the dot on the energy landscape. The landscape shows the gravitational potential energy of the system. What is Q for this system? What is state 1 and state 2? Which state is stable and which state is metastable? What does the transition state look like?

Answer: The following shows the energy landscape for the box. The box has a metastable configuration, in which the box is standing on a short edge, and a stable configuration, in which the box is laying down on a long edge. To transition between these states, the box must stand up on a corner, which corresponds to the activated state.



III. The energy landscape

In this activity, we explore the factors that establish the energy landscape.



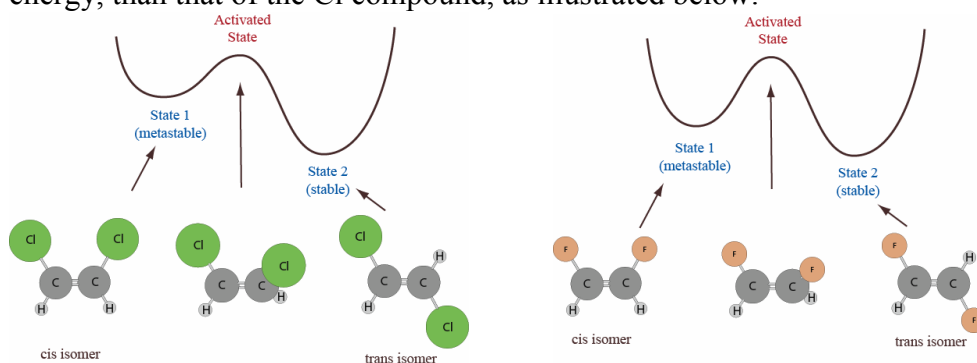
Activity Try moving the “aspect ratio” slider and see what it alters.

Q: For which aspect ratios is the reaction uphill in energy (energy of state 2 > energy of state 1)? For which aspect ratios is it a downhill reaction?

Q: The driving force of a reaction is the magnitude of the energy difference between states 1 and 2. For what aspect ratio is the driving force the greatest? For what aspect ratio is it easiest to knock the box over, i.e. requires the smallest kick?

This activity illustrates that the energy landscape is established by the structure of the system. For a chemical system, it is established by the molecular structure. For instance, if we replace the chlorines of the molecule shown in lesson 2 with fluorines, we alter the energy landscape for the cis-trans isomerization. The van der Waals ratio (i.e. size) of Fluorine is less than that of Chlorine. How do you think the energy landscape changes when you replace Cl with F?

Answer: Since F is smaller than Cl, the steric interaction between F atoms is less than that between Cl atoms. The metastable state for the fluorine substituted compound is then more stable, i.e. has lower energy, than that of the Cl compound, as illustrated below.

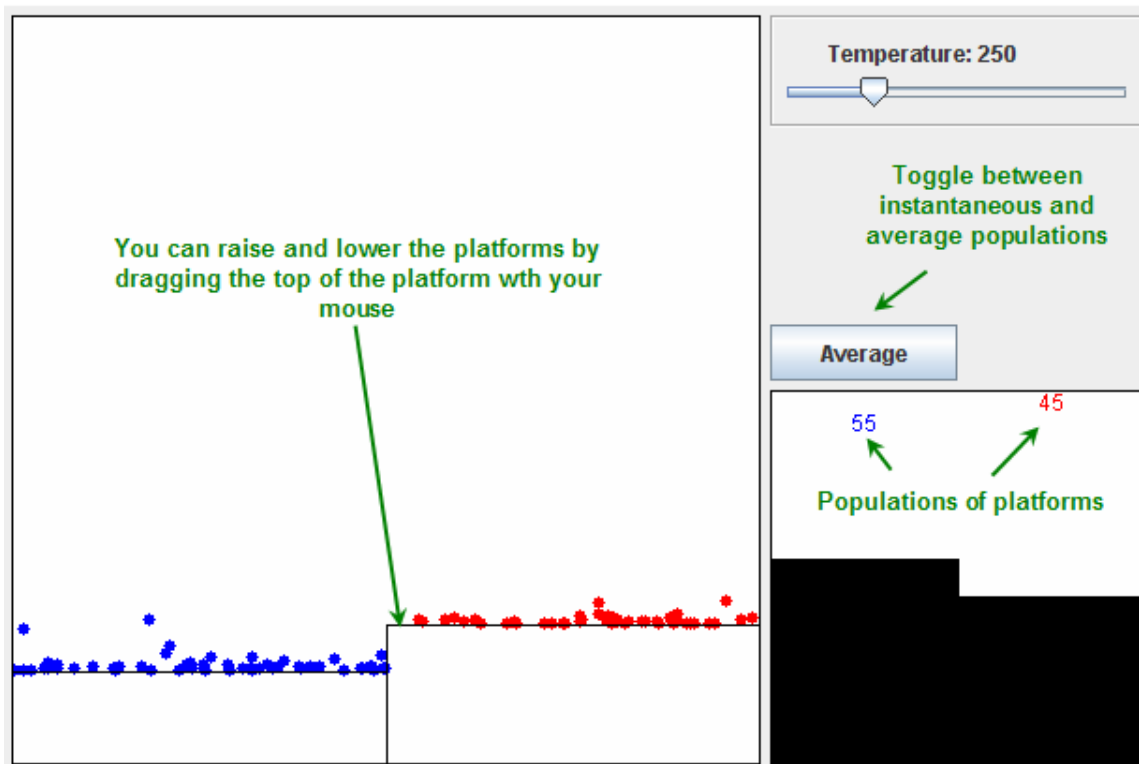


Changing Cl to F is analogous to changing the aspect ratio of our box. For the box, we can choose any aspect ratio we want. For molecular systems, we often have discrete choices, such as choosing one of the halogens (F, Cl, Br, or I) or replacing an amino acid of a protein with another amino acid.

IV. Population distributions

In the above simulations, you determined the strength of kick needed to knock the box over or stand it up. Molecules are always being kicked by their surroundings, and the strength of these kicks is related to the temperature of the system. For molecules in solution, the kicks come from the surrounding solvent molecules. However, the details of the surroundings are not essential to making predictions of how the system will behave. In fact, we can just view the surroundings as a "heat bath" that exchanges energy (heat) with the system through random kicks.

For our box, a good analogy of a heat bath is to consider placing the box on a shaking platform. The platform kicks the box randomly, with the strength of the kicks being set by the temperature of the heat bath. Before putting boxes on a shaking platform, let's consider placing balls on the platform. The height to which a ball rises after being kicked by the platform is an indication of how hard it was kicked. The average height of the balls is then an indication of the average strength of the kicks.



The balls on the upper platform can be viewed as being "activated", since they have higher energy than those on the lower platform. To denote this activation, the balls change their color to red when they transition to the upper platform.

Activity Turn the temperature up to 700 and let the simulation run for a while. The populations on each of the platforms will change at first, and then reach a steady-state where the number of particles on the lower platform is 3 to 4 times greater than that on the upper platform. (Note that the populations will fluctuate quite a bit, with the number of particles on the upper platform going from about 14 to 28.)

Q: Try lowering the temperature to 300. Let the simulation run for a while (so that the particles can reach thermal equilibrium). Is the average population on the upper platform larger or smaller than it was at $T=700$?

The ratio between the number of particles in state 2 and the number in state 1 is equal to

$$\frac{P_2}{P_1} = e^{-\frac{(E_2-E_1)}{RT}} = e^{-\frac{\Delta E}{RT}}$$

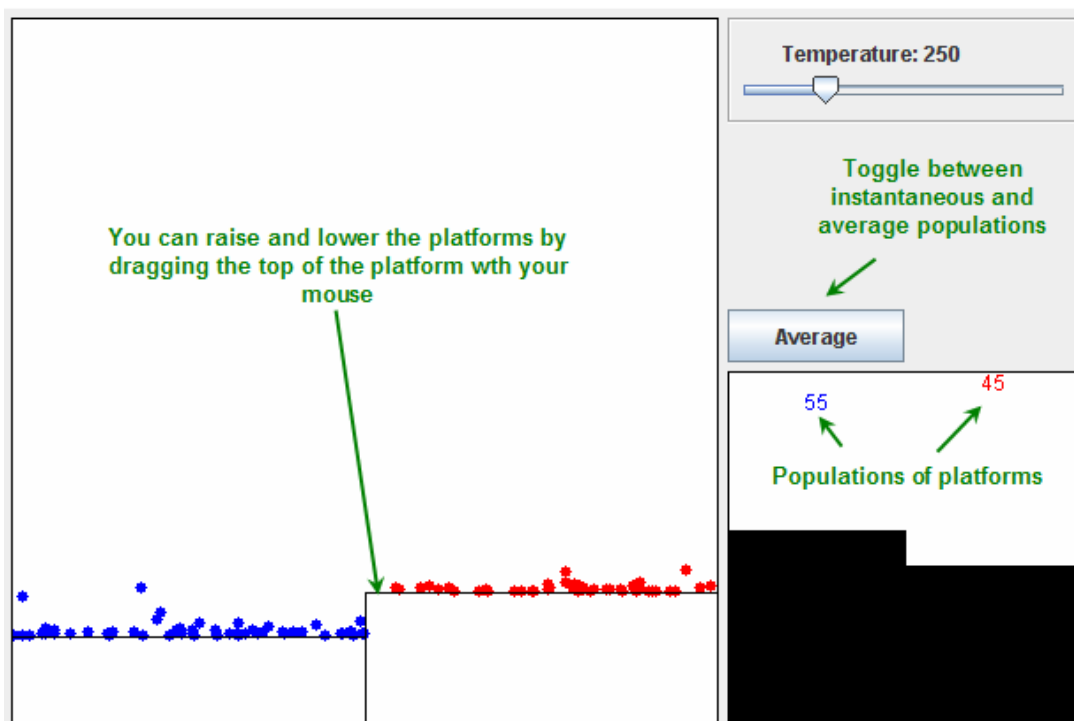
Where P_2 and P_1 are the "populations" of state 2 and state 1, i.e. the average number of particles in each of these states.

Note that P_2/P_1 depends only on ΔE and RT . ΔE is the difference in energy between the two states, and RT is the thermal energy (i.e. a measure of the average kinetic energy of the particles, or in our example, the average height of the bouncing balls). To predict P_2/P_1 , we don't need to know the detailed pathway between the states, we just need to know the difference in state energies and the

temperature. (The pathway can change how long it takes to reach thermal equilibrium, i.e. how long it takes the populations of the two platforms in our simulation to reach steady state.)

If you watch the simulation for a while, you'll notice that every so often a ball gets a very strong kick from the platform. Although these strong kicks are rare, they are important since they give the system enough energy to make it to a high-energy platform. Even small increases in temperature can substantially increase the number of times a system gets a strong enough kick to reach a highly activated state, which would be represented here as a high energy platform. Try changing the temperature and noting how often a ball gets a strong kick.

V. Motion at constant temperature, and exchange of energy with the heat bath



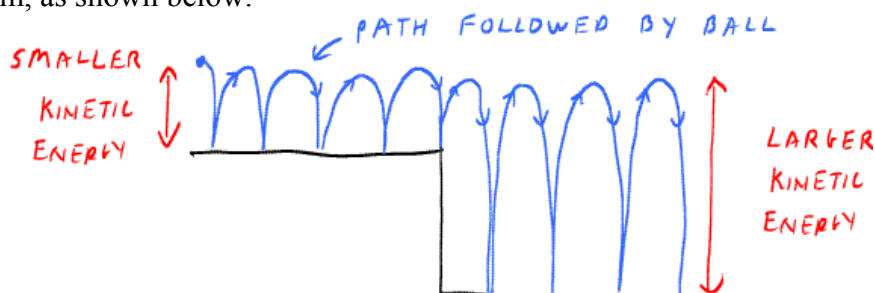
Activity Increase the temperature of the system. What happens to the average height of the bouncing particles? Compare the average height of the bouncing balls on the upper platform to the lower platform. Are they different?

You should have found that the average height of the particles on the two platforms is the same. This is an important aspect of molecular motion at constant temperature. The motion of particles is referred to as kinetic energy and temperature is a measure of the average kinetic energy of the atoms and molecules,

$$\langle \text{Kinetic energy per degree of freedom} \rangle = \frac{1}{2} k T$$

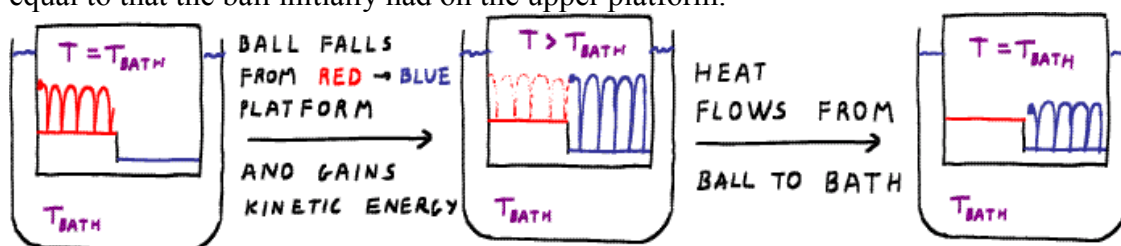
where k is the "Boltzmann constant" with a value $1.3806503 \times 10^{-23}$ J/K. (The units are Joules (energy) per Kelvin (degrees).) The heat bath ensures that the average kinetic energy of the particles is equal to $1/2 kT$ per degree of freedom.

Dynamics at constant temperature, i.e. on a shaking platform, is considerably different than everyday dynamics. Consider a ball bouncing on the above platforms. The height of the bounce sets the average kinetic energy of the ball. Suppose the ball falls off the upper platform and onto the lower platform, as shown below.

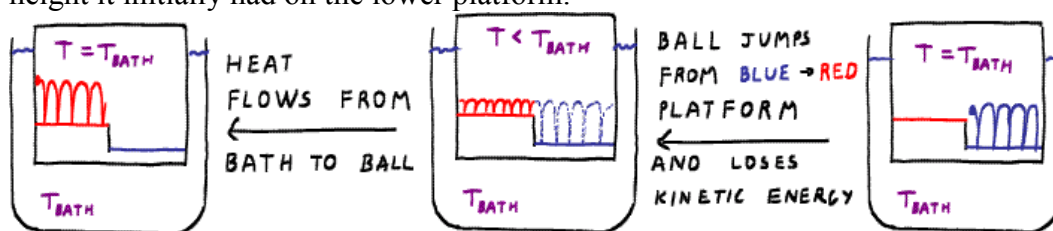


When the ball falls to the lower platform, gravitational potential energy is converted into kinetic energy, so the degree of bouncing is higher on the lower platform than it was on the upper platform. This means the average kinetic energy of the ball has increased. Since temperature is directly proportional to the average kinetic energy, this means the temperature of the system has increased.

In contact with a heat bath (shaking platform), energy will flow into or out of the heat bath to keep the system at constant temperature. The heat bath is constantly giving and taking kinetic energy from the ball, in such a way that the average height of the bouncing ball remains constant. When the ball falls off the platform, transitioning from state 1 to state 2, the potential energy decreases. This energy initially appears as an increase in kinetic energy, corresponding to an increase in temperature. The temperature of the ball is now higher than that of the heat bath ($T > T_{\text{bath}}$), so heat flows into the heat bath until the temperature of the ball becomes equal to that of the heat bath ($T = T_{\text{bath}}$). As heat flows into the heat bath, the kinetic energy of the ball decreases until the average height of the bouncing is equal to that the ball initially had on the upper platform.



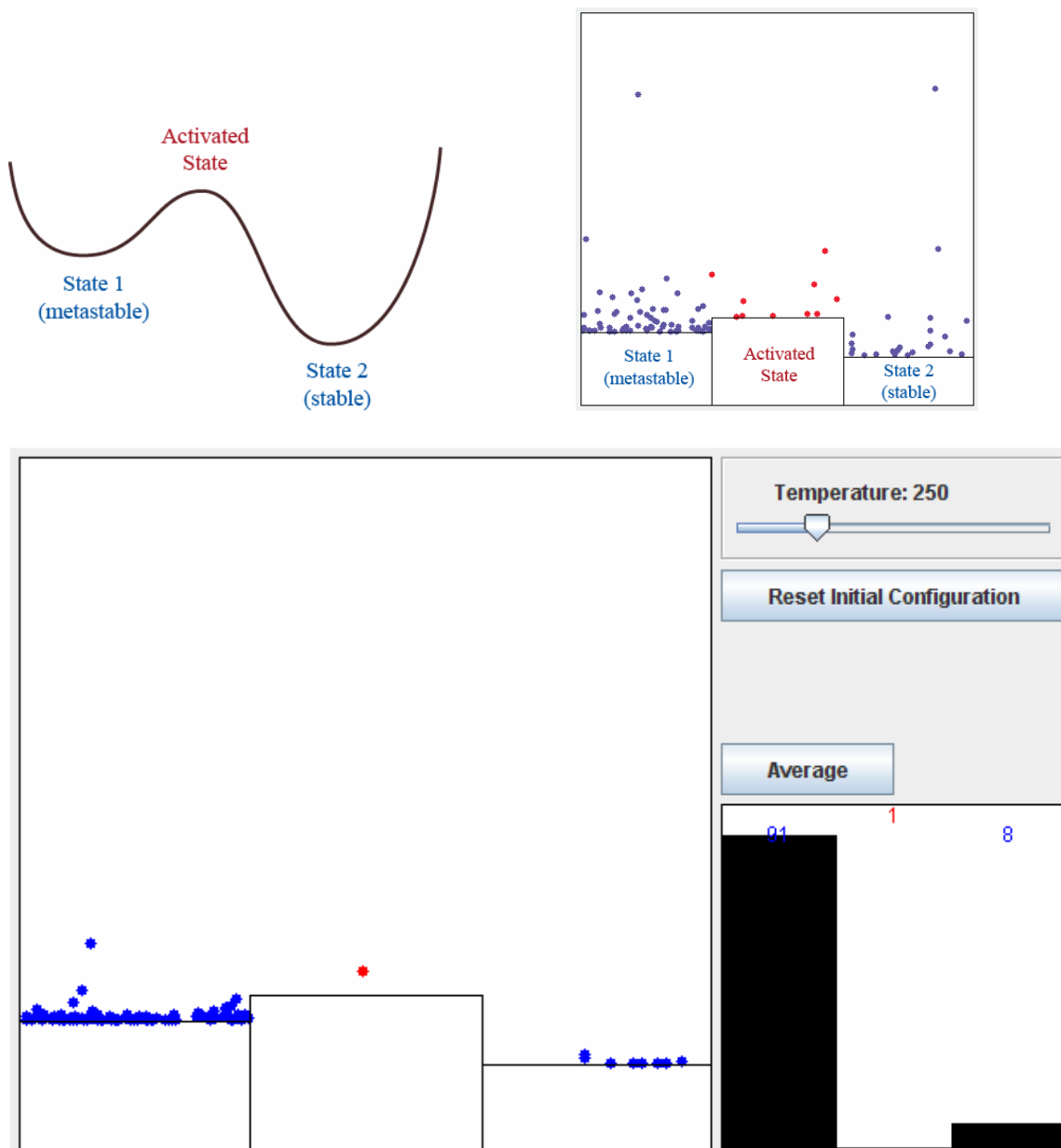
As the ball moves from state 1 (upper platform) to state 2 (lower platform), heat flows into the heat bath. The opposite is true for a transition from state 2 to state 1. Following the figure below from right to left, we see that as the ball transitions from the lower to the upper platform, it loses kinetic energy and its temperature drops below that of the bath. Heat then flow into the system from the heat bath, increasing the average kinetic energy so that the ball is now bouncing with the same average height it initially had on the lower platform.



Q: Supposed that the difference in energy between the upper and lower platform in the above diagrams is 5 kJ/mol. When the ball falls from the upper to lower platform, what is the flow of energy (both magnitude and direction) between the ball and the heat bath?

VI. Thermally activated processes

Above, we considered the number of molecules that will be on a high-energy vs. low-energy platform. In this activity, we explore the consequences of this on the rate of thermally activated processes. In the simulation, we will mimic the energy landscape with three platforms that represent the metastable, activated and stable states as shown below.



Activity The simulation starts with all of the balls in the metastable state.

Q: What happens to the number of activated molecules, i.e. balls on the activated platform, as you increase the temperature?

Q: How does this affect the rate of the reaction, i.e. the rate at which balls reach the platform on the right that represents the stable state?

In order to reach the stable state, a ball must first be activated by getting sufficient energy from the bath to reach the activated (middle) platform. Once on the activated platform, some balls will fall to the right onto the stable platform. The number of balls reaching the stable platform in a given time is then proportional to the number of activated molecules, which we saw above is proportional to $e^{-\frac{E_a}{RT}}$ where E_a is the difference in energy between the activated and stable platforms. The rate of a thermally activated process is therefore proportional to $e^{-\frac{E_a}{RT}}$.

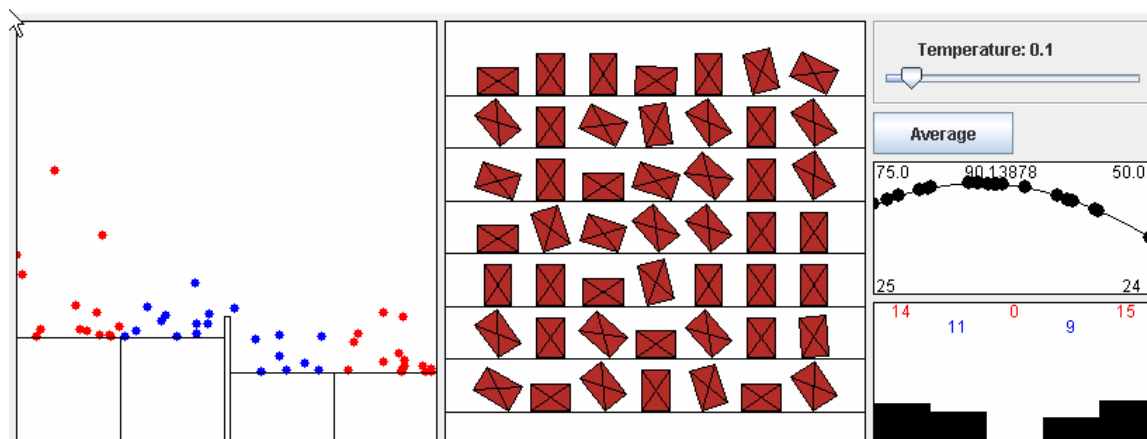
If you watch the simulation for a while, you'll notice that every so often a ball gets a very strong kick from the platform. Although these strong kicks are rare, they are important since they give the system enough energy to make it to the activated state. Even small increases in temperature can substantially increase the number of times a system gets a strong enough kick to reach the activated state, represented here by the middle platform. Some thermally-activated processes take minutes or hours to occur. For instance, when you cook an egg, it takes a few minutes for the egg white to solidify and even longer for the yolk to solidify. On a molecular scale, the molecules are bouncing at about 10^{12} times per second. If we were to use our simulation to model a reaction takes one second to occur, a ball would have to bounce an average of about 10^{12} times before it got a kick strong enough to knock it onto the activated platform.

VII. Energy and temperature determine the populations

Once a system reaches thermal equilibrium, the relative populations of two states is related only to the difference in energy between the states, ΔE , and the temperature T , through the relation $P_2/P_1 = e^{-\Delta E/kT}$. The details of the dynamics do not play a role. This next activity places the balls and the boxes on platforms that are shaking with the same temperature, which you can control with the slider bar. The two simulations are set to have the same number of states and state energies.

The box has four states corresponding to the four sides of the box. There are two ways to stand up (two short sides) and two ways to lie down (two long sides).

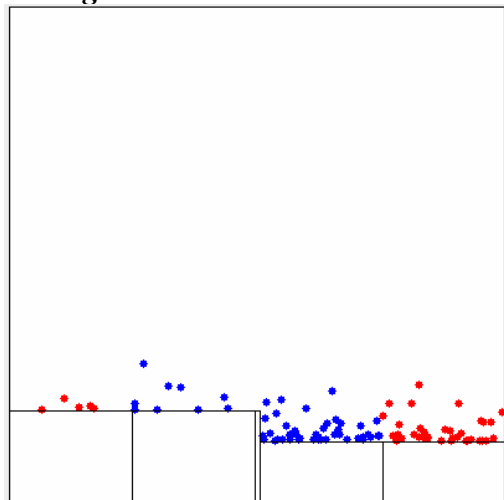
The bouncing ball simulation also has four states, corresponding to four platforms. Two platforms are at high energy (modeling the box standing up) and two are at low energy (modeling the box laying down). The narrow bar in the middle is present to model the transition state between the stable and metastable states.



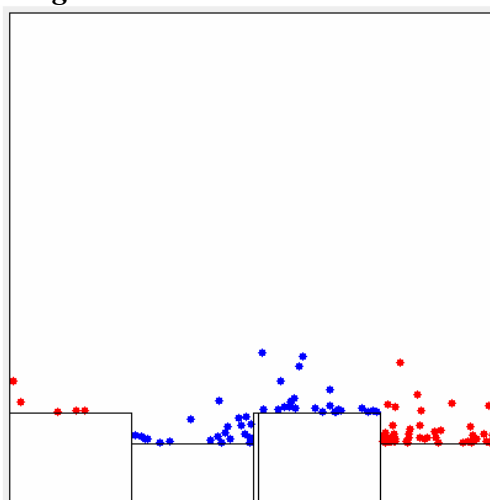
Activity Compare the populations of the balls on the upper and lower platform, to the population of boxes standing up and laying down. Try changing the temperature. Note that although the population ratios P_2/P_1 reach similar values after long time, the time it takes to reach this steady-state (or equilibrium) condition is different for the two systems. This is because the steady state P_2/P_1 depends only on ΔE and T , however, the detailed manner in which the system reaches this steady state depends on the details of the dynamics.

Consider the following two arrangements of platforms. The energies of the platforms are the same in both arrangements, but the order of the platforms is different.

Arrangement 1



Arrangement 2

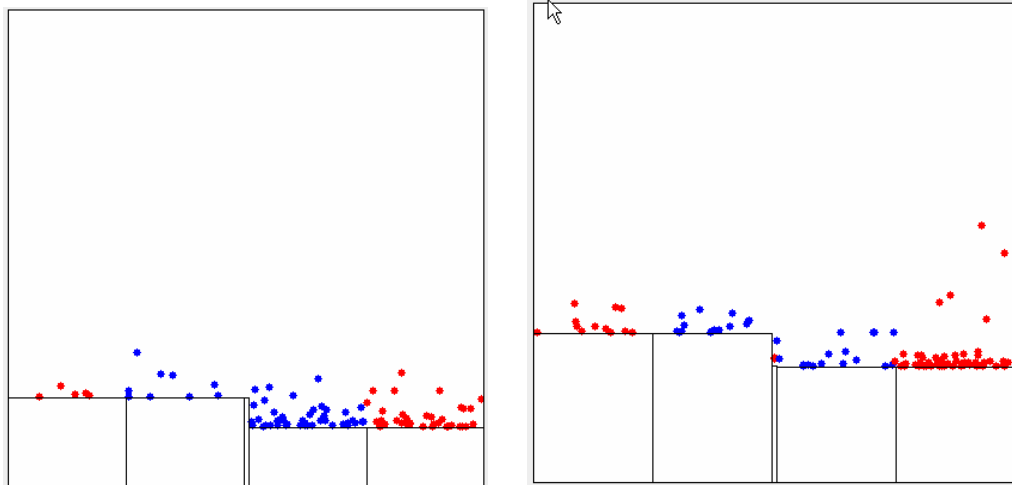


Q: At thermal equilibrium, will the populations of the upper and lower energy platforms be the same for both arrangements?

Consider the following two arrangements of platforms (The difference in energy between the platforms is the same in both arrangements. In the arrangement 2, both platforms have been raised to a high energy.)

Arrangement 1

Arrangement 2



Q: At thermal equilibrium, will the ratio of populations between the higher and lower platforms (P_2/P_1) be the same for both arrangements?

At thermal equilibrium, the ratio between the populations of any two individual platforms is given by:

$$\frac{P_2}{P_1} = e^{-\frac{(E_2-E_1)}{RT}} = e^{-\frac{\Delta E}{RT}}$$

Is there a temperature for which a higher energy platform can have a larger population than a lower population, i.e. can $P_2/P_1 > 1$ when $E_2 > E_1$?

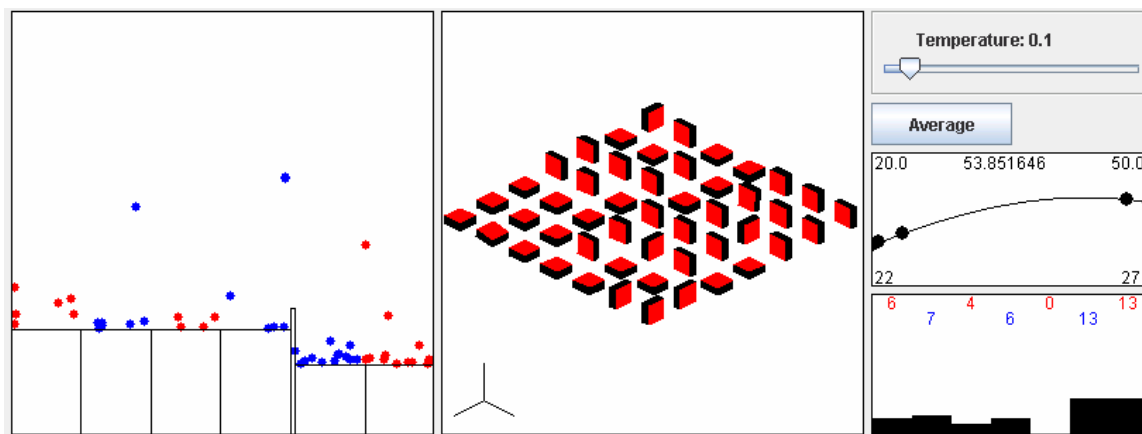
Answer: No. At low temperature, there will be more particles on the lower-energy platform. As we heat the system up, the population of the upper platform increases. At infinitely high temperature, the population of the higher-energy platform will become equal to that of the lower-energy platform ($P_2/P_1 = 1$), but P_2/P_1 will never be greater than one. This can be seen mathematically as:

$$\frac{P_2}{P_1} = e^{-\frac{\Delta E}{R\infty}} = e^{-0} = 1$$

Where we have used the fact that $\frac{1}{\infty} = 0$.

VIII. Entropy and free energy

This simulation introduces entropy into the systems. The simulation extends the above two-dimensional boxes to three dimensions, as shown in the middle panel below. Each box has six sides and the shape is such that there are four ways to stand up (have higher energy), and two ways to lie down (have lower energy). To mimic this in the bouncing ball simulation, we have created six platforms, four platforms with higher energy and two platforms with lower energy.



Activity Notice how the populations of the higher and lower energy states behave at different temperatures?

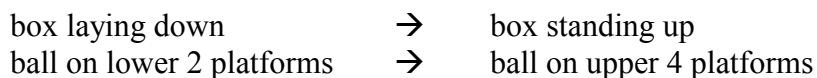
Q: Is there a temperature at which the higher-energy state (the total population of the four higher-energy platforms, or the total number of boxes standing up) has a larger population than the lower-energy state (the total population of the two lower-energy platforms, or total number of boxes laying down)?

You should have found that at high temperature, more boxes are standing up and most of the balls are on the upper platforms. Why does most of the population move to the higher-energy state? The concept we use to explain this is entropy. The summary explanation is: "Although energy prefers that the boxes lie down, entropy prefers that they stand up. At low temperature, energy wins and most boxes are lying down. At high temperature, entropy wins and more boxes are standing up." We will now examine this explanation in more detail.

Entropy refers to the number of ways a system can be in a certain state. For the above rectangular box there are 4 ways to have high energy and only 2 ways to have low energy, so the entropy is larger in the higher energy state. We can summarize this with the following table: (We do not need to make a distinction between energy and enthalpy here, and so will use E and H interchangeably.)

	Energy (E or H)	Entropy (S)
Standing-up boxes/higher platforms		favored
Laying-down boxes/lower platforms	favored	

Or, equivalently, we can say the following reactions:



entropy-driven but not enthalpy-driven.

This interplay of energy and entropy is captured mathematically by the free energy:

$$G = H - T S$$

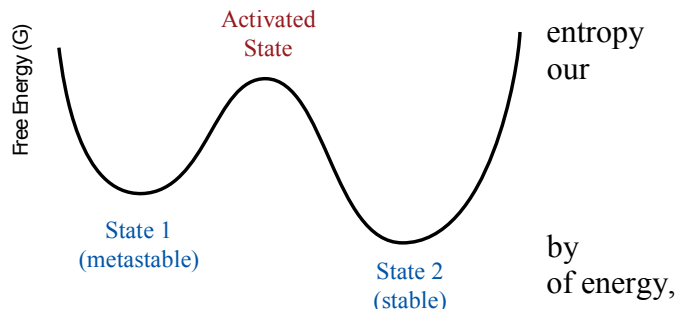
Systems always favor the state with the lowest free-energy. We can understand the above expression for G as follows. Since the entropy is multiplied by temperature, T, entropy becomes more important

at high temperature. The energy and entropy terms have opposite sign (E vs. $-TS$) because systems prefer *low* energy and *high* entropy. At low temperature, energy (H) dominates the free energy: most of the boxes are lying down and most of the balls are on the lower platforms. At sufficiently high temperature, entropy ($-TS$) begins to dominate: most of the boxes are standing up and most of the balls are on the upper platform.

We will show below that we can include the effects by replacing energy with free energy in population expression:

$$\frac{P_2}{P_1} = e^{-\frac{(G_2-G_1)}{kT}} = e^{-\frac{\Delta G}{kT}}$$

We include this in our reaction path diagram labeling the y-axis with free energy, G, instead of E.



IX. Mathematical derivation of free energy

Above, we used the expression

$$\frac{P_2}{P_1} = e^{-\frac{\Delta E}{kT}}$$

for the ratio of populations between two states. This ratio holds between any two specific states, such as individual platforms for the bouncing balls, or individual sides on which the box can stand:

$$\frac{P_{\text{a short side}}}{P_{\text{a long side}}} = e^{-\frac{\Delta E}{kT}}$$

(A box is standing up if it is standing on a short side of the rectangular box, and is lying down if it is standing on a long side.)

We will refer to these specific states (a box standing on a specific side) as configurations. Now suppose that we want to group configurations together into states such as "box standing up" and "box lying down". For the three-dimensional box of the previous section, four configurations are grouped into the "box standing up" state and two configurations are grouped into the "box lying down" state. The total population of boxes standing up is a sum of the populations in the four standing-up configurations, and since these states have equal energy, they have equal populations:

$$P_{\text{all standing-up configurations}} = P_{\text{short side 1}} + P_{\text{short side 2}} + P_{\text{short side 3}} + P_{\text{short side 4}} = 4 P_{\text{a short side}}$$

Similarly, the total population of boxes lying down is

$$P_{\text{all lying down configurations}} = P_{\text{long side 1}} + P_{\text{long side 2}} = 2 P_{\text{a long side}}$$

The ratio is then

$$\frac{P_{\text{all standing-up configurations}}}{P_{\text{all lying-down configurations}}} = \frac{4P_{\text{a short side}}}{2P_{\text{a long side}}} = \frac{4}{2} e^{-\frac{\Delta E}{kT}}$$

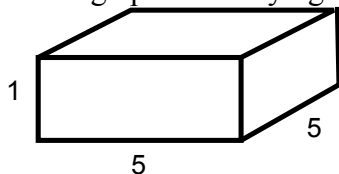
More generally, we can write that the population between two states is

$$\frac{P_2}{P_1} = \frac{\Omega_2}{\Omega_1} e^{-\frac{\Delta E}{kT}} = \frac{\Omega_2}{\Omega_1} e^{-\frac{(E_2-E_1)}{kT}}$$

where Ω_n is the number of configurations grouped together to make the state.

For our box example, $\Omega_2=4$ (the number of ways the box can stand up) and $\Omega_1=2$ (the number of ways the box can lie down).

Q: Consider a box with dimensions as shown below. Suppose the difference in energy between the box standing up and laying down is ΔE . What is the ratio between the total pollution of boxes standing up versus laying down, $P_{\text{standing up}}/P_{\text{laying down}}$, at a given temperature T.



We can get from the expression:

$$\frac{P_2}{P_1} = \frac{\Omega_2}{\Omega_1} e^{-\frac{\Delta E}{kT}}$$

to free energy through the following mathematical manipulations. First, we re-write the above ratio as

$$\frac{P_2}{P_1} = \frac{\Omega_2}{\Omega_1} e^{-\frac{\Delta E}{kT}} = \frac{\Omega_2}{\Omega_1} e^{-\frac{(E_2-E_1)}{kT}} = \frac{\Omega_2 e^{-E_2/kT}}{\Omega_1 e^{-E_1/kT}}$$

If we want the effects of Ω to be comparable to the effects of energy, we need to move Ω into the exponential. Since \ln and \exp cancel one another, we can write

$$\Omega = e^{\ln \Omega}$$

We also want to have kT in the denominator of the exponent, so we multiply and divide by kT

$$\Omega = e^{\frac{kT \ln \Omega}{kT}}$$

If we define entropy S as $k \ln \Omega$, then the above becomes

$$\Omega = e^{\frac{TS}{kT}}$$

We can now put this back into the population ratio to get

$$\frac{P_2}{P_1} = \frac{\Omega_2 e^{-E_2/kT}}{\Omega_1 e^{-E_1/kT}} = \frac{e^{\frac{TS_2}{kT}} e^{-\frac{E_2}{kT}}}{e^{\frac{TS_1}{kT}} e^{-\frac{E_1}{kT}}}$$

Combining the exponentials together (recall that $e^x e^y = e^{x+y}$),

$$\frac{P_2}{P_1} = \frac{e^{\frac{TS_2}{kT}} e^{-\frac{E_2}{kT}}}{e^{\frac{TS_1}{kT}} e^{-\frac{E_1}{kT}}} = \frac{e^{\frac{E_2 - TS_2}{kT}}}{e^{\frac{E_1 - TS_1}{kT}}} = \frac{e^{-\frac{G_2}{kT}}}{e^{-\frac{G_1}{kT}}} = e^{-\frac{\Delta G}{kT}}$$

Where we have used $G = E - TS$. This leads us to the result we introduced at the end of the previous section: when you group configurations together into states, the energy should be replaced with the

free energy. It also gives us a molecular-level definition of entropy: $S = -k \ln \Omega$, the formula inscribed on Boltzmann tombstone (Boltzmann rightly considered this expression the ultimate achievement of his life's work, the ability to connect the entropy measured in thermodynamic experiments on macroscopic systems to the atomic/molecular world.)

